MARINE & COASTAL HABITAT MANAGEMENT ALASKA DEPT. OF JISH & CAUE 333 Raspberry Roade, ALASKA Anchorage, Alaska 99562 1997

U.S. DEPARTMENT OF COMMERCE National Technical Information Service

P-2-103

17, 141, 165

PB-283 658

IMPACTS OF COAL-FIRED POWER PLANTS ON FISH, WILDLIFE, AND THEIR HABITATS

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ARGONNE NATIONAL LABORATORY, ILLINOIS

PREPARED FOR FISH AND WILDLIFE SERVICE, WASHINGTON, D.C. OFFICE OF BIOLOGICAL SERVICES

**March 1978** 

## **Biological Services Program**

FWS/OBS-78/29 March 1978



Impacts of Coal-Fired Power Plants on Fish, Wildlife, and their Habitats

QH 540 .U56 no.78/29

and Wildlife Service

# **Department of the Interior**

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Stock Number 024-010-00458-4

### FWS/OBS-78/29 March 1978

QH 540 .U.56 Mo.75/

# IMPACTS OF COAL-FIRED POWER PLANTS ON FISH, WILDLIFE, AND THEIR HABITATS

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> Argonne National Laboratory is operated for the U.S. Department of Energy under contract W-31-109-Eng-38.

#### ABSTRACT

This report contains an assessment of expected impacts to terrestrial and aquatic biota and their habitats which are associated with the operation of coal-fired power stations, from the point at which coal is delivered to the site through disposal of process wastes. Emphasis is placed on discussion of impacts unique to coal combustion, although some features of gas- and oil-fired stations are also addressed. Impacts arising from thermal effluents, condenser cooling facilities, and power transmission are not discussed.

Gaseous, liquid, and solid discharges from power plants are characterized and quantities estimated, based on the use of Western, Northern Appalachian, and Eastern Interior coal at each of four model plants with rated capacities of 100, 350, 700, and 2100 MWe, respectively. The major physical components of coal-fired power plants are described, and methods are included for estimating requirements for coal, land, water, lime, and limestone.

The features of a coal-fired power plant that have potential for adverse impacts to fish and wildlife include coal slurry pipelines, coal cleaning and storage, limestone preparation (in cases where flue-gas desulfurization is employed), particulate and gaseous emissions, ash, and desulfurization sludge. Coal slurry pipeline impacts arise from rights-of-way construction effects and accidental coal slurry spills. Coal cleaning and storage result in noise, dust, loss of habitat, and introduction of material similar to acid mine drainage into surface waters via runoff. Limestone dust and runoff from limestone storage piles may have measurable effects on soils and vegetation, and can increase surface-water hardness and turbidity. Disposal of combustion waste products (collected ash and flue-gas desulfurization sludge) requires sizable land areas and has the potential for adverse effects that include seepage of trace and other elements into groundwater, soils, and surface waters.

The effects of air pollutants  $(SO_2, NO_x)$ , and particulates) on plants and animals can be acute, chronic, and/or long-term. The latter effects are, at present, difficult if not impossible to evaluate due to the absence of long-term studies of the subject. In particular, ecosystem impacts due to exposure to low but persistent concentrations of trace elements in power plant particulate emissions can only be surmised. Acid precipitation, a secondary pollutant associated with coal-fired power plant emissions, is known to cause direct and indirect effects on terrestrial and aquatic ecosystems. Such effects include injury to foliage, leaching of nutrients from plants and soils, and elimination of certain fish species from lakes and streams.

Mitigative measures to reduce the magnitude of some of these adverse impacts are described, and include pollution abatement devices, erosion control, proper siting and lining of ash and sludge disposal ponds, and reclamation of inactive waste-disposal sites.

Included in the report is a list of research topics suggested to improve impact assessment capabilities.

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#### INTRODUCTION

The projected increases in the use of coal in steam-electric plants, both new and those converted from burning oil or gas, give concern for the environmental impacts of the concomitant increase in the discharge of waste products from such power plants. The U.S. Fish and Wildlife Service has the responsibility for input into the maintenance and enhancement of the environmental quality of the nation's fish and wildlife resources. To carry out these responsibilities, the Fish and Wildlife Service must have adequate information to advise federal and state agencies and industrial groups regarding protection of fish and wildlife and their habitats during electric power development.

The purpose of this report is to serve as a data or resource base for individuals in the Fish and Wildlife Service who, as a part of their job, are called upon to review and comment on either an environmental report or an environmental impact statement for a proposed coal-fired electric generating facility. The use of this report will be increased by the forthcoming publication of a user's manual--a condensation of appropriate material from the report--which will provide guidelines for identifying the potential environmental impacts associated with the siting of a coal-fired electric generating facility.

This report contains an assessment of expected impacts to biota and their habitat associated with the operation of coal-fired power plants. The scope of the report limits discussion of impacts to the operation of the facility from the point at which coal is delivered to the plant site through final disposal of waste products. In order to provide a comparison of the environmental trade-offs of substituting coal for petroleum products or natural gas in electric generating stations, those impacts associated with oil-fired stations, natural-gas-fired stations, and stations converted from oil- or natural-gas-fired to coal-fired that are different from coalfired stations are addressed. The impacts of features that are not unique to steam-electric stations--e.g., condenser cooling systems, cooling-water intakes and discharges, cooling towers or other off-stream methods of cooling and cooling-water treatment, and transmission lines--are not addressed.

Stations with rated capacities (plant sizes) of 100 MWe, 350 MWe, 700 MWe and 2100 MWe were chosen as model power plants to estimate the raw materials required for combustion, combustion wastes, and airborne emissions for each fossil fuel. These four station sizes will provide information to account for the wide array of sizes that could be encountered by an individual reviewing a proposed facility. The description of the plants includes ancillary structures, daily fuel requirements assuming a thermal efficiency of 38% and a 70% plant capacity factor, coal storage piles, and wastes generated. Three types of coal were chosen, based on (1) sulfur content and (2) representation of those coals in the various coal-supplying regions of the United States. Therefore, the estimates vary for each coal type and power plant size.

Each coal-fired model plant is assumed to be equipped with an electrostatic precipitator (with an efficiency of 99.5%) for fly ash removal and, if high-sulfur coal is used, with fluegas desulfurization lime/limestone scrubbers (with 85% efficiency) for  $SO_2$  reduction. These two pollution-control technologies and resultant by-products and/or wastes are described.

For each of the four model plants and three coal types, the daily fuel requirements are used to quantify the following: (1) the amount of waste from coal washing, (2) nonairborne wastes produced from combustion, i.e., fly ash and bottom ash, (3) by-products from pollutioncontrol technology, (4) ultimate airborne emissions, and (5) land area for waste disposal and coal storage. The terrestrial and aquatic impacts associated with each of the above are discussed to the extent that existing literature allows. Mitigative measures which may be feasible to reduce or eliminate the potential impacts are described. Topical areas in which insufficient data exists or limits the impact assessment are identified.

Metric units, mostly SI units (International System of Units), are used in this report, with a few exceptions where they seemed inappropriate (e.g., Btu/lb). The definitions of SI units and conversion factors follow the 1976 "Standard for Metric Practice" of the American Society for Testing and Materials, Philadelphia, Pa.

1

#### MAJOR PHYSICAL COMPONENTS, RAW MATERIALS, AND SITING CONSIDERATIONS FOR COAL-FIRED POWER PLANTS

#### MAJOR PHYSICAL COMPONENTS OF A TYPICAL COAL-FIRED POWER PLANT

A coal-fired power plant transforms the chemical energy in coal into electrical energy by a sequence of three conversion processes. Physical components required for these processes include furnaces and boilers (where chemical energy is converted to heat energy and heat is transferred to water to make steam), turbines (where heat energy of the steam is converted to mechanical energy), and generators (where mechanical energy is converted to electrical energy). Ancillary equipment includes cooling systems (where low-temperature heat is rejected), coal storage and handling facilities, and, frequently, stack-gas cleaning equipment to remove particulates and noxious gases released during coal combustion. These basic components and processes are described below. A flow chart of the conversion process is shown in Figure 1.



## Figure 1. Conversion of Coal into Electrical Energy in a Coal-Fired Power Plant.

#### Furnace

Furnaces in common use include: stoker-fired, cyclone-furnace-fired, and pulverized-coalfired units. Stokers are mechanisms which feed fuel onto a grate within the furnace. Stokerfiring is only practical for atypically small (< 40 MWe) power plants. Cyclone furnaces burn crushed coal in a horizontal cylinder. A high velocity stream of air is injected into the cylinder and moves along the cylinder boundary to create a cyclonic flame pattern. Although they offer a number of significant advantages, cyclone furnaces produce relatively high concentrations of nitrogen oxides. For this reason, it is expected, and assumed within the remainder of this report, that new coal-fired plants will utilize pulverized-coal firing rather than cyclone-furnace firing.

With a pulverized-coal system, the coal is pulverized to a powder, mixed with air, and then blown into the furnace. Figure 2 shows air and flue gas circulation patterns for a somewhat simplified pulverized-coal boiler. A modern pulverized-coal-fired power plant will typically produce steam at 2400  $\times$  10<sup>4</sup> Pa (3500 psi) superheated to 538°C (1000°F) with 538°C (1000°F) reheat.



Figure 2. Boiler Air and Flue-Gas Circulation Paths. From University of Oklahoma, Science and Public Policy Program (1975). [Originally from Shields (1961).]

### Boiler

A coal-fired boiler can be either the water-tube or the fire-tube type. In a water-tube boiler, the water and steam are inside the tubes and the hot gases are outside. The opposite is the case with fire-tube boilers. Modern boilers are of the water-tube type because these boilers can be constructed for greater capacity and higher pressures than fire-tube boilers.

To maximize thermal efficiency, a power plant boiler generally contains the following components: superheater, reheater, economizer, and air preheater. The superheater is a system of tubes located at the top of the boiler in which saturated steam is superheated by combustion gases. The reheater is a system of tubes which reheats partially expanded steam that has passed through the turbine's initial stages; the reheated steam is then returned to the final stages of the turbine. The economizer transfers heat from the combustion gases (after the superheater and the reheater) to the boiler feedwater. The air preheater extracts additional

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heat from the flue gases (after the economizer) and transfers it to the combustion air before the air is fed into the furnace. In addition to these components, a boiler typically utilizes steam separators, fans, pumps, and fuel-handling equipment.

#### Turbine

The turbine converts heat energy from the boiler to mechanical energy. In the turbine, steam expands, exerting force on the turbine blades. This force turns the turbine shaft which is connected to the generator shaft. Basically, the turbine is a sophisticated, steam-driven windmill.

#### Generator

The generator converts mechanical energy from the turbine to electrical energy by utilizing a basic natural phenomenon--i.e., the movement of an electrical conductor relative to a magnetic field creates a voltage within the conductor. In the generator, the movement (rotation) is maintained by torque transmitted from the turbine. Power plant generators have energy conversion efficiencies ranging from 96 to 99% (Univ. Okla. Sci. Public Policy Prog. 1975).

#### Water/Steam Cycle

The water/steam cycle in a coal-fired power plant is schematically presented in Figure 3. In the boiler, heat from coal combustion is transferred to water to, produce steam. The steam does work (in the technical sense) against the turbine blades and emerges at lower temperature and lower pressure; it is then condensed into water and the water is returned to the boiler to complete the cycle. The heat extracted by the condenser is rejected to a lake, river, pond, or to the atmosphere.



Figure 3. The Water/Steam Cycle in a Coal-Fired Power Plant. Modified from U.S. Atomic Energy Commission (1974).

In a modern system, after passing through the early stages of the turbine, moderatetemperature/moderate-pressure steam is reheated in the boiler to make high-temperature/moderatepressure steam, which is then returned to the final stages of the turbine. This is called reheat and it improves the efficiency of the heat-to-mechanical-energy conversion process. Some power plants have two reheat stages. (Figure 3 does not show a reheat cycle.)

The electrical power that a generating plant is capable of producing is measured in megawatts electric (MWe) (1 MWe =  $10^6$  watts =  $10^3$  kilowatts). The sizes of coal-burning power plants range from less than 10 MWe to more than 2000 MWe. For purposes of illustration, sizes of 100, 350, 700, and 2100 MWe will be considered in this report. Power plants do not operate continuously over long periods at full capacity. Averaging over a year, electrical energy output is typically 70% of capacity. The average output expressed as a percent of capacity is called the capacity factor or plant factor. As indicated above, the power generating station rejects low-temperature heat; because of this and other losses, more than one kilowatt-hour  $(kW \cdot h)$  of heat energy must be supplied by the coal for each kW  $\cdot h$  of electrical energy output. In a modern coal-burning power plant, the numbers are typically 2.5-2.8 kW  $\cdot h$  (8500-9500 Btu) of coal energy input per kW  $\cdot h$  of electrical energy output (Babcock and Wilcox Co. 1972). This corresponds to plant efficiencies of 36-40% (efficiency = kW  $\cdot h$  of electrical output per kW  $\cdot h$  of coal energy input).

#### Cooling Systems

All electrical power plants require a cooling system to reject heat. Further discussion of cooling systems is outside the scope of this report.

#### Coal Storage and Handling

<u>Coal storage</u>. Coal is consumed continuously by the furnace, but is delivered in periodic bulk shipments of large tonnage which must be stored at the plant. The storage of coal is discussed on page 28.

<u>Coal handling</u>. Coal is unloaded at the receiving facility and stored. From storage, coal is transported by conveyor to a crusher house, then to a surge bin, and finally to the silos or bunkers which feed the furnaces (Babcock and Wilcox Co. 1972; U.S. Energy Res. Dev. Admin. 1975; Dvorak et al. 1977). The surge bin serves to smooth out the flow of coal to the burners. On the conveyor feeding the surge bin, coal samples are taken for measurement of the Btu content of the coal to determine how many metric tons/minute are needed by the furnace. Collectors in the surge bin remove dust, thereby reducing the possibility of explosion. The collected coal dust is conveyed to the bunkers and is subsequently burned in the furnace. For boilers utilizing pulverized coal burners, the feed system from each silo includes a pulverizer. The pulverized coal is mixed with a certain proportion of preheated air and delivered to the furnace for combustion. With pulverizers it is desirable to include a magnetic separator in the feed system. A coal-handling system for a large plant is shown in Figure 4.

#### Stack-Gas Cleaning

The U.S. Environmental Protection Agency (USEPA) has developed New Source Performance Standards (NSPS) which place limitations on particulates and oxides of sulfur and nitrogen emitted in the stack gases from power plants (see Appendix A). The methods employed to meet these standards are presented below.

<u>Particulates</u>. Particulate (fly ash) emissions are that part of the uncombustible residue which is carried out of the stack by the flue gas. With pulverized-coal firing (dry ash unit), 80% of the ash becomes entrained in the flue gas; the remaining 20% settles in hoppers (at the boiler base) from which it is removed for disposal. This fly ash level is relatively high (compared to stoker and cyclone-furnace firing) due to the fact that pulverized coal is burned in suspension. The fly ash level is reduced to about 50% for a pulverized-coal furnace with a slag-tap capability. With cyclone-furnace firing, only 20 to 30% of the total ash is carried away as fly ash (Babcock and Wilcox Co. 1972).

There are four types of fly ash control systems: electrostatic precipitators, wet scrubbers, fabric filters, and mechanical collectors.

<u>Electrostatic precipitators</u>. Electrostatic precipitators cause the fly ash particles to become electrically charged. The charged particles are then pulled, by electrostatic forces, to collecting electrodes. Four steps are involved:

- 1. A powerful electric field is maintained between the negative discharge electrode and the positive collecting electrode. The discharge electrode is a wire, and the collecting electrode is a tube or plate.
- 2. A direct-current, high-voltage corona is established in the interelectrode space. This corona ionizes molecules of electronegative gases such as  $0_2$ ,  $C0_2$ , and  $S0_2$  present in the flue gas. These ions, in turn, charge the fly ash particles by colliding with them and transferring charge.
- 3. The particles of fly ash, now negatively charged, are pulled by electrostatic forces to the positive (grounded) collecting electrode.
- 4. The collecting electrode is periodically rapped to dislodge the accumulated fly ash. Upon rapping, the ash falls into a hopper beneath the electrodes.



Figure 4. Coal-Handling System for a 1000-MWe Power Plant. From Babcock and Wilcox Co. (1972) (with permission, see credits).

A parallel plate precipitator utilizes a series of flat parallel collector plates spaced from 15 to 30 cm (6 to 12 inches) apart, with a wire (the discharge electrode) between each pair of plates (Gottschlich 1968; Ottmers et al. 1975). The particulate-laden flue gas passes between the plates.

High collection efficiencies, ranging from 99% to 99.9%, can be achieved with a low pressure drop through the precipitator and a low power requirement (Southern Research Institute 1975). A 99% efficiency or less is obtained at a generally lower cost than with other types of equipment (Babcock and Wilcox Co. 1972). Further, electrostatic precipitators are relatively compact, and have low maintenance costs and low downtime. The fly ash escaping from the precipitator (generally 1% or less of the total) is smaller than 2  $\mu$ m in size (Locklin et al. 1974).

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The precipitator collection efficiency increases with increasing time of particle residency in the electrostatic field and with the strength of the field. Efficiency declines with increasing fly ash resistivity. The resistivity of the fly ash is, in turn, a function of the ash temperature and sulfur content. Low-sulfur coal produces a high resistivity fly ash which reduces collection efficiency. This problem can be overcome by using a "hot" precipitator, placed upstream of the air heater and operated at  $315^{\circ}C$  ( $600^{\circ}F$ ) or more, instead of the conventional "cold" precipitator, placed downstream from the air heater. The higher temperature in the hot precipitator compensates for the low sulfur content so that a high removal efficiency is obtained even with low-sulfur coal. With the growing dependence on low-sulfur coal, hot precipitators are coming into increasing use.

<u>Wet scrubbers</u>. A wet scrubber removes fly ash particles from the flue gas by transferring the particles to water. The transfer is accomplished by: inertial impaction (primarily effective for > 1  $\mu$ m particles), interception (primarily effective for 0.1 to 1  $\mu$ m particles), and diffusion into collector droplets (for < 0.1  $\mu$ m particles) (Dvorak et al. 1977).

Collection efficiency, particle size, and the pressure drop across the scrubber are closely related. For a given efficiency, pressure drop varies inversely with particle size; for a given particle size, efficiency increases with increasing pressure drop.

Venturi and moving-bed scrubbers are the most widely used wet scrubbers in power plant applications.

Venturi scrubbers utilize a venturi throat to obtain a high-velocity flow of stack gas. Velocities are typically in the range of 60-120 m/s (200-400 ft/s). Absorbing liquid is injected (at the throat) into the fly-ash-laden stream of high-velocity stack gas. The gas stream atomizes the liquid into droplets. Internal impaction of the fly ash particles into the droplets is fostered by the high relative velocity between the gas and the droplets. Impaction is considered to be the primary collection mechanism in venturi scrubbers.

Venturi scrubbers have a nominal efficiency of 99% (Ottmers et al. 1975). With an acrossscrubber pressure drop of 2500 to 3750 Pa (10 to 15 inches of water) and a liquid-to-gas ratio of 1.3 to 2 L/m<sup>3</sup> (10 to 15 gal/1000 ft<sup>3</sup>), they can reduce fly ash content of the flue gas by 0.7 g/m<sup>3</sup> (0.02 g/ft<sup>3</sup>) (Southern Research Institute 1975).

A moving-bed scrubber consists of a bed of plastic or glass spheres, packed loosely to permit movement and supported underneath by a perforated plate; the spheres and plate are mounted within a cylindrical container (Ottmers et al. 1975; Southern Research Institute 1975). Flue gas passes upward through the sphere bed as the scrubber liquid percolates downward. The spheres provide an extensive surface for gas-liquid contact, and create turbulence in the flue gas which further enhances contact.

In addition to extracting fly ash particles, moving-bed scrubbers are effective in simultaneously removing  $SO_2$  from the flue gas. This effectiveness is due in part to the long residence time of the gas in the scrubber. By contrast, venturi scrubbers provide a short residence time (due to the high velocities) and are correspondingly poor in  $SO_2$  removal.

Particle collection efficiencies are high for moving-bed scrubbers, ranging from 98.7 to 99.9%. These percentages are obtained with pressure drops of 1350 to 2500 Pa (5.5 to 10 inches of water), liquid-to-gas ratios of 4.3 to 10.6  $L/m^3$  (32 to 80 gal/1000 ft<sup>3</sup>), and gas velocities of 2.4 to 3 m/s (8 to 10 ft/s) (Southern Research Institute 1975). Increasing the pressure drop increases the collection efficiency.

<u>Fabric filters</u>. These consist of fabric bags through which the stack gas flows. Fly ash is trapped by the fine threads composing the fabric. As particles accumulate on the filter, its efficiency increases. The bags are periodically cleaned, after which their efficiency returns to the original, lower value.

Fabric filters must be applied in situations where temperature and humidity are not excessive. They are generally not competitive with electrostatic precipitators at efficiencies of 99% or less. However, efficiencies above 99% are economically achievable with fabric filters, and for this reason, their utilization in urban areas may increase.

<u>Mechanical collectors</u>. Mechanical collectors utilize centrifugal forces to separate fly ash particles from the flue gas. The ash-bearing gas stream is introduced tangentially into the collector. The particles are thrown to the collector's outside wall where they are removed.

Mechanical collectors are most effective for particles of > 10  $\mu m$ . For < 10  $\mu m$  size particles, the efficiency drops well below 90%.

<u>Nitrogen oxides</u>. Combustion-generated nitrogen oxides  $(NO_X)$  are produced by two reactions: the combination of nitrogen from the combustion air with oxygen and the oxidation of nitrogen chemically bound in the coal. The formation of nitrogen oxides depends on combustion conditions in the primary flame zone of the boiler.

Four techniques are available to control  $NO_X$  emissions from coal-fired boilers: (1) modification of combustion conditions, (2) modification of the coal, (3) extraction of  $NO_X$  from the flue gas, and (4) utilization of an alternative, low  $NO_X$  combustion process (catalytic combustion, fluidized-bed combustion). Of these, modification of combustion conditions constitutes the best developed and most effective technique for the short and long term (Shimizu et al. 1975). The capital cost of combustion modifications is an order of magnitude lower than that for flue gas cleaning.

To avoid poor combustion, with the consequent production of smoke and unburned fuel, utility boilers always take in more air than is stoichiometrically required. Burning with low-excess air is the most widely used combustion modification strategy. This approach reduces the quantity of oxygen available for combination with atmospheric or coal-bound nitrogen. It also reduces the quantity of atmospheric nitrogen in the furnace. However, if the excess air level becomes too low, smoke and CO are produced.

Staged combustion is a second strategy for the control of  $NO_X$  via the modification of combustion (Shimizu et al. 1975; Brown et al. 1974). With this approach, the furnace is fired in such a way as to make the primary flame zone rich in fuel. Sufficient air is introduced above the flame zone to complete combustion, while maintaining overall excess air at a low level. The fuel-rich primary flame zone is kept comparatively cool by radiative heat transfer. [Nitrogen oxide formation proceeds rapidly at temperatures above 1650°C (3000°F).] Thus, the main  $NO_X$ -forming region of the furnace--the primary flame zone--is maintained in a cool, oxygen-poor state; the coolness and the oxygen scarcity both tend to inhibit  $NO_X$  development. The staged combustion technique is constrained by the occurrence of convective section fouling, unburned hydrocarbon emissions, or poor ignition characteristics when the primary zone is too rich in fuel.

The use of staged combustion leads to emission reductions in the 50 to 65% range; the lowexcess-air approach is somewhat less effective (Shimizu et al. 1975; Armento 1975).

<u>Sulfur oxides</u>. The following flue-gas desulfurization (FGD) processes are used for controlling sulfur oxide  $(SO_X)$  emissions: lime/limestone scrubbing, double alkali scrubbing, magnesia scrubbing, and the Wellman-Lord process.

<u>Lime/limestone scrubbing</u>. The lime/limestone scrubbing process extracts  $SO_2$  from the flue gas by reacting it with lime (CaO) or limestone (CaCO<sub>3</sub>) in a slurry to form a precipitate. The slurry recirculates as shown in Figure 5. The relevant chemical reactions are:

Lime:	$SO_2 + Ca(OH)_2 \longrightarrow H_2O + CaSO_3$ ;	(1)

Limestone:  $SO_2 + CaCO_3 \longrightarrow CO_2 + CaSO_3$  (2)

 $2 \operatorname{CaSO}_3 + O_2 \longrightarrow 2 \operatorname{CaSO}_4 . \tag{3}$ 

The flue gas and the slurry come into contact in the scrubber, and it is there that the first two reactions take place. From the scrubber, the reacted slurry flows to the reaction tank where fresh lime or limestone is added to make the calcium sulfite and sulfate precipitate out (as hydrates). Part of the slurry leaving the reaction tank is pumped back to the scrubber. The remainder is sent to a solid/liquid separator, which may be a centrifuge, filter, or holding pond. Solids (sludge) from the separator--consisting of hydrated calcium sulfite and sulfate, unreacted lime or limestone, and some fly ash--are removed for disposal. The liquid-output stream of the separator is split, one portion being sent back to the reaction tank and the remaining portion to the scrubber, thus completing the cycle. Makeup water is added to the scrubber-bound portion to compensate for evaporation losses and water lost with the sludge. Large quantities of sludge are produced by the lime/limestone system.

After scrubbing, the flue gas is reheated above its dew point and released up the stack.

With reasonable maintenance, lime/limestone scrubbing systems can function at least 80% of the time (Herlihy 1977). These systems are effective in removing  $SO_2$ ; removal efficiencies of 80% or more are achieved in normal operation (Herlihy 1977). Lime/limestone scrubbing is the most widely utilized of the available flue-gas desulfurization techniques and it is expected that this predominance will continue well into the 1980's.

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<u>Double alkali scrubbing</u>. The double alkali scrubbing process uses two solutions-one for absorbing  $SO_2$  from the flue gas and one for regenerating the spent absorbing liquid. Of the many possible combinations, usually a solution of sodium hydroxide or sodium sulfite is used as the absorbing medium and lime or limestone as the regenerating agent. A sodium sulfitelime/limestone system is described here. Figure 6 shows the basic flow scheme for such a system. As with lime/limestone scrubbing, a solid waste of calcium sulfite and calcium sulfate is generated

A sodium sulfite  $(Na_2SO_3)$  liquor is brought into contact with the flue gas; the flue-gas  $SO_2$  reacts with the  $Na_2SO_3$  as follows:

$$SO_2 + Na_2SO_3 + H_2O \longrightarrow 2 NaHSO_3$$
. (4)

The  $NaHSO_3$ -bearing effluent from the scrubber is regenerated in the reaction tank according to either of the following reactions:

Lime: 
$$2 \text{ NaHSO}_3 + \text{Ca}(OH)_2 \longrightarrow \text{Na}_2\text{SO}_3 + \text{CaSO}_3 + 2 \text{H}_2\text{O}$$
. (5)

Limestone: 
$$2 \text{ NaHSO}_3 + \text{CaCO}_3 \longrightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{CaSO}_3 + \text{CO}_2$$
. (6)

Sodium sulfate ( $Na_2SO_4$ ) is also formed in the process. This is soluble and is removed by a purge stream.

The solid/liquid mixture from the reaction tank goes to a separator, which discharges the sludge and the scrubbing liquid. Makeup water and alkali are added to the scrubbing liquid which is returned to the scrubber. As in the lime/limestone scrubbing process, the sludge from the separator must be disposed of.

Double alkali absorbers have less potential for scaling and are more efficient than lime/ limestone systems. Removal efficiencies for  $SO_2$  of 90-97% have been reported for double alkali units (Cooper 1975; Yeager 1975; Herlihy 1977).

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<u>Magnesia scrubbing</u>. The magnesia scrubbing process (Fig. 7) reacts flue-gas  $SO_2$  with a magnesium sulfite slurry (Ottmers et al. 1975; Herlihy 1977), as follows:

$$SO_2 + MgSO_3 + H_2O \longrightarrow Mg(HSO_3)_2$$
 (7)

Magnesium oxide is used to regenerate magnesium sulfite from the spent absorbing liquor:

$$Mg(HSO_3)_2 + MgO \longrightarrow 2 MgSO_3 + H_2O$$
 (8)

The precipitated  $MgSO_3$  is concentrated by a separator, dried, and sent to a sulfuric acid plant. At the plant, the magnesium sulfite is heated to regenerate the magnesium oxide.

$$MgSO_3 \longrightarrow MgO + SO_2 . \tag{9}$$

The  $SO_2$  driven off during heating is converted into 98% sulfuric acid.

Magnesia scrubbing is regenerative, producing no throwaway sludge and requiring no input analogous to the lime or limestone used in the two scrubbing processes described above (except for a minor amount of makeup MgO). Further, the magnesia scrubbing process offers low scaling potential, high SO<sub>2</sub> removal efficiency (90% or more), and a salable end product (Herlihy 1977).

<u>Wellman-Lord process</u>. The Wellman-Lord process (Fig. 8) removes flue-gas  $SO_2$  by reacting it with a solution of sodium sulfite,  $Na_2SO_3$  (Ottmers et al. 1975; Herlihy 1977):

$$SO_2 + Na_2SO_3 + H_2O - 2 NaHSO_3$$
.

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(10)



Figure 7. Basic Flow Scheme for Magnesia Scrubbing Processes. From Ottmers et al. (1975) (with permission, see credits).



Figure 8. Basic Flow Scheme for the Wellman-Lord Scrubbing Process. From Ottmers et al. (1975) (with permission, see credits).

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The spent absorbing solution is then regenerated by heating in an evaporator/crystallizer:

$$2 \text{ NaHSO}_3 \longrightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{SO}_2$$
 (11)

The gas stream from the evaporator/crystallizer, consisting of  $H_2O$  and  $SO_2$ , is sent to a condenser to condense out the  $H_2O$ , and then to a separator to separate the water and  $SO_2$ . The condensed water is mixed with the regenerated sulfite slurry, makeup alkali, and makeup water to provide scrubber-feed solution. The  $SO_2$  can be processed to sulfuric acid, liquid  $SO_2$ , or elemental sulfur. Some of the sodium sulfite is oxidized to sulfate, which is unreactive. To prevent sulfate build-up, a sulfate purge stream is required. The makeup water compensates for losses in this purge stream as well as in the scrubber.

The SO<sub>2</sub> removal efficiency of Wellman-Lord system is high. For the 17 units in operation, efficiency is over 90% in normal operations at all installations (Pedroso 1976).

#### RAW MATERIALS REQUIRED FOR POWER PLANT OPERATION

The raw materials used by a coal-fired power plant are (1) coal, (2) oil or natural gas for the ignitors, (3) lime or limestone, assuming a lime/limestone scrubber is used to remove  $SO_2$ from the flue gas, and (4) water. Of the various  $SO_2$  control processes, lime/limestone scrubbing is receiving the widest application (Ottmers et al. 1975; Commerce Technical Advisory Board Panel on Sulfur Oxide Control Technology 1975). For this report, a plant utilizing either lime or limestone scrubbing is assumed if  $SO_2$  emissions exceed NSPS.

### Coal

The daily coal requirement (DCR) of a coal-fired electric power plant is given by the formula:

DCR (tons/day)

$$= \left(\frac{P}{100}\right) C(MWe) \times 10^3 \frac{kW}{MW} \times 24 \frac{hr}{day} \times 3412 \frac{Btu}{kW \cdot h} \times \frac{100}{E} \times \frac{1 \ 1b \ coal}{B_C(Btu)} \times \frac{1 \ ton}{2000 \ 1b}$$
(12)

where

- C = The rated capacity of the plant in megawatts (MWe).
- P = The capacity or plant factor, i.e., the percentage of capacity at which the plant operates, averaged over one year. A typical value for P is 70%.
- E = The efficiency of the plant in %. E/100 = kW•h (kilowatt hours) of electrical energy output from the plant per kW•h of coal energy input into the plant. Typically, E ranges from 36-40% because: (1) heat must be rejected in order to convert heat energy into mechanical energy, (2) some of the generated electrical energy must be used to power auxiliary equipment within the plant, (3) heat and combustibles are lost "up the stack," (4) heat is lost from the boiler walls by radiation and convection, and (5) there are energy losses in the generators (Dvorak et al. 1977).
- $B_c$  = The heat content in Btu (British thermal units) of one pound of coal.

Three coals with sulfur, ash, and heat contents reflecting regionally observed variations will be used hereafter in this report as the basis for discussion and impact assessment (Table 1). The three coals chosen are bituminous coal from the Pittsburgh seam of West Virginia in the Northern Appalachian Region, bituminous coal from the Illinois No. 5 seam in the Eastern Interior Region, and subbituminous Western coal from the Anderson, Canyon, and Wyodak-Anderson seams of the Powder River Region of Wyoming. The daily coal requirements of the four model plants considered in this report are given in Table 2 for the three coal types. Information on coal classification and composition of these and other coals is presented in Appendix B.

#### Oil or Natural Gas

During start-up and shutdown and for flame stabilization while in operation, the furnaces of coal-burning power plants use ignitors which burn oil or natural gas. The required amounts of oil or natural gas are quite small, contributing less than one percent of the heat generated by the boiler furnace (Natl. Coal Assoc. 1976).

Coal type	Coal seam	Ash (%)	Sulfur (%)	Heat value (Btu/lb) <sup>a</sup>
Western (Powder River)	Anderson, Canyon, and Wyodak-Anderson (Wyoming)	6.0	0.48	8,200
Northern Appalachian	Pittsburgh (West Virginia)	7	2.2	13,800
Eastern Interior	No. 5 (Illinois)	10	3.5	11,400

Table 1. Ash, Sulfur, and Heat Values of the Three Coals Chosen for Sample Calculations

<sup>a</sup>To convert Btu/lb to J/kg, multiply by 2.324  $\times$  10<sup>3</sup>.

「able	2,	Daily	/ Coal	Require	nents (	of t	he F	our	Mode1	Power
	P	lants	Burnir	ng Three	Standa	ard	Coal	Тур	esa	

Diant circ		Dail	y coal requirem	ent per coal t	ype	
	West	ern	Northern A	ppalachian	Eastern I	nterior
(MWe)	(MT/day)	(t/day)	(MT/day)	(t/day)	(MT/day)	(t/day)
100	834	919	495	546	600	661
350	2,920	3,220	1,730	1,910	2,100	2,310
700	5,830	6,430	3,460	3,820	4,200	4,630
2100	17,500	19,300	10,400	11,500	12,600	13,900

<sup>a</sup>The plants are assumed to use pulverized-coal furnaces, have a thermal efficiency of 38%, and operate at 70% capacity. Ash, sulfur, and heat contents of these coals are given in Table 1.

#### Lime/Limestone

Lime scrubbing. In lime scrubbing (Eq. 1), an atom of calcium is required for each sulfur atom "removed." However, more than one calcium atom must be fed into the scrubber for each sulfur atom removed because some of the  $Ca(OH)_2$  does not participate in the above reaction, but rather reacts to form  $CaCO_3$  or remains as unreacted  $Ca(OH)_2$ . Typically 1.2 calcium atoms are supplied to the scrubber per sulfur atom removed. Using this number, and assuming that the scrubber removes 85% of the SO<sub>2</sub> passing through it (this percentage is typical), the amount of lime consumed by the scrubber/day, i.e., the daily lime requirement (DLR), is given in terms of the daily coal requirement (DCR) by:

$$DLR(MT/day) = DCR(MT/day) \frac{\% \text{ sulfur in coal}}{100} \times \frac{85}{100} \times \frac{56 \text{ (mol. wt. Ca0)}}{32 \text{ (At. wt. S)}} \times 1.2$$
$$= DCR(MT/day) \frac{\% \text{ sulfur in coal}}{100} \times 1.785 . \tag{13}$$

Limestone scrubbing. In limestone scrubbing (Eqs. 2 and 3), typically 1.5 atoms of calcium are supplied to the scrubber for each sulfur atom "removed" (for reasons analogous to those for lime scrubbing). Using this number, and again assuming an 85% scrubber efficiency, the amount of limestone consumed by the scrubber/day, i.e., the daily limestone requirement (DLSR), is given by:

$$DLSR(MT/day) = DCR(MT/day) \frac{\% \text{ sulfur in coal}}{100} \times \frac{85}{100} \times \frac{100 \text{ (mol. wt. CaCO_3)}}{32 \text{ (At. wt. S)}} \times 1.5$$
  
= DCR(MT/day)  $\frac{\% \text{ sulfur in coal}}{100} \times 3.98$ . (14)

The daily lime/limestone requirements for the four model coal-burning plants are presented in Table 3 for the same plant sizes and coal types as given in Table 2, except for Western coal which meets NSPS for  $SO_2$  emissions without scrubbing.

and the second	and the first state of the second state of the	and the second	A CONTRACTOR OF A CONTRACTOR O	<u></u>	The second s	
and an and a second	Daily lime or	limestone req	uirement	per coa	l type (MT/day)	
Plant size (MWe)	Northern	Appalachian		Easter	Interior	
	Lime	Limestone		Lime	Limestone	
100	19.5	43.5		37.5	83.6	
350	68.2	152		132	292	
700	136	304		262	585	
2100	409	912	- 11 J.A.	787	1756	

Table 3. Daily Lime or Limestone Requirements for the Four Model Power Plants, Equipped with a Lime or Limestone Scrubber, for Two Coal Types<sup>a</sup>

<sup>a</sup>The entries were determined from the corresponding daily coal requirements in Table 2. Ash, sulfur, and heat contents of these coals are given in Table 1. A scrubber efficiency of 85% is assumed.

#### Water

Water is consumed in the lime and limestone scrubbing processes, in the sluicing of bottom ash and captured fly ash, and in cooling. Assuming the cooling is accomplished by cooling towers, 0.4 gallons of water will be consumed per output kW+h due to evaporation (Parker and Krenkel 1969). The daily water consumption by the cooling towers, i.e., the daily water requirement (DWR<sub>c</sub>), is given by:

$$DWR_{C} (gallons/day) = 0.7 \times C(MW) \times 24 \frac{hr}{day} \times 10^{3} \frac{kW \cdot h}{MW \cdot h} \times 0.4 \frac{gallon}{kW \cdot h}$$
$$= 0.672 \times 10^{4} C(MW) gallons/day .$$
(15)

This equation assumes a 70% capacity factor. The 100, 350, 700, and 2100 MWe power plants have daily water requirements of  $0.7 \times 10^6$ ,  $2.3 \times 10^6$ ,  $4.7 \times 10^6$ , and  $14 \times 10^6$  gallons/day, respectively.

The consumption of water for lime/limestone scrubbing and for ash sluicing amounts to 16 to 30% of the cooling water requirement (Ottmers et al. 1975), depending on the solids content of the ash slurry and whether the  $SO_2$  scrubber also removes fly ash.

#### SITING CONSIDERATIONS

The siting of a coal-fired electric generating station is a complex process involving many basic social, economic, and environmental considerations and their alternatives upon which the final decision of site selection is based. The screening process for site selection should take into account numerous environmental parameters such as water availability, water quality, visual amenities, public use areas, migratory routes of important species, important habitats, etc. If the potential impacts are identified for these parameters before a site is chosen, the impacts may be mitigated by proper modifications or alterations in plans; if not, another site should be selected.

The site selection process employed by a utility places economics as the major consideration for choosing a candidate site once the need for power has been established. Costs are estimated for land acquisition, construction of the plant and ancillary facilities, and transportation and transmission corridors. The distance required to transmit the electrical energy to the demand area is also taken into consideration. The ecological implications of developing a site are given only minor consideration by a utility.

The factors discussed below do not include all parameters evaluated by the utility in their site-selection process. Only those factors are considered which deal primarily with the ecological aspects of siting. Because of regional differences which affect the importance given to these factors (e.g., water availability is of greater concern in the arid West than in the humid East), no attempt is made to prioritize the siting factors.

#### Water Availability

The primary siting consideration for a power plant regardless of fuel source is the availability of water for waste heat dissipation. This will account for the major water requirement of the plant. The amount of water needed will depend on the cooling system used, i.e., oncethrough cooling systems will require much greater amounts of water than a closed-cycle system which employs cooling towers or another offstream cooling system. The source of cooling waters may be natural lakes, rivers, or salt water. Ocean sites will obviously have sufficient water available, although salt water introduces special problems of corrosion in the cooling system. Inland sites have several options for water supplies.

A vast majority of the existing aquatic resources of the country have competing water uses. The addition of a power plant to a system which already receives industrial and municipal wastes, which has impoundments, which is subjected to navigation and dredging, and which is also managed for fish and wildlife, increases the burden to that aquatic system. It may be that the impacts associated with the individual uses are not deemed significant. However, the combined effects should be considered.

#### Land Use

The area required for siting a typical power station is a function of engineering design and generating capacity (Table 4). In addition to the buildings and ancillary facilities, the land converted to such things as access roads, parking lots, and landscaping around buildings, would be permanently disturbed (Dvorak et al. 1977). Larger stations (e.g., 2100 MWe) will obviously require more area, especially for waste disposal and coal storage. The impacts to surrounding areas originate from construction and operation of the plant, transmission lines, and transportation corridors.

Areas should be identified which are deemed ecologically unique in natural resources and may be degraded, destroyed, or made totally or partially inaccessible to important species because of construction or operation of the station. For example, certain restrictive structures, such as fences constructed around a forest site, may interfere with the movements of many of the larger mammals (e.g., deer) and in some cases cause increased mortality if adverse weather causes them to seek less favorable shelter.

Regional terrestrial data needed in considering land-use categories include evaluation of the types and extent of candidate areas, the occurrence of critical wildlife habitats within these areas, and alternatives to these areas. Some of these areas may include deciduous forests, wetlands (estuaries), and lands used for agricultural, residential, and industrial purposes; some may also be unsuitable for siting because of public interest in future use for recreational or cultural involvements. Thus, future uses for potential sites will largely depend on the existing impacts from industrial, commercial, and all other developments.

#### Waste Disposal

In coal-related energy facilities, waste streams are generated from cleaning of stack gases, collection of bottom ash, coal cleaning, and runoff from coal storage piles. Slurry and gob resulting from the cleaning of coal and the problems associated with this aspect of refuse material are limited, for the most part, to the Eastern Interior and Appalachian coal regions of the country, since most western coals are not cleaned. These waste materials can involve sizable amounts of surface land as shown in Table 4.

The geological and hydrological parameters important in minimizing impacts from waste disposal are discussed in the section on Measures to Mitigate Impacts (p. 139).

	Area requirements of coal-fired plants							
	100 MWe		350 MWe		700 MWe		2100 MWe	
Component	(ha)	(acres)	(ha)	(acres)	(ha)	(acres)	(ha)	(acres)
Coal storage, handling <sup>b</sup> Rail siding Reserve storage Live storage, crusher, surge bins	0.3 1.0 0.2	0.8 2.4 0.4	0.5 1.5 0.3	1.2 3.6 0.7	0.8 2.4 0.4	1.9 5.9 1.1	2.1 6.5 1.2	5.2 16.0 3.0
Subtotal	1.5	3.6	2.3	5.5	3.6	8.9	9.8	24.2
Power generation Boiler Turbine/generator	0.3	0.7 0.7	0.3	0.8 0.8	0.4	1.0	1.1 1.1	2.6
Subtotal	0.6	1.4	0.6	1.6	0.8	2.0	2.2	5.2
Waste heat dispersal <sup>C</sup> (Cooling towers)	1.1	2.8	3.4	8.4	6.5	16.	18.6	46.
Waste handling <sup>b</sup> Ash ponds Sludge ponds Subtotal	0.4 0.4 0.8	1.1 1.1 2.2	0.8 0.8 1.6	2.0 2.0 4.0	1.5 1.5 3.0	3.8 3.8 7.6	4.5 4.5 9.0	11. 11. 22.
TOTAL	4.0	10.0	7.9	19.5	13.9	34.5	39.6	97.4
Area permanently disturbed <sup>d</sup>	29.	71.	57.	140.	97.	240.	283.	700.

## Table 4. Approximate Area Requirements for Coal-Fired Power Plants of Various Sizes<sup>a</sup>

<sup>a</sup>Data from Dvorak et al. (1977); Montana State Dep. Nat. Resour. Conserv. Energy Plan. Div. (1974); Fed. Energy Admin. (1977a, 1977b); and staff communications with personnel of the Commonwealth Edison Co., Chicago, and the Southern Illinois Power Cooperative, Merion, Ill. Data are annual estimates. Actual values are a function of the heat (Btu/lb), sulfur, and ash content of the coals being burned.

<sup>C</sup>Where cooling lakes are used, approximately 0.4~0.8 ha/MWe (1-2 acres/MWe) is required. <sup>d</sup>Includes roads, parking areas, switchyards, landscaping, etc., not included in rest of table.

#### Coal Storage

Coal storage areas are needed to maintain a continuous supply between shipments. Although the problems associated with the storage of coal will probably not have significant bearing on siting, prior regards for loss of terrestrial habitat and the potential impacts of dust generation, especially in arid regions, should be considered. Dusting of surrounding vegetation reduces palatability of forage to animals and retards vegetative growth. The process of selecting a site for coal storage piles should include an assessment of potential impacts to the surrounding area from surface-water runoff.

#### Airborne Effluents

Atmospheric dispersion considerations are also important to the siting of power plants because of the effects of airborne effluents on local climate and air quality. Sulfur dioxides, particulates, and trace elements can, in increased amounts, affect both terrestrial and aquatic ecosystems. Stack height and diameter, topography, and the meteorology of the site influence the ultimate ground-level concentrations of these stack-gas effluents. The effects of these four parameters on atmospheric dispersion are discussed in the section on Dispersion of Combustion Emission Products (p. 33).

#### Terrestrial Ecosystems

One of the major issues which must be evaluated during the siting process is the potential terrestrial impact that may occur during station construction and operation. Impacts to terrestrial ecosystems include a reduction or loss in carrying capacity, destruction or modifications of food webs, changes in population densities, and losses or changes in habitat (U.S. Nucl. Reg.

Comm. 1975). In general, animal populations which are stable have the appropriate reproductive capacities to withstand losses of a few individuals without drastic changes in overall population densities. However, if these losses become too great, shifts in the community structure may become prevalent and stability is lost. Structures which would result in restricting or limiting the use of foraging areas by wildlife should also be evaluated. The size of the feeding territory both onsite and offsite, the food availability and usage relative to the plant site, and access roads and other pertinent physical structures all warrant consideration.

The growing public concern about the large numbers and diversity of life forms dependent on wetlands, especially on the role of wetlands as nurseries for aquatic fauna, has stimulated fears that the destruction of wetlands might have very far-reaching consequences, not only for such "quality of life" factors as diversity of species but also for key processes essential to the survival of the overall ecosystem itself (Ramsay and Reed 1974). Many coastal states have passed laws to protect exploitation of wetlands and have also established land-use regulations to control any alteration of wetland usage. It is widely believed that wetlands, among other attributes, also provide natural cushions which help to mitigate the effects against floodings.

The Middle Atlantic states region--including New Jersey, Pennsylvania, Delaware, Maryland, Virginia, West Virginia, Ohio, and the District of Columbia--is the area of the largest estuaries in the United States. Waterfowl dependence on the estuarine environment is varied. Species such as mallards and canvasbacks have adapted to some of the man-made environmental changes and have survived them with no ill-effects to their nesting sites. These waterfowl and other species such as geese, coots and swans winter on the salt marshes from New York to North Carolina each year (Clark and Brownell 1973). They rely on a healthy marsh environment for food sources, which include aquatic plants, fish, insects, and various other nutritives found in this environment. Shore and sea birds are more dependent upon estuarine conditions, and have shown in the past a high degree of sensitivity to any changes in the estuarine environment.

#### Aquatic Ecosystems

<u>Natural lakes</u>. Many power plants have been sited on large natural lakes. Factors to be considered for lake sites are the volume of the lake relative to the amount of water required for plant operation. Reductions in the volume of the lake will have several impacts to aquatic biota: (1) lake drawdown will reduce the volume and quality of aquatic habitat available to biota; pelagic species will become more concentrated, and species interactions will be increased due to a reduction in carrying capacity and the volume of the system, and (2) the location of the littoral zone will change. Although this effect may not be serious in lakes which occupy gradually sloping basins, in lakes with limited shallow areas which then drop steeply, the littoral zone may be greatly reduced. The littoral zone is highly productive in terms of aquatic macrophyte growth and associated epiphytes and invertebrates, and reduction of the littoral zone can have significant effects on the biota of this type of lake.

Cold-water fish species (salmonids) could be adversely affected by drawdown whereas warmwater species (bass) may be benefited. Drawdown has been used as a management technique for enhancing bass populations in many impoundments. Temporary drawdown displaces small prey species from refuge areas afforded in the littoral zone. Because available plant cover is reduced, prey species are more susceptible to predation. Reestablishing predrawdown water levels stimulates production and, in many cases, improves both fish production and yield (Wegner and Williams 1974). Cool-water percids (yellow perch, walleye, and sauger) occupy intermediate habitat between the shallow littoral zone and the deep profundal zone (Kitchell et al. 1977). Displacement or elimination of this sublittoral area would reduce the populations of these species.

<u>Estuaries</u>. The major siting consideration for power plants on estuaries is with regard to location of cooling-water intakes and discharges. Estuaries are utilized by many resident fish species as well as migrants and are very productive aquatic systems. Although this report does not address the impacts from cooling-water systems, other effects of plant construction and operation can impact fish species of estuaries, i.e., discharges from solid-waste-disposal areas, coal storage-pile runoff, and siltation.

The dominant physical feature of an estuary is the tidal cycle. The intrusion of usually colder, denser salt water into a freshwater system provides unique conditions for many species. The major estuarine systems on the East Coast are Long Island Sound, Hudson Bay, and Chesapeake Bay. The Sacramento-San Joaquin and Columbia river areas are the major estuaries on the West Coast. These systems are major resources for both sport and commercial fisheries.

The site selection process should consider the life history requirements of the major aquatic species, primarily with respect to spawning and nursery areas. Many of the species, e.g., striped bass and oysters, have either spawning or developmental requirements which are associated with salinity gradients. Some species utilize estuaries as feeding grounds, preying upon other species which reproduce in estuaries or fresh water. Such associations are known--i.e., bluefish and menhaden, and striped bass and alewife--and timing of presence and locations of these species in various estuaries have been documented.

<u>Rivers</u>. The important physical feature of a river is that the water mass present in a given area at any time flows through that area. Any change in water quality from additions, such as silt from construction runoff or discharge effluents, is constantly being diluted and the additions carried downstream by the river. The potential impacts downstream from a proposed site should be evaluated as part of the siting criteria. The majority of the large rivers in the United States are not, however, free-flowing. Many impoundments have been created primarily for flood control and navigation.

Increased electrical demand within a geographical region may necessitate siting of power plants on smaller rivers. In order to meet water requirements, construction of impoundments or reservoirs may be necessary. The construction of an impoundment can have significant effects on the river system, both upstream and downstream of the dam. Construction impacts include siltation and habitat destruction. Once the dam is built and the pool allowed to fill, a new set of impacts will occur. The dam itself forms a physical barrier which blocks the movement of fish and invertebrates. The life cycles of migrant fish such as forage species (suckers and minnows) and game species (salmonids) can be interrupted. When this occurs, the populations of these and other species with similar life cycles could be impacted by reduced recruitment.

Above the dam, the lotic habitat (riverine) has been replaced by lentic habitat (lake). Those species which are riverine and cannot adapt to the newly formed lake environment will be replaced by more adaptable species. Fish species diversity will be initially low but will increase through time. The additional area covered by the pool introduces new substrate for invertebrate populations to colonize. The invertebrate fauna may shift from predominantly drifting types such as mayflies, stone flies, and caddis flies to more benthic and fossorial forms such as dragonflies and chironomids. Productivity of new impoundments is usually high due to the availability of inundated organic matter and the rapid population growth of species expanding into new habitat now available for colonization. The energy base shifts from predominantly allochthonous inputs, such as leaf litter, to higher levels of primary production from phytoplankton aquatic macrophytes.

Downstream from the dam, water quality will usually improve because the impoundment serves as a settling basin for suspended matter carried by the river (Neel 1963). The water velocity entering the impoundment is reduced, thereby reducing the sediment-load carrying capacity of the water. Water discharged from the impoundment is therefore usually less turbid than water entering the impoundment.

Temperature of discharge water will depend on the type and location of the dam discharge structure, i.e., whether water is discharged from the surface over a spillway or from depth through gates. In the former case, water temperatures will be warmer in summer and cooler in winter whereas if discharged from depth, the reverse will occur. Although the thermal requirements for survival, growth, and reproduction differ among species, a change in the thermal regime of a river can cause changes in the species composition of the downstream community (Lehmkuhl 1972; Spence and Hynes 1971a, 1971b).

The source of organic matter to the river downstream will change from a detritus/terrestrialinput/invertebrate-drift system to an autotrophic-plant/phytoplankton-export system. The impoundment pool will provide a large water volume, increased water temperature, and longer water residence time--all of which will promote planktonic algal growth. Export of planktonic biomass can cause a change in the trophic structure of the river downstream. River detritivores and those invertebrates and vertebrates which are part of a detritus-based trophic structure will no longer be supplied with particulate detrital inputs from upstream due to sedimentation in the impoundment. Instead, increased planktonic input will dominate. Those species which can utilize this food source will increase while the original trophic structure will change in response.

The overall effect of an impoundment on the river downstream will be similar to the effects of mild organic pollution (Spence and Hynes 1971a). Increasing organic matter supplies, changing thermal regimes, and stabilization of discharge will all have consequences on the river biota. The addition of a coal-fired power plant which will utilize the impoundment as a cooling lake and as receiving waters for discharges will further compound the impact of the impoundment.

<u>Artificial lakes</u>. An alternative to siting power plants on existing aquatic resources is the construction of an artificial lake. The use of the lake would be primarily to provide cooling water. However, many artificial lakes are multipurpose in that they provide an additional resource for aquatic sports and fish and wildlife. Implementation of this alternative has both positive and negative attributes. Although a new aquatic resource is generated, terrestrial habitat is lost with consequential impacts to the terrestrial system. Usually an artificial lake would be selected as a water source where existing water resources are insufficient to supply the water requirements of the plant. In such instances, the overall effect of adding a new aquatic resource for the region may be beneficial as long as multiple use is possible. Lack of sufficient surface water for plant operation also suggests that groundwater resources are valuable, and impacts from reduction of groundwater supplies should be investigated.

#### REFERENCES

Armento, W. J. 1975. Effects of Design and Operating Variables on  $NO_X$  from Coal-fired . Furnaces - Phase II. EPA-650/2-74-002-b; PB 241283. Prepared by Babcock and Wilcox Co. for the U.S. Environmental Protection Agency, Office of Research and Development.

- Babcock and Wilcox Co. 1972. Steam, Its Generation and Use, 38th ed. New York. 1 v. (various pagings).
- Brown, R. A., H. B. Mason, and R. J. Schreiber. 1974. Systems Analysis Requirements for Nitrogen Oxide Control of Stationary Sources. EPA-650/2-74-091; PB 237 367. Prepared by Aerotherm/Acurex Corp. for the U.S. Environmental Protection Agency, Office of Research and Development. 165 pp.
- Clark, J., and W. Brownell. 1973. Electric Power Plants in the Coastal Zone: Environmental Issues. American Littoral Society Spec. Publ. No. 7. The Striped Bass Fund, Baylon, N.Y., and the American Littoral Society, Highlands, N.J. 1 v. (various pagings).
- Commerce Technical Advisory Board Panel on Sulfur Oxide Control Technology. 1975. Report on Sulfur Oxide Control Technology. Prepared for the U.S. Department of Commerce, Washington, D.C.
- Cooper, H. B. 1975. The ultimate disposal of ash and other solids from electric power generation, pp. 183-195. <u>In</u> E. F. Gloyna, H. H. Woodson, and H. R. Drew (eds.), Water Management by the Electric Power Industry. Water Resources Symposium No. 8, Center for Research in Water Resources, University of Texas at Austin.
- Dvorak, A. J., et al. 1977. The Environmental Effects of Using Coal for Generating Electricity. NUREG-0252. Prepared by Argonne National Laboratory, Argonne, Ill., for the U.S. Nuclear Regulatory Commission. 221 pp.
- Federal Energy Administration. 1977a. Environmental Assessment, Lawrence Generating Station, Kansas Power and Light Company, Power Plants 3, 4 and 5. FEA/G-77-150. 99 pp.
- Federal Energy Administration. 1977b. Draft Environmental Impact Statement, McManus Generating Station, Georgia Power Company, Power Plants 1 and 2. FEA/G-77-147. 202 pp.
- Gottschlich, C. F. 1968. Source control by electrostatic precipitation, pp. 437-456. <u>In</u> A. C. Stern (ed.), Air Pollution, 2nd ed. Vol. III, Sources of Air Pollution and Their Control. Academic Press, New York.
- Herlihy, J. 1977. Flue Gas Desulfurization in Power Plants, Status Report. U.S. Environmental Protection Agency, Division of Stationary Source Enforcement, Office of Enforcement, Washington, D.C. 1 v. (various pagings).
- Kitchell, J. F., M. G. Johnson, C. K. Minns, K. H. Loftus, L. Greig, and C. H. Olver. 1977. Percid habitat: the river analogy. J. Fish. Res. Board Can. 34:1936-1940.
- Lehmkuhl, D. M. 1972. Change in thermal regime as a cause of reduction of benthic fauna downstream of a reservoir. J. Fish. Res. Board Can. 29:1329-1332.
- Locklin, D. W., et al. 1974. Power Plant Utilization of Coal, a Battelle Energy Program Report. Battelle-Columbus Laboratories. 96 pp. + App. (mimeo).
- Montana State Department of Natural Resources and Conservation, Energy Planning Division. 1974. Draft Environmental Impact Statement on Colstrip Electric Generatings Units 3 & 4, 500 Kilovolt Transmission Lines and Associated Facilities. Volume One, Summary. Helena, Montana. 368 pp.

National Coal Association. 1976. Steam Electric Plant Factors. Washington, D.C. 128 pp.

- Neel, J. K. 1963. The impact of reservoirs, pp. 575-593. <u>In</u> C. G. Frey (ed.), Limnology in North America. University of Wisconsin Press, Madison.
- Ottmers, D. M., Jr., P. S. Lowell, and J. G. Noblett. 1975. Energy and water requirements for air quality control, pp. 358-370. <u>In</u> E. F. Gloyna, H. H. Woodson, and H. R. Drew (eds.), Water Management by the Electric Power Industry. Water Resources Symposium No. 8, Center for Research in Water Resources, University of Texas at Austin.

Parker, F. L., and P. A. Krenkel. 1969. Thermal Pollution: Status of the Art. Report No. 3. Department of Environmental and Water Resources Engineering, Vanderbilt University, Nashville, Tenn. 1 v. (various pagings).

- Pedroso, R. I. 1976. An update of the Wellman-Lord flue gas desulfurization process. Presented at the EPA Flue Gas Desulfurization Symposium, New Orleans, March 1976.
- Ramsay, W., and P. R. Reed. 1974. Land Use and Nuclear Power Plants, Case Studies of Siting Problems. WASH-19. U.S. Atomic Energy Commission, Directorate of Regulatory Standards, Washington, D. C. 58 pp.
- Shields, C. D. 1961. Boilers: Types, Characteristics, and Functions. F. W. Dodge Corp., New York. [As cited in Univ. Okla. Sci. Public Policy Prog. (1975).]
- Shimizu, A. B., R. J. Schreiber, H. B. Mason, G. G. Poe, and S. B. Youngblood. 1975. NO<sub>X</sub> Combustion Control Methods and Costs for Stationary Sources, Summary Study. EPA-600/2-75-046; PB 246730. U.S. Environmental Protection Agency, Washington, D.C. 104 pp.
- Southern Research Institute. 1975. Survey of Information of Fine-Particle Control. EPRI-259; PB 242 383. Prepared for the Electric Power Research Institute, Palo Alto, Calif.
- Spence, J. A., and H. B. N. Hynes. 1971a. Differences in benthos upstream and downstream of an impoundment. J. Fish. Res. Board Can. 28:35-43.
- Spence, J. A., and H. B. N. Hynes. 1971b. Differences in fish populations upstream and downstream of a mainstem impoundment. J. Fish. Res. Board Can. 28:45-46.
- U.S. Atomic Energy Commission. 1974. Draft Environmental Statement: Liquid Metal Fast Breeder Reactor Program. U.S. Government Printing Office, Washington, D.C. 4 v.
- U.S. Energy Research and Development Administration. 1975. Baseline Data Environmental Assessment of a Large Coal Conversion Complex. R & D Report No. 101, Interim Report No. 1, Volume 22. Report No. FE-1508-TI (Vol. 2). 128 pp.
- U.S. Nuclear Regulatory Commission, Office of Standards Development. 1975. Regulatory Guide 4.7, General Site Suitability Criteria for Nuclear Power Stations. Revision 1. Washington, D.C. 30 pp.
- University of Oklahoma, Science and Public Policy Program. 1975. Energy Alternatives: A Comparative Analysis. U.S. Government Printing Office, Washington, D.C. 1 v. (various pagings).
- Wegner, W., and V. Williams. 1974. Fish population responses to improved lake habitat utilizing an extreme drawdown. Proc. 28th Annu. Conf. Southeast. Assoc. Game Fish Comm. 24 pp.
- Yeager, K. E. 1975. Stacks vs. Scrubbers. Report FF-3. Electric Power Research Institute, Palo Alto, Calif.

#### FEATURES OF COAL-FIRED ELECTRIC GENERATING STATIONS THAT POSE POTENTIAL IMPACTS TO THE ENVIRONMENT

The features of a coal-fired power plant that are described in this section (1) pertain to an operating plant (i.e., construction impacts are not covered), and (2) exclude the indirect aspects of the coal cycle, i.e., mining and transportation. The exception to the latter is coal slurry pipelines which are described because of their uniqueness and the proposed developments for this mode of coal transportation in the future.

#### COAL SLURRY PIPELINES

Coal slurry pipelines provide a means whereby coal is pumped in the form of a slurry (pulverized coal and water of approximately equal proportions by weight) and transported directly from a mine to a power plant through an underground, welded-steel piping system. Currently, most mined coal is shipped to generating stations via rail and/or barge. By the 1980's, some 180 million MT (200 million tons) of coal will be produced annually from western coal mines, compared with 70 million MT (75 million tons) mined in 1975. Much of this coal will be used 1300 to 2400 km (800 to 1500 mi) from the mine (Ross and Martinka, 1975). Coal slurry pipelines may thus become an alternative for transporting some of this coal since one of the major advantages of coal slurry pipelines is that under some circumstances they are more economical than rails for long-distance, high-volume transportation (Campbell and Katell 1975).

To date, only two coal slurry pipelines have operated in the United States. The first was a 174-km (108-mi), 25.4-cm (10-inch) diameter pipeline running from Cadiz to Eastlake Station, Ohio, that operated from 1957 to 1963. This pipeline ceased service due to the advent of the coal unit trains which became more economical for short distance hauls (Campbell and Katell 1975). The second pipeline is the Black Mesa pipeline which began operation in 1970. The Black Mesa pipeline extends 439 km (273 mi) from the Peabody Black Mesa Mine near Kayenta, Arizona, to the 1500-MW Southern California Edison Mohave Power Station near the southern tip of Nevada. This pipeline is currently operational and is the only means used for delivering coal to the generating station. It has the capability of delivering 5 million MT (5.5 million to the (660 MT (660 tons) per hour], requiring some four billion liters (one billion gallons) of water per year (Ross and Martinka 1975).

The major obstacles in the construction of other coal slurry pipelines are securing water rights and, more importantly, the acquisition of rights-of-way. Right-of-way widths range from 15 to 30 m (50 to 100 ft), requiring approximately 1.5-3 ha/km (6-12 acres/mi) (Bisselle et al. 1975). A 1600-km (1000-mi) long right-of-way can include 2,400-4,800 ha (6,000-12,000 acres) pf land. Four major pipelines proposed or in the planning stage are:

Colorado to Texas - 1770 km, 45.7-cm pipe, 6.4 million MT/year capacity (1100 mi, 18-inch pipe, 7 million tons/year capacity)

Wyoming to Arkansas - 1650 km, 96.5-cm pipe, 23 million MT/year capacity (1030 mi, 38-inch pipe, 25 million tons/year capacity)

Utah to Nevada - 290 km, 61-cm pipe, 9 million MT/year capacity (180 mi, 24-inch pipe, 10 million tons/year capacity)

New Mexico to Arizona - 290 km, 40.6-cm pipe, 3.6 million MT/year capacity (180 mi, 16-inch pipe, 4 million tons/year capacity)

If the above pipelines are constructed, slurry pipelines will account for  $\sim$  5% of the coal transported in the United States (Ross and Martinka 1975).

Major components of a slurry pipeline consist of a slurry preparation plant, the pipeline and associated pumping stations, and a slurry dewatering plant which removes water from the slurry leaving a filter cake of coal which is dried and then burned in the generating station. At the coal-slurry preparation plant, the coal is received, cleaned (if necessary), crushed to a 5.1-cm (2-inch) diameter, and held in storage tanks. The coal is then brought from storage and undergoes a series of size reductions by grinding to a final consist size (particle size) of  $\leq$  1 mm (Thompson and Wasp 1971). The slurry water, approximately 50% by weight, is also added during the final grinding stages. Chemical treatment may be employed after grinding to improve slurry characteristics. The coal slurry is then conveyed to agitated storage tanks prior to pumping (Cowper et al. 1972). These steps are associated with the preparation of lowash, low-sulfur coals for slurry transport. For transporting high-ash coal by slurry, a coalwashing step prior to grinding may be needed (Gold et al. 1977). In addition to crushers and grinders, the slurry preparation facility contains water storage ponds which serve as backup sources for slurry-water processing and transport, and a dump pond to serve as a reservoir for any slurry imperfections (this water can be recycled as a slurry water source) (Bechtel Corp. 1974). The quantity of water needed to pump 9 million MT/yr (10 million tons/yr) ranges from 7 million m<sup>3</sup> or 6000 acre feet (Bechtel Corp. 1974) to 9 million m<sup>3</sup> or 7500 acre feet (Freudenthel et al. 1974). Water to be used for slurry must have less than 100 ppm of dissolved solids to assure marketability of coal (Freudenthel et al. 1974).

The slurry is pumped through the pipeline, which is buried to a depth of 0.8 to 0.9 m (2.5 to 3 ft) underground (Aude et al. 1974), under pressure, e.g., 6,900 to 10,300 kPa (1000 to 1500 psi) for the Black Mesa pipeline (Montfort 1972), at about 1.5 m (5 ft) per second. Pumping stations are required at intervals of every 97 to 129 km (60 to 80 mi), depending upon terrain, to maintain flow rates above critical velocities that will prevent separation and deposition of coal from the slurry. Each pumping station requires a water storage pond with the capacity to hold 1.25 times pipeline volume to the nearest downpipe pumping station and a slurry storage pond capable of holding at least 1.25 times the pipeline volume to the nearest up-pipe pumping station. These ponds [approximately 20 ha (50 acres) each] are necessary to store slurry, when the pipeline is flushed during emergency shutdowns, to prevent the coal from settling out of suspension and collecting in the bottom of the pipes (Bechtel Corp. 1974). It should, however, be noted that one significant property of slurries is that they are designed to settle in the pipeline in such a manner that they can be restarted (Aude et al. 1974). Automated communication systems run the length of the pipeline to facilitate normal operation and/or emergency shutdowns (Bechtel Corp. 1974).

The slurry received at the dewatering facility is initially delivered to agitated storage tanks; e.g., for the Black Mesa pipeline, 30-million-liter (7.8-million-gallon) storage tanks receive the slurry (Montfort 1972). The slurry dewatering facility can make use of centrifugation, vacuum filtration, and/or thermal drying methods to produce a filter cake of coal from slurry (Wilson and Miller 1974). Spent water from the dewatering process can be used for makeup water for the generating station, and/or will have to be stored in evaporation ponds or treated and discharged into receiving waters. The filter cake is sent to dryer feed bins, then to dryers, and finally to a coal storage area (Bechtel Corp. 1974).

#### COAL CLEANING AND STORAGE

#### Coal Cleaning

Newly mined or raw coal frequently contains high percentages of sulfur and unwanted noncombustible materials (ash), and is therefore often mechanically cleaned (prepared) to reduce the concentrations of these substances. Cleaning increases the uniformity of the chemical and physical properties of coal (Wolfson 1968). Cleaning also reduces the quantity of particulates in flue gases (Walker 1975), increases the heating value, and reduces the sulfur content of the coal, thereby improving its properties and reducing sulfur dioxide emission during combustion.

The amount of waste material may be particularly high in deep-mined coal excavated by continuous mining machines, which fail to discriminate between coal and roof or bottom slate (Schmidt 1975). Cleaning is therefore commonly practiced for deep-mined coal, and on a much more limited basis for strip- and auger-mined coal (Deurbrouck 1974; Anderson et al. 1968). Practically all anthracite is cleaned, but this represents a small fraction of coal production. Bituminous coals account for perhaps 95% or more of cleaned coal production, with only small amounts of subbituminous coals and practically no lignite being cleaned (Yancey and Geer 1968).

Cleaning at the mine site prior to shipping often presents less of a waste-disposal problem than at the point of use. In addition, removal of noncombustible materials from coals before shipment reduces transportation costs (Walker 1975). However, if a coal-fired power plant is adjacent to the mining operation (mine-mouth facility), coal-cleaning equipment may be a part of the ancillary facilities of the power plant.

<u>Coal washability</u>. Washability refers to the potential for reducing sulfur and ash components of a coal by cleaning. The fraction removable varies and depends upon the chemical and physical forms of the impurities and the acceptable percentage of coal losses during the cleaning process.

The sulfur content of U.S. coals is in the range of 0.2 to 7.0% by weight, with the average between 1.0 and 2.0% (Walker 1975). Sulfur occurs in coals as organic compounds, sulfates, and pyritic materials (Walker and Hartner 1966). Organically bound sulfur is an integral part of
the coal's organic matrix and therefore is not removed by conventional cleaning processes; it is generally the dominant form in low-sulfur coals (Walker and Hartner 1966). Sulfur also occurs in coals as calcium and iron sulfates, but generally these forms amount to less than 0.05% of unweathered coals, an insignificant quantity (Walker and Hartner 1966). Pyritic sulfur is present in the form of the minerals pyrite and marcasite (both FeS<sub>2</sub>) in a wide range of particle sizes. Sulfur in this form may be removed by conventional cleaning processes. The fraction removed depends upon the particle size distribution; large particles are most easily removed (Walker and Hartner 1966).

Since the removable sulfur fraction is concentrated in high-density pyritic minerals (the specific gravity of pyrite is about 5.0, compared to 1.7 or less for coals) (Cavallaro et al. 1976), the same cleaning practices used for sulfur reduction also reduce ash.

Trace elements may be associated with either the organic coal fraction or with minerals which are included in the coal in particulate form. The potential for reduction of an element's concentration by normal coal washing processes depends upon its association with a mineral with sufficiently high specific gravity to permit separation. Data on the washability of trace elements are scarce, but some work by the Illinois State Geological Survey (Ruch et al. 1971; Gluskoter and Lindahl 1973; Ruch et al. 1974) suggests that the concentrations of many of these elements may be reduced by conventional cleaning processes. However, because there are so few data, it is difficult to make quantitative determinations of trace-element reductions during cleaning.

Regional data on coal washability obtained in float-sink tests on crushed coals are summarized in Table 5. The data are based upon 195 coal samples from the Northern Appalachian Region, 13 samples from the Southern Appalachian Region, and 82 samples from the Eastern Interior Region.

Approximately two-thirds of the total sulfur in Northern Appalachian coals is pyritic, and pyritic sulfur reductions of 56% and 75% were obtained, with clean coal yields of 90% and 60%, respectively. The corresponding reductions in total sulfur were 33% and 46%. Data are not presented on washability of Southern Appalachian coals since their pyritic sulfur content is so low that cleaning would be of only small benefit. Eastern Interior coals have higher pyritic sulfur content, and cleaning results in sizable sulfur reductions, although decreases are somewhat lower on a percentage basis than for Northern Appalachian coals.

Coals vary in washability within a bed and between beds, and the data presented in Table 5 represent averages for the regions described. In particular, coals from the Pittsburgh bed in the Northern Appalachian Region and the Kentucky No. 9 bed in the Eastern Interior Region have high organic sulfur contents, so that total sulfur remains high even with good pyritic sulfur removal (Research and Education Association, 1975).

<u>Cleaning methods</u>. Most conventional cleaning methods make use of the fact that slate, rock, and sulfur-containing pyrites and marcasites have higher specific gravities than coal, and the methods employ centrifugal force or gravity to separate these wastes from the coal.

Since mechanical cleaning methods are based on the principle of separation of coal particles from particles of impurities, the coal is first crushed to free the waste matter from the coal matrix. This is often followed by screening, which separates the coal into size fractions; each size fraction is then diverted into individual cleaning units. When the friability of coal and waste differ sufficiently, rough cleaning may be achieved at the screening stage by rejection of the oversize impurities (Palowitch and Deurbrouck 1968).

Disposal of cleaning wastes. The amounts of waste vary with the type of coal cleaned and the degree of treatment employed, but they are generally large. In 1973, 361 million MT (398 million short tons) of bituminous coal and lignite were mechanically cleaned in the United States, yielding 262 million MT (289 million tons) of product and 99 million MT (109 million tons) of refuse. Thus, the average yield of the cleaning processes was 73%, with the remaining 27% of raw coal disposed of as waste.

Data on mechanical cleaning of U.S. lignite and bituminous coals are presented in Table 6. These data indicate that virtually all of Illinois and Indiana coal production and the major portion of Alabama's production are cleaned. Yields (clean coal tonnage/ton of raw coal), refuse generated per ton of clean coal (refuse tonnage/ton of raw coal), and ratio of refuse to clean coal for Appalachian and Eastern Interior coals are summarized in Table 7. Clean coal yields vary between 64% and 78% with a mean of 73%. Refuse generated per ton of raw coal produced varies from 22% to 36%, with a mean of 27%, and the ratio of refuse to clean coal ranged from 0.29 to 0.57 with a mean of 0.38.

The coal cleaning process removes combustible material as well as pyritic and other unwanted substances. Wastes from this process are divided into two fractions: (1) gob, rock or large-sized fragments which are denser than coal and are separated from the coal by gravity,

				Sulfur reduction obtained in washability tests for 0.95-cm (3/8-inch) top size coal					
		x.		90% y	ield <sup>b</sup>	60% y	ield <sup>b</sup>		
Coal type	Ash (%)	Pyritic S (%)	Total S (%)	Pyritic S reduction (%)	Total S reduction (%)	Pyritic S reduction (%)	Total S reduction (%)		
Northern Appalachian (Pa., northern W. Va., Ohio, Md.)	14.7	2.03	3.07	56	33	76	46		
Southern Appalachian <sup>C</sup> (southern W. Va., Va., Tenn.)	11.2	0.29	0.93	-	-	<b>-</b> 1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.	an <mark>-</mark> la an An Airte		
Eastern Interior (Ill., Ind., western Ky.)	14.1	2.29	3.92	47	23	70	39		

Table 5. Average Ash, Total and Pyritic Sulfur Content, and Washability Data for Coals from the Appalachian and Eastern Interior Regions

<sup>a</sup>From Dvorak et al. (1977). Data from Research and Education Association (1975). <sup>b</sup>Clean coal yield expressed as a percentage of raw coal. <sup>C</sup>Alabama coals are not included in these data.

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· · · ·	Total pr	oduction	Number of	Raw	Raw coal		d coal	Refuse	
State	(10 <sup>3</sup> MT)	(10 <sup>3</sup> t)	plants	(10 <sup>3</sup> MT)	(10 <sup>3</sup> t)	(10 <sup>3</sup> MT)	(10 <sup>3</sup> t)	(10 <sup>3</sup> MT)	(10 <sup>3</sup> t)
Alabama	17,445	19,230	19	16,722	18,433	10,619	11,705	6,104	6,728
Alaska	630	694	1 a <b>1</b>	64	70	45	50	18	20
Colorado	5,654	6,233	3	1,754	1,933	1,508	1,662	245	270
Illinois	55,857	61,572	36	56,596	62,386	43,627	48,091	12,968	14,295
Indiana	22,909	25,253	• 10	22,979	25,330	17,871	19,699	5,108	5,631
Kentucky (eastern)	67,101	73,966	33	27,541	30,359	20,198	22,264	7,344	8,095
Kentucky (western)	48,697	53,679	18	23,590	26,004	18,148	20,005	5,442	5,999
Ohio	41,534	45,783	17	18,869	20,799	13,234	14,588	5,635	6,211
Oklahoma	1,980	2,183	3	346	381	283	312	63	69
Pennsylvania	69,312	76,403	68	57,190	63,041	41,486	45,731	15,703	17,310
Tennessee	7,456	8,219	2	1,429	1,575	1,039	1,145	390	430
Utah	4,990	5,500	7	3,770	4,156	3,243	3,575	527	581
Virginia	30,809	33,961	32	24,094	26,559	16,054	17,696	8,040	8,863
Washington	2,966	3,270	2	4,046	4,460	2,959	3,262	1,087	1,198
West Virginia	104,733	115,448	124	97,540	107,520	68,648	75,672	28,892	31,848
Other states <sup>C</sup>	54,743	60,344	7	4,208	4,639	3,139	3,460	1,070	1,179
Total <sup>d</sup>	536,816	591,738	382	360,738	397,646	262,102	288,918	98,636	108,728

Table 6. Mechanical Cleaning at Bituminous Coal and Lignite Mines in 1973<sup>a,b</sup> 1. 40

aData (English units) from Westerstrom (1975). Data (English units) quoted directly from source. CIncludes Arizona, Arkansas, Iowa, Kansas, Maryland, Missouri, Montana (bituminous coal and dlignite), New Mexico, North Dakota (lignite), Texas (lignite), and Wyoming. Data may not add to totals shown because of independent rounding.

Table 7. Clean Coal and Refuse as Percentages of Raw Coal and Refuse/Clean Coal Ratios for Appalachian and Eastern Interior Coals<sup>a</sup>

	Clean coal as percent of raw coal	Refuse as percent of raw coal	Ratio of refuse to clean coal
Alabama	64	36	0.57
Illinois	77	23	0.30
Indiana	78	22	0.29
Kentucky (eastern)	73	27	0.36
Kentucky (western)	77	23	0.30
Ohio	75	25	0.33
Pennsylvania	73	27	0.38
Tennessee	73	27	0.38
Virginia	67	33	0.50
West Virginia	<u>70</u>	30	0.42
Average	73	27	0.38

<sup>a</sup>From Dvorak et al. (1977).

and (2) slurry, extremely small particles (fines) which are generally transported to the disposal site in slurry form and allowed to dewater in an impoundment. Gob and slurry are often disposed of separately, but may be mixed.

Most of these wastes are disposed of on or near the surface as fill in strip mine cuts, landfill, or valley fill, or are stored in surface piles.

Some cleaning wastes are disposed of locally in underground mines, but this practice is uncommon because of economic considerations, possible interference with active mining operations, and efforts to minimize worker exposure to underground health and safety hazards. For these reasons, underground disposal of coal processing wastes is practiced only when filling of voids created by mining contributes to control of ground subsidence (Falkie et al. 1974).

Coal cleaning wastes are also used to a limited extent as fill material in highway construction and for winter antiskid use on highways (Falkie et al. 1974; Butler 1974).

## Coal Storage

There are two types of coal storage: live storage and reserve storage. The live storage stockpile serves as the buffer between the furnace's continuous demand and the intermittent arrivals of bulk shipments. Reserve storage coal is held in reserve in case the periodic shipments are interrupted (by labor problems, mine disasters, derailments, or weather conditions).

Live storage. Assuming there is daily arrival of coal shipments, the minimum size of the live storage stockpile will be the amount of coal consumed per day by the plant. For a 700 MWe plant operating at 70% capacity, having a 38% efficiency, and utilizing coal with a heat content of 11,400 Btu/lb, the amount of coal required is 4200 MT/day (4630 tons/day) (see Table 2). Hence, for this plant, the minimum size of the live storage stockpile will be 4200 MT (4630 tons). At 1.1 MT/m<sup>3</sup> (1490 tons/acre foot) of coal (U.S. Bureau of Land Management 1974), this tonnage converts to 3800 m<sup>3</sup> (3.1 acre feet).

The daily coal requirements listed in Table 2 for various coal types and plant sizes are equal to the minimum tonnages of the live storage stockpiles for those types and sizes (assuming one coal shipment per day). In practice, the live storage stockpile must be larger than the coal tonnage consumed between shipments, since the shipments will not arrive at precisely the same time each day. However, the live storage stockpile should not be much larger than the minimum size, because the stored coal begins to oxidize, losing some of its heat content in the process.

The oxidation, due to contact with air, is a surface phenomenon. The oxidation produces heat which can build up and cause spontaneous combustion in the coal pile. To avoid this, the live storage coal can be kept in small piles. The high surface-to-volume ratio of small piles maximizes heat dispersal. Unfortunately, it also maximizes exposure to the air.

<u>Reserve storage</u>. The reserve storage usually consists of a 100-day supply, although minemouth plants may stockpile only a 30-day supply (Dvorak et al. 1977; U.S. Energy Res. Dev. Admin. 1975).

For the 700-MWe plant mentioned in the discussion of live storage coal, the 100-day supply would amount to 420,000 MT (463,000 tons). Coal put into reserve storage is compacted to eliminate air spaces, typically to 1.3  $MT/m^3$  (1750 tons/acre foot) (Babcock and Wilcox Co. 1972). Using this value, the 420,000 MT (463,000 tons) converts to 325,000 m<sup>3</sup> (264.6 acre feet).

Multiplying the daily coal requirement figures listed in Table 2 by a factor of 100 yields the tonnages of the reserve stockpiles for the coal types and plant sizes of that table.

The reserve stockpile must be checked periodically (usually daily) for hot spots produced by coal oxidation. Once discovered, the hot spots should be sent to the boiler; otherwise spontaneous combustion will probably occur, resulting in significant losses. Bituminous coal in reserve storage can be capped by a 0.3-m (1-ft) layer of sized lump coal over a 0.3-m (1-ft) compacted layer of fines to help seal out air (Babcock and Wilcox Co. 1972). Oxidation within the pile is thereby reduced.

## LIMESTONE PREPARATION

Crushed limestone is prepared for injection into the scrubbing stream by being mixed with water and then pulverized. The limestone is carried by conveyors from a storage pile to a silo from which it feeds into the pulverizer. Water is added to the limestone inside the pulverizer. As the pulverizer cylinder rotates, steel balls (about 75 cm in diameter) pulverize the wet limestone to about 320 mesh. The limestone slurry--a mixture of pulverized limestone and water--is withdrawn at the bottom of the pulverizer and pumped to a classifier.

separates the oversize limestone grains for return to the pulverizer. The remaining slurry is injected into the scrubbing stream as makeup slurry. This makeup slurry contains about 20% solids by weight.

#### COAL COMBUSTION WASTE PRODUCTS

# Ash Production

The production rates of bottom ash, collected fly ash, and atmospheric fly ash for each of the four model plant sizes and three standard coal types are presented in Tables 8, 9, and 10. It was assumed in calculating these data that the furnace type being used is a pulverized coal burner and that 20% of ash production appears as bottom ash, with the remaining 80% being fly ash. The electrostatic precipitator is assumed to have a 99.5% collection efficiency.

#### Trace-Element Emissions

Estimates of trace-element emission rates for a 100-MWe plant burning Eastern Interior coal are summarized in Table 11. These data are based upon trace-element contents of the coals as summarized in Table B.3 (Appendix B). The trace-element content of the coal burned in the course of a day is partitioned among bottom ash, collected fly ash, and emitted fly ash using mass balance procedures described by Klein et al. (1975a) and Gorman et al. (1976). The few studies performed concerning trace-element flow through a power plant show large variability in the fraction removed in bottom ash and collected fly ash, indicating the imprecise nature of such calculations and the need to regard them as only rough estimates.

Plant size	Western coal		North Appalachi	ern an_coal	Eastern Interior coal		
(MWe)	(MT/day)	(t/day)	(MT/day)	(t/day)	(MT/day)	(t/day)	
100	9.9	11.	6.9	7.6	12.	13.	
350	35.	39.	25.	27.	42.	46.	
700	70.	77.	49.	54.	84.	93.	
2100	210.	230.	150.	160.	250.	280.	

Table 8. Average Bottom Ash Production Rates for the Four Model Plants and Three Standard Coal Types<sup>a</sup>

<sup>a</sup>Ash, sulfur, and heat contents of these coals are given in Table 1.

## Table 9. Average Fly Ash Collection Rates for the Four Model Plants and Three Standard Coal Types<sup>a</sup>

Plant size	Western coal		North Appalachi	ern an coal	Eastern Interior coal		
(MWe)	(MT/day)	(t/day)	(MT/day)	(t/day)	(MT/day)	(t/day)	
100	40.	44.	27.	30.	47.	52.	
350	140.	150.	100.	110.	160.	180.	
700	280.	310.	190.	210.	340.	370.	
2100	830.	920.	580.	640.	1000.	1100.	

<sup>a</sup>Ash, sulfur, and heat contents of these coals are given in Table 1.

Plant sizo	Western coal		North Appalachi		Eastern Interior coal			
(MWe)	(MT/day)	(t/day)	(MT/day)	(t/day)		(MT/day)	(t/day)	
100	0.20	0.22	0.14	0.15		0.24	0.26	
350	0.70	0.77	0.49	0.54		0.84	0.93	
700	1.4	1.5	1.0	1.1		1.7	1.9	
2100	4.2	4.6	2.9	3.2	· .	5.1	5.6	

Table 10. Average Atmospheric Fly Ash Emission Rates for the Four Model Plants and Three Standard Coal Types<sup>a</sup>

<sup>a</sup>Ash, sulfur, and heat contents of these coals are given in Table 1.

# Table 11. Estimated Average Trace-Element Emission Rates by a 100-MWe Power Plant Burning the Standard Eastern Interior Coal<sup>a</sup>

	Emission rate				
Element	(MT/day)	(t/day)			
Arsenic	0.00011	0.00012 <sup>b</sup>			
Barium	0.00034	0.00037			
Boron	0.0049	0.0054 <sup>b</sup>			
Cadmium	0.000090	0.000099			
Chromium	0.00036	0.00040			
Cobalt	0.00011	0.00012			
Fluorine	0.034	0.039 <sup>b</sup>			
Lead	0.0013	0.0014			
Manganese	0.00044	0.00048			
Mercury	0.00016	0.00018			
Molybdenum	0.0014	0.0015 <sup>b</sup>			
Nickel	0.0060	0.0066 <sup>b</sup>			
Selenium	0.00031	0.00034			
Vanadium	0.00039	0.00043			
Zinc	0.00028	0.00031			

<sup>a</sup>Unless indicated otherwise, partition factors published by Klein et al. (1975a) were used.

were used. Conservative estimates of partition factors published by Gorman et al. (1976) were used for these elements. These are expected to overestimate actual emissions.

# Sulfur Oxide Emissions and Flue-Gas Desulfurization Sludge Production

The sulfur and heat contents of the standard coals for the Western (Powder River), Northern Appalachian, and Eastern Interior regions give  $SO_2$ /heat value ratios of 1.17, 3.19, and 6.14 lb SO<sub>2</sub>/million Btu, respectively. The first of these meets the USEPA New Source Performance Standard of 1.2 lb  $SO_2$ /million Btu (see Table A.1, Appendix A), whereas the remaining two do not. For this reason, further calculations for plants utilizing West Virginia coal from the Pittsburgh seam (Northern Appalachian) and Illinois coal from the No. 5 seam (Eastern Interior) will include flue-gas scrubbers in the plant configuration, whereas calculations for plants utilizing coal from the Powder River Region (Western) will not include the effects of scrubbers.

Sulfur dioxide emission rates for all combinations of model plant sizes and standard coal types are presented in Table 12. Scrubbing is assumed to remove 85% of the sulfur in the flue gases. The sulfur emission rates from the plants utilizing Northern Appalachian and Eastern Interior coals are lower than those from the plants burning Western (Powder River) coals, indicating that use of a scrubber with 85% sulfur removal efficiency reduces sulfur emission well below USEPA (1971) New Source Performance Standards for these coals.

Dlant cizo	Western coal <sup>b</sup>	Northern Appalachian coal	Eastern Interior coal		
(MWe)	(MT/day) (t/day)	(MT/day) (t/day)	(MT/day) (t/day)		
100	8.0 8.8	3.3 3.6	6.3 6.9		
350	28. 31.	12. 13.	22. 24.		
700	56. 62.	23. 25.	44. 49.		
2100	170. 190.	69. 76.	140. 150.		

Table 12. Average Atmospheric SO<sub>2</sub> Emission Rates for the Four Model Plants and Three Standard Coal Types<sup>a</sup>

Ash, sulfur, and heat contents of these coals are given in Table 1. No scrubbing assumed for this coal.

Scrubber sludge production rates for limestone and lime scrubbers at the four model plants are summarized in Table 13. The quantities given are for sludge consisting of 50% solids by weight. The values in the table were derived by reference to Figure 9, in which sludge (dry solids) production per MWe-year is plotted against the sulfur content of coal for three scrubbing

> Table 13. Average Lime and Limestone Scrubber Sludge<sup>a</sup> Produced at the Four Model Plants for Two Standard Coal Types

mil arrequirteration		Scrubber sludge produced (MT/day)						
Plant cizo	Northern A	ppalachian coal	Eastern	Interior coal				
(MWe)	Lime	Limestone	Lime	Limestone				
100	80	105	130	165				
350	280	370	455	570				
700	560	735	910	1145				
2100	1680	2205	2730	3435				

<sup>a</sup>Assumes the sludges are 50% solids by weight. The plants are assumed to use pulverized-coal furnaces having a thermal efficiency of 38% and operating at 70% capacity. Ash, sulfur, and heat contents of the coals are given in Table 1.



Figure 9. Lime/Limestone Sludge Generation from Coal-Fired Boilers. From Cooper (1975) (with permission, see credits).

agents (Cooper 1975). Values in the table were converted to 50% solids by weight and corrected to the 70% capacity factor assumed for the four model plants. The calculation is as follows:

$$\frac{\text{Ordinate value from Fig. 9 \times MWe \times 2 \times .70}}{365 \text{ days/year}} = \text{tons sludge/day}$$
(16)

To convert tons sludge/day to MT sludge/day, multiply by 0.907.

# Nitrogen Oxide Emissions

Since  $NO_X$  formation is due to the thermal fixation of atmospheric nitrogen and the conversion of chemically bound nitrogen in coal, there is no practical way to relate  $NO_X$  emissions to the type or chemical composition of the coal burned. For the purpose of calculating the amount of  $NO_X$  formed, an emission figure of 758 lb  $NO_X$  per  $10^9$  Btu of heat input has been reported for an average coal with a heating value of 11,867 Btu/lb (Brown et al. 1974). This figure does not include the effect of emission controls.

Where excess air is controlled or staged combustion is practiced, leading to a 50% reduction in  $NO_X$  formed, the emission rate for a 1000 MWe coal-fired unit, operating at 70% capacity with a thermal efficiency of 40%, is estimated to be 27.2 tons  $NO_X/day$  (Dvorak et al. 1977). Assuming a linear relationship between plant size and  $NO_X$  emissions, and correcting for a reduction in thermal efficiency from 40% to 38%, each 100 MWe of rated capacity would result in 2.47 MT (2.72 tons) of  $NO_X$  emitted per day.

## DISPERSION OF COMBUSTION EMISSION PRODUCTS

The ground-level concentrations of pollutants emitted by a coal-fired power plant are the result of dilution of the combustion gases emitted from the stack during the time those gases travel from the stack to the ground. The variation in ground-level concentrations results from temporal and spatial variations of atmospheric conditions. The dispersion of the pollutants of interest and the ground-level concentrations that affect plants, animals, soils, and water surfaces are determined by the complex interaction of the (1) physical characteristics of the plant stack, (2) physical and chemical properties of the emitted effluents, (3) meteorological conditions at and near the site during the time the effluent travels from stack to ground-level receptor, and (4) nature of the vegetation, i.e., plant heights and density of cover, and topography of the power plant site and surrounding areas. By determining applicable values of each of these variables, estimates of ground-level concentrations resulting from plant operations can be made using suitable models.

# Stack Description

The power plant stack is a chimney, designed to remove combustion gases and entrained particles from the plant area and to inject those gases and particles into the atmosphere. Gases leave the stack with an upward velocity, and the high temperature of the gases also causes the effluent to rise until it reaches a temperature equilibrium with the ambient air. The combined effects of the effluent velocity, thermal buoyancy, and the physical stack height result in a parameter known as the effective stack height. Methods of estimating this effective stack height are available (Moses and Carson 1968; Turner 1969). Once the effluent plume leaves the stack, it begins to disperse horizontally. At times, portions of the plume can be drawn into the aerodynamic wake generated by the stack and associated buildings. During these times, an effect known as downwash occurs in which plume height is decreased as is the ultimate dilution of the effluent, resulting in increased ground-level concentrations (Strom 1976). An effluent exit velocity 1.5 times the wind speed at stack height will eliminate downwash (Am. Soc. Mech. Eng. 1973). Due to the wakes generated by other associated buildings, the stack should be 2.5 times as high above ground level as any of these buildings (Strom 1976).

The plant stack diameter and volume of gas emitted determine the velocity of the effluent as it leaves the stack, whereas the stack height determines the level of the atmosphere into which combustion gases and entrained particles are injected. By injecting the gases high into the atmosphere with high exit velocities, maximum ground-level concentrations are generally lowered, but the area affected by these lower ground-level concentrations is increased. Very tall stacks have been used in the past to reduce ground-level concentrations (Am. Soc. Mech. Eng. 1973), but recent rulings by the USEPA (Amendments to Clean Air Act, 7 August 1977--see Appendix A) no longer allow credit for large stack heights when predicting the effects of a proposed facility.

Plant stacks must be built to withstand high wind speeds, as well as the corrosive effects of the effluents. Tall stacks do have significant visual impacts, and can be hazardous to airplane traffic as well as to migrating birds (Williams and Jackson 1974).

#### Influence of Topography

The topography of the site and the surrounding areas affect the concentrations of effluents. Hills and mountains upwind of the plant site may alter the wind direction and velocity at the plant, causing downwash (see Fig. 10), whereas mountains downwind of the site may intercept a plume of concentrated effluents. Valleys and canyons influence local circulations. At night, cold air drains into valley floors, carrying plant effluents with the drainage winds as shown in Figure 11. By decreasing the circulation, valleys and river basins reduce the dilution of effluent with unpolluted air, thereby increasing concentrations throughout the valley or basin. Large bodies of water near a plant site may significantly alter circulation patterns that might not be reflected in data derived from facilities further inland. Because land and water heat differentially, diurnal variations in ground-level concentrations may result. Vegetative cover strongly influences surface heating patterns as well as channeling or blocking local wind effects. Different vegetation types also filter the air, selectively removing airborne pollutants.



VALLEY LOCATION ("WIND CROSS AXIS")

Figure 10. Terrain-Induced Aerodynamic Downwash. From American Society of Mechanical Engineers (1973) (with permission, see credits).

The primary influence of topography is upon the meteorological characteristics of the area over which the plant effluent is dispersed. Care should be exercised in comparing data from other facilities to a proposed site if differences in topography, elevation, or bodies of water exist. If great differences are noted, and no site-specific data are available, laboratory (wind tunnel) modeling can be helpful (Snyder et al. 1976; Huber and Snyder 1976; Snyder and Lawson 1976).

## Meteorological Influence

The meteorology of the site and surrounding areas ultimately determine the ground-level concentrations of the stack effluents. The wind speed, wind direction, and stability of the atmosphere all strongly influence the areas affected by the effluents and the concentrations at ground level.

The direction of the wind at and below the level of final plume rise determines the direction in which the effluent will travel. The wind direction often changes through the level of interest, thereby widening and changing the direction of travel of the plume as it disperses downward. Wind direction data are generally available as a wind rose (e.g., Fig. 12), which depicts the percentage of time the wind blows from a particular direction (Am. Soc. Mech. Eng. 1973). Drainage winds cause near-ground air to flow down into valleys or depressions, and often down the center of a valley.

The speed of the wind affects not only the travel time of the effluent from stack to ground-level reception, but also the final concentration of the effluents. Significant chemical and physical transformations may occur during the time the effluent leaves the stack, mixes with the ambient air, and reaches ground level. In addition, increased wind speed increases dilution, decreasing final concentrations. Light winds allow the plume to disperse quite slowly, and can lead to very high concentrations. Wind speed typically increases with height throughout the layer of atmosphere, and the speed increases with height more rapidly over smooth, flat, rural areas than over built-up urban areas. Wind speeds are generally slower at night than during the day, leading to higher average ground-level concentrations at night.

The turbulence of the atmosphere, which is the rapid fluctuation in the wind flow, strongly affects the ability of pollutants to mix with the surrounding air. The enhancement (or suppression) of the turbulence regime in a portion of the atmosphere is expressed by the instability (or stability) of the atmosphere. Stable air strongly suppresses vertical motions, leading to decreased dilution and, for low stacks, to higher ground-level effluent concentrations; unstable air enhances vertical motions and increases dilution. However, with tall stacks and a stable atmosphere, ground-level concentrations will be very low.

The stability of the atmosphere is generally modified by the flow of air over rough terrain and by thermal convection caused by the differences in air and surface temperatures. At night, and during cloudy days, the thermal effect is less, thereby stabilizing the atmosphere during those times. A measure of the stability is the rate of decrease of temperature with height as compared with a standard, or adiabatic (occurring without loss or gain of heat), decrease. The



# VALLEY LOCATION ("WIND ALONG AXIS")

Figure 11. Plume Trapped by Valley Drainage Winds. From American Society of Mechanical Engineers (1973) (with permission, see credits).

dispersion of effluents during periods of variable vertical temperature profiles is shown in Figure 13.

During periods of change in surface temperature or wind speeds, discontinuities in vertical temperature gradients can occur, with stable layers occurring over or under unstable layers. Because the ability of plumes to penetrate stable layers is limited, extremes in ground-level concentrations often occur during these events, as shown in Figure 14. If a stable layer forms at or near a given level, as occurs at many sites across the country, the plant should be designed so that the effective stack height is above that level.

Since wind velocity and atmospheric stability are independent parameters, joint frequencies of these variables are important in predicting impacts of proposed facilities. These joint frequencies are available for many sites from the National Climatic Center, Asheville, N. C.

Other meteorological phenomena that affect ground-level concentrations include precipitation scavenging, dry deposition, and effluent transformations. Precipitation may remove gaseous, liquid, or solid effluents from the plume, thereby reducing the pollutant source and decreasing ground-level airborne concentrations (Johnson et al. 1977). Gases may adsorb onto particulate





matter and fall from the plume to the soil or vegetative cover. In addition, other chemicals or particles in the plume or the atmosphere may react with the effluents and sunlight to form different products, or decay to stable gaseous or solid compounds. Chemical reaction times are well known for certain effluents, but may be highly variable, depending upon availability of water vapor, other chemicals, sunlight, or suitable particulates before reactions occur.

## Dispersion Analyses

Many techniques exist for predicting the dispersion of effluents (Slade 1968). By assuming uniform turbulence throughout the portion of the atmosphere through which the effluent disperses, the concentration of pollutants will be "normal," or Gaussian. By using Gaussian statistical methods, results are easily obtained for many different combinations of wind speed and direction, atmospheric stability in the horizontal and vertical planes, and effective stack heights.

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Plume Behavior During Constantly Varying Vertical Temperature Profiles (Characterized in Graphical Form at the Left of Plume Illustration). Z = vertical height above ground level; T = temperature (dashed line = standard, adiabatic decrease; solid line = actual temperature profile);  $\mu$  = wind vector. From Strom (1976) (with permission, see credits). Figure 13.



Figure 14. Plume Behavior During Discontinuous Vertical Temperature Profiles. Legend the same as for Figure 13. From Strom (1976) (with permission, see credits).

Empirical estimates of dispersion parameters for various stability classes have been made (Turner 1969), and are generally used. The general equation used in Gaussian dispersion estimate is:

$$X = \frac{Q}{2\pi\sigma_{y}\sigma_{z}^{u}} \exp\left[\frac{1}{2}\left(\frac{y}{\sigma_{y}}\right)^{2}\right] \times \exp\left[\frac{1}{2}\left(\frac{h_{e}}{\sigma_{z}}\right)^{2}\right]$$

$$X = \text{Plume concentration, } q/m^{3}$$
(17)

where

Q = Effluent emission rate, g/s

 $\sigma_{\rm o}$  = Horizontal crosswind dispersion parameter, m

 $\sigma_{\star}$  = Vertical crosswind dispersion parameter, m

u = Downwind velocity, m/s

h\_ = Effective stack height, m

y = Distance from centerline of plume, m

As wind is generally tabulated in 16 sectors (e.g., see Fig. 12), concentrations are typically calculated at various distances along these 22-1/2° radii. Wind speeds are also divided into classes, and the midpoint of the class intervals are used in the dispersion equations. All possible combinations of wind speed and direction, stability, and downwind distance are calculated, then multiplied by the percentage of time each combination is expected to occur. In order to find the total effect of all pollutant emitters (multiple sources), the concentration predicted to result from each source is calculated, and the arithmetic sum of all sources is calculated.

Dispersion models were originally developed for ground-level releases over flat terrain (Slade 1968). As concern increased regarding pollution emitted from elevated sources, modifications have been made to the original models to include the effects of elevated sources, plume rise, chemical transformations, dry deposition, precipitation scavenging, and complex terrain. Other models have been developed that track individual "puffs" of pollution through the atmosphere, allowing meteorological conditions to change during travel. Still other models have been developed to calculate concentrations resulting from multiple stack releases and plume interactions. Unfortunately, no available models can predict concentrations with great accuracy. Variations in atmospheric conditions, source characteristics, topographical influences, vegetative cover, and a host of other variables all influence dispersion and the accuracy of predicted concentrations.

Turner (1969) believes that centerline concentrations for a ground-level release are accurate to a factor of 3, but elevated stacks and uneven terrain lead to predictions that disagree with observation by even larger factors. Thus, annual average concentrations for elevated releases with climatological input data are probably accurate to a factor of 10 to 20. Under conditions of complex terrain or nonconstant emissions, concentrations are predicted with less accuracy, possibly a factor of 20 to 50 (Van der Hoven 1976). In all predictive models, accurate input data are required, along with judicious interpretation of the effects of local terrain and meteorological conditions.

#### Calculated Meteorological Dispersion of SO<sub>2</sub>, Particulates, and NO<sub>X</sub>

The short-term concentrations of  $SO_2$ , particulates, and  $NO_X$  are presented in Table 14 for the four model plants and three coal types. The values were calculated using maximum Xu/Qvalues from Turner (1969) and estimates of wind speed, stability class, and plume chosen to give maximum ground-level concentrations. These conditions may in fact last for up to three hours. To estimate 24-hr concentrations, the empirical relationships found in Montgomery and Coleman (1975) were used.

Annual average concentrations were calculated using xu/Q values from Turner (1969). Realistic values of wind speed, plume rise, frequency of wind direction, and local inversion heights were chosen to give reasonable bounds to anticipated concentrations. A stack height of 75 m was used for all calculations. Primarily due to this limitation of stack height used for calculating effluent concentrations, many of the short-tern (3-hour and 24-hour) averages exceed the National Ambient Air Quality Standards set by the USEPA (see Appendix A). However, this is an example of what may be encountered in the evaluation of an oil- or gas-fired plant (which is likely to have short stacks) that will be converted to coal combustion. If the plant being considered has or will have a stack substantially greater than 75 m, the short-term concentrations will be reduced (Lucas 1974). Each value in Table 14 is for the power plant contribution only. To estimate total ambient concentrations for a particular geographic area,

<u> </u>				$SO_2 (\mu g/m^3)$		Partic	ulates (µg/m <sup>3</sup> )	b	
Plant size (MWe)	Distance to maximum (m)	Sampling time <sup>C</sup>	Western	Northern Appalachian	Eastern Interior	Western	Northern Appalachian	Eastern Interior	<u>NO<sub>X</sub> (µg/m<sup>3</sup>)</u> All coal types
100	600	3 hours 24 hours	967 267	395 109	760 210	24 7	17 5	29 8	316 92
350	700	3 hours 24 hours	1,667 460	681 188	1,312 362	42 12	29 8	50 14	554 158
700	750	3 hours 24 hours	1,853 511	757 209	1,457 402	46 13	32 9	56 15	606 171
2100	1030	3 hours 24 hours	3,059 844	1,249 345	2,404 663	76 21	53 15	92 25	1,002 277

# Table 14. Maximum Short-Term Ground-Level Concentrations of ${\rm SO}_2,$ Particulates, and NO $_X$ from the Four Model Plants and Three Coal Types^a

<sup>a</sup>Assumes no scrubber for Western coal and 85% scrubber efficiency for Northern Appalachian and Eastern Interior coal. <sup>b</sup>Assumes 99.5% efficiency precipitators. <sup>c</sup>Data from Turner (1969) for 3-hour sampling time; data from Montgomery and Coleman (1975) for 24-hour sampling time.

local background concentrations must be added to the calculated values. Concentrations lower than the low figures and higher than the high figures are possible, but these numbers do provide realistic bounds. Because ambient air quality standards (USEPA 1971) may be exceeded by certain coal types, care in the siting of large power plants in relation to local meteorology is important.

Deposition was calculated and is based on two assumptions. All fly ash is assumed to fall within the 100 km area, and the deposition pattern exactly follows the airborne concentration pattern. The x/Q values were summed, set equal to 1, yielding normalized x/Q values. These normalized (x/Q) values were then multiplied by the fly ash released, and divided by the area of each ring, the centerpoint of which is given. These values are then expressed in terms of  $\mu g/m^2/day$ .

Short-term, annual average, and deposition calculations were made to provide the staff with realistic concentrations upon which to base other decisions. Individual plants should be examined in a case-by-case manner, and estimates of possible damage then made.

SOLID WASTE PRODUCTS FROM COMBUSTION AND EMISSION ABATEMENT

#### Introduction

Solid wastes generated by burning coal in steam electric generating stations and by pollutionabatement processes include (1) slag and bottom ash, (2) fly ash, and (3) scrubber sludge. Impacts to terrestrial and aquatic environments arise during and after disposal of these wastes, specifically due to the physical quantity and chemical quality of the wastes. In turn, the quantity and quality of the wastes produced at a given power plant will depend upon the characteristics of the coal that is burned, the type of boiler and operating conditions, and the efficiency of the particular pollution-control equipment employed. A generalized description of these wastes follows.

<u>Slag</u>. Slag (also termed "boiler slag" or "Black Beauty") is that portion of the total ash that melts to a viscous fluid at burner operating temperatures. It is usually recovered from the bottom of the boiler by tapping the slag from the furnace in a molten state into a tank of water. This produces a glassy, angular material that is predominantly one-sized, usually ranging from #30 to #4 mesh. Some coarse "clinker" is also produced, which is usually crushed to a 5-cm (2-inch) maximum size prior to disposal. This coarse fraction comprises less than 10-20% of the boiler slag. The slag may be vesicular if gasses are trapped in it as it is withdrawn from the furnace (Usmen and Anderson 1976).

Bottom ash. Bottom ash (also called "cinders") is dry ash that does not melt but is too heavy to be entrained in the flue gas. It is recovered from the bottom of the boiler through a grate into an ash hopper filled with water. Slag and bottom ash are usually combined, and together are called "aggregate." The amounts of bottom ash produced by three coal types are listed in Table 8. Slag and bottom ash comprise, in general, about 30% of the total coal ash.

If pulverized coal is burned over sinter grates, 20-25% of the total ash remains at the bottom of the furnace as dry bottom ash. Some of the bottom ash may solidify on the surfaces inside the furnace and have the appearance of boiler slag (Usmen and Anderson 1976).

Bottom ash has a coarse texture (similar to sand) and its pH can range from 6 to 11. Its uncompacted permeability ranges from about  $10^{-1}$  to  $10^{-3}$  cm/s (U. S. Dep. Agric. 1977).

<u>Fly ash</u>. Fly ash is the proportion of the total ash carried up the flue; it is assumed that  $\overline{99.5\%}$  of the ash is retained by pollution-abatement equipment. Fly ash comprises about 70% of the total ash produced at coal-burning power plants. It is similar in texture to sandy silt, with pH ranging between 6 and 11. The uncompacted permeability of fly ash is about  $10^{-3}$  to  $10^{-4}$  cm/s (U. S. Dep. Agric. 1977).

Fly ash from lignite differs in some respects from that of bituminous coal; i.e., it has a higher index of refraction, coarser particle size, and includes some free lime. The presence of the free lime gives lignite fly ash the tendency to set after being moistened, due to reactions between hydrated lime and the glassy particles (Manz 1976).

The amount of fly ash collected at each of the four model power plants is given in Table 9.

The major impacts of ash disposal (see page 109) arise in part from the chemical nature of the ash. In turn, the chemical composition of the ash will depend on the particular coal and the boiler operating conditions. In general, about 50-90% of the ash is in the glass state, with smaller quantities of quartz, mullite, magnetite, and hematite (Hecht and Duvall 1975). The major chemical constituents of coal ash are listed in Table 15 as ranges of values. A number of the trace or "heavy metal" elements found in coal ash can be deleterious to terrestrial and aquatic biota. Examples of the composition of the ash from a particular coal are given in Tables 16 and 17. The chemical constituents of coal ash can be grouped into three general

Constituents	Range (%)			
Silica (SiO <sub>2</sub> )	20-60			
Alumina (Al <sub>2</sub> O <sub>3</sub> )	10-35			
Ferric oxide (Fe <sub>2</sub> 0 <sub>3</sub> )	5-35			
Calcium oxide (CaO)	1-20			
Magnesium oxide (MgO)	0.25-4			
Titanium dioxide (TiO <sub>2</sub> )	0.5-2.5			
Potassium oxide (K <sub>2</sub> 0)	1.0-4.0			
Sodium oxide (Na <sub>2</sub> 0)	0.4-1.5			
Sulfur trioxide (SO <sub>3</sub> )	0.1-12			
Carbon (C)	0.1-20			

Table 15. Major Chemical Constituents of Coal Ash<sup>a</sup>

<sup>a</sup>From Dvorak et al. (1977). Data from Hecht and Duvall (1975).

Table 16.	Trace-Element	Constituents	of	Coal	and	Coal	Asha

Element	Coal (ppm)	Bottom ash (ppm)	Precipitator ash (ppm)
Antimony	.08	< 1.0	4.4
Arsenic	.87	4.4	61.
Barium	440.	5600.	15,000.
Beryllium	. 29	.40	5.2
Boron	37.7	83.2	1040.
Cadmium	.11	1.1	4.2
Chromium	1.8	15.6	8.9
Copper	5.2	68.	238.
Fluorine	78.5	44.6	2880.
Germanium	.48	< .1	9.2
Lead	.15	1.0	4.0
Manganese	26.2	56.7	374.
Mercury	.131	< .010	< .010
Molybdenum	.87	3.2	12.
Nickel	3.67	14.5	92.9
Selenium	. 98	.14	16.4
Vanadium	< 13.	< 100.	< 100.
Zinc	16.2	< 8.0	386.

<sup>a</sup>From Dvorak et al. (1977). Data from Holland et al. (1975). Data are for a particular batch of coal and are not necessarily representative of all coal. Sulfur content of the coal (4%) indicates use of Eastern coal.

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		Concentra	tion (ppm or as i	ndicated)	
,		<u>Units 1, 2, &amp; 3<sup>b</sup></u>		Units 4 & 5 <sup>b</sup>	
Element	Coal <sup>C</sup>	Bottom ash	Stack particulates	Bottom ash	Fly ash from precipitator
Arsenic	1.1	0.8	30	1.1	11
Beryllium	1.5	5	5	5	6
Cadmium	<]	3.2	<4	<0.7	<1.6
Chromium	4	20	20	20	60
Copper	14	57	65	53	80
Fluorine	44	· 7	900	17	100
Mercury	0.08	0.03	0.30	0.06	0.13
Manganese	40	200	200	200	300
Nickel	4	20	20	20	30
Lead	6.3	23	50	26	62
Antimony	0.13	<0.05	0.9	0.08	0.4
Selenium	2.7	0.2	27	1.5	6.6
Vanadium	20	70	60	50	200
Zinc	6	10	<10	<10	100
Silver	<0.2	<]	<1	<]	<]
Boron	80	200	300	200	700
Bismuth	<1	<10	<10	<10	<10
Cobalt	<2	<10	<10	<10	<10
Molybdenum	0.8	3	3	3	10
Niobium	<2	<10	<10	<10	<10
Tin	<0.6	<3	<3	.<3	<3
Zirconium	40	200	300	200	300
Gallium	8	30	40	30	400
Germanium	<6	<30	<30	<30	<30
Lithium	50	200	200	200	200
Strontium	40	300	300	300	500
Barium (%)	0.1	0.5	0.5	0.5	1.0
Water (wt., %)	6.0	0.2	0.2	0.2	0.2
Organic (wt., %)	72.5	0.6	1.8	0.8	1.1
Ash (wt., %)	21.5	99.2	98.0	99.0	98.5

Table 17. Trace Elements in Coal and Ashes<sup>a</sup>

<sup>a</sup>From Roffman et al. (1977).

The units refer to the five pulverized coal-burning units at the Four Corners Power Generating Plant. Units 1, 2, and 3 are equipped with scrubbers. No stack particulates could be obtained for a complete trace-element analysis since the quantity was too small. Units 4 and 5 are \_equipped with electrostatic precipitators.

equipped with electrostatic precipitators. <sup>C</sup>The coal sample was a composite of daily samples from the Navajo Coal Mine in Arizona collected during the 1973 trace-element meteorological study at the Four Corners Power Plant.

classes, as follows [the classification is based on a study of 37 elements at a particular power plant (Klein et al. 1975b)]:

- Class I. Elements that are not volatilized in the combustion zone, but instead form a rather uniform melt that becomes both fly ash and slag. These elements include Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, and Ti.
- Class II. Elements that are volatilized on combustion, and condense or adsorb on the fly ash as the flue gas cools, leading to depletion from the slag and concentration in the fly ash. These elements include As, Cd, Cu, Ga, Pb, Sb, Se, and Zn.
- Class III. Elements that remain almost completely in the gas phase. These elements include Hg, Cl, and Br.

Intermediate between Classes I and II are the elements in coal that could not definitely be assigned to either class on the basis of the data obtained in the study.

Coal ash also contains radioactive elements that were originally present in the coal. For example, fly ash collected at one station contained 30 ppm uranium and 26 ppm thorium; fly ash at another station contained 25 ppm of uranium (McBride et al. 1977). The concentrations of Ra-226, Ra-228, Th-228, and Th-232 in fly ash from a number of coal types are listed in Table 18.

		Concentration	(pCi/g dry fly ash)	
Source of coal sample	Ra-226	Ra-228	Th-228	Th-232
Appalachia <sup>b</sup>	3.8	2.4	2.6	No analysis
Utah	1.3	0.8	1.0	No analysis
Wyoming	No analysis	1.3	1.6	No analysis
Alabama	2.3	2.2	2.3	No analysis
Unidentified power plant	4.3	2.9	2.9	2.9
Hartsville power plant <sup>C</sup>	2.3	3.1	No analysis	3.1
Colbert power plant <sup>d</sup>	3.1	6.9	1.6e	6.9e
Widows Creek power plant	1.6	2.7	2.8	2.7

Table 18. Radioactivity in Fly Ash from Coal Combustion<sup>a</sup>

<sup>a</sup>Adapted from McBride et al. (1977). <sup>b</sup>Average values for samples of fly ash obtained from combustion of 6 samples of semibituminous coal from Appalachian mines. Average values for Ra-226 and Th-232 in 5 samples of fly ash; Ra-228 assumed in secular

dequilibrium with Th-232.

Average of 12 samples; Ra-228 assumed in secular equilibrium with Th-232.

One of these numbers appears to be in error. In secular equilibrium, the actitivites of Th-228 and Th-232 should be the same.

Scrubber sludge. Scrubber sludge is the waste material generated by "throw-away" flue-gas desulfurization methods, e.g., methods that employ lime or limestone scrubbing. The quantity of sludge produced at a given power plant will depend on the sulfur content of the coal and the efficiency of the scrubbers; estimates for sludge produced at the four model power plants are listed in Table 13. Lime and limestone scrubber sludges consist mainly of calcium sulfite, calcium sulfate, and calcium carbonate, as indicated in Table 19. The proportion of solids and water in the sludges can vary from 30 to 70% water by weight, depending on the process that is used for dewatering of the sludge (Table 20). The sludges are thixotropic (i.e., become fluid when disturbed, and set to a gel when allowed to stand), which is disadvantageous for most types of disposal. To overcome this property, the sludges are sometimes treated with a chemical fixative before ultimate disposal.

Scrubber sludges also contain trace elements derived from the flue gas. One study indicated that the trace-element concentration of scrubber liquors was mainly dependent on the type of coal burned, and only secondarily dependent on the type of absorbent used. The trace-element concentration measured in sludge liquor was two orders of magnitude lower than the corresponding concentrations measured in the solids (Leo and Rosoff 1976). The ranges of scrubber liquor constituents found at five power plants are listed in Table 21. Trace elements in scrubber solids and liquors, as found in another study (Cooper 1975), are listed in Table 22.

	Composition (% by	by dry weight)	
Chemical compound	Limestone sludge	Lime sludge	
CaCO <sub>3</sub>	33	5	
CaSO3•2H20	58	73	
CaSO4 • 2H20	9	11	
Ca(OH) <sub>2</sub>	0	11	

4.5

Table 19. Chemical Compositions of Lime and Limestone Scrubber Sludges<sup>a</sup>

<sup>d</sup>From Cooper (1975) (with permission, see credits).

Type of treatment	Solids content (% by weight)
No treatment	30
Pond sedimentation only	40
Pond and vacuum filtration	60
Pond and filter and centrifugation	70

Table 20. Effect of Dewatering on the Solids Content of Lime/Limestone Scrubber Sludge<sup>a</sup>

 $^{\rm a}{\rm From}$  Cooper (1975) (with permission, see credits).

Constituent	Range of concentration at potential discharge point (mg/L)
Aluminum Antimony Arsenic Beryllium Boron	0.03 to 0.3 0.09 to 2.3 < 0.004 to 0.3 < 0.002 to 0.14 8.0 to 46.
Cadmium Calcium Chromium Cobalt Copper	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Iron Lead Magnesium Manganese Mercury	$\begin{array}{cccccc} 0.02 & \text{to} & 8.1 \\ 0.01 & \text{to} & 0.4 \\ 3.0 & \text{to} & 2,750. \\ 0.09 & \text{to} & 2.5 \\ 0.0004 & \text{to} & 0.07 \end{array}$
Molybdenum Nickel Potassium Selenium Silicon	0.91 to 6.3 0.05 to 1.5 5.9 to 32. < 0.001 to 2.2 0.2 to 3.3
Silver Sodium Tin Vanadium Zinc	0.005 to 0.6 14.0 to 2,400. 3.1 to 3.5 < 0.001 to 0.67 0.01 to 0.35
Carbonate $(CO_3)$ Chloride Fluoride Sulfite $(SO_3)$ Sulfate $(SO_4)$	<pre>&lt; 1.0 to &lt; 10. 420. to 4,800. 0.07 to 10. 0.8 to 3,500. 720. to 10,000.</pre>
Phosphate (PO <sub>4</sub> ) Nitrogen (total) Chemical oxygen demand TDS Total alkalinity (as CaCO <sub>3</sub> )	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Conductance, mho/cm Turbidity, Jackson units	0.003 to 0.015 < 3. to < 10.
pH	3.04 to 10.7

Table 21. Range of Concentration of Constituents in Scrubber Liquors<sup>a</sup>

<sup>a</sup>Adapted from Leo and Rosoff (1976).

	Concentra	ation (ppm)
Element	Solids	Liquors
Aluminum (%)	>10	2.4
Antimony	0.22	<1
Arsenic	7.3	3.1
Barium (%)	0.5	<0.2
Beryllium	<5	<0.02
Bismuth	<10	<0.2
Boron	300	6.0
Cadmium	<4	4.2
Calcium (%)	≥1.0	>0.03
Chromium	20	200
Copper	57	59
Fluorine	310	4.2
Gallium	40	0.2
Germanium	<30	<0.2
Iron (%)	>1.0	<0.2
Lead	38	14
Lithium	200	2.4
Magnesium (%)	∿1	0.0001
Manganese	200	<0.2
Mercury	0.09	<0.001
Molybdenum	3	1.8
Nickel	20	<0.2
Niobium	<10	<0.2
Potassium (%)	≥1.0	0.0016
Scandium	īo	<0.1
Selenium	3.5	0.5
Silicon (%)	>10	0.0009
Sodium (%)	>1.0	>0.031
Silver	<]	0.04
Tin	400	6.0
Titanium	1.0	<0.2
Vanadium	60	<0.2
Zinc	<10	<0.2

Table 22. Trace Elements in Solids and Liquors of Scrubber Slurry<sup>a</sup>

<sup>a</sup>Adapted from Cooper (1975). Concentrations in ppm or as indicated.

The environmental impacts of power-plant waste disposal are dependent not only on the physical and chemical nature of the wastes but also on the method and site for disposal. It is not possible to describe a "typical" disposal method due to site-specific factors that determine the choice of a method. However, a description of the more common methods of disposal may prove helpful and is given below. A summary flow diagram is presented in Figure 15.

# Fly Ash and Bottom Ash Disposal

Fly ash wet-sluiced to impoundment. The prevalent method for disposal of fly ash is by wetsluicing of fly ash from electrostatic precipitators or fabric filters to onsite ash ponds. The water requirement for wet-sluicing can range from 5,000 to 165,000 L/MT (1,200 to 40,000 gal/ton) of ash (Frascino and Vail 1976). The ash pond may be lined or unlined. The usual lining material is clay; synthetic plastic or rubber liners are commercially available but there is little experience with such liners to determine efficacy in retarding seepage or long-term durability. Where artificial liners are employed, attention to proper ground preparation and liner installation appear to be essential to proper liner function (Staff 1967).

In many cases, effluent from the ash pond is discharged directly to natural surface waters. New Source Performance Standards require that there be no discharge of total suspended solids or oil and grease in fly ash transport water (see Appendix A). However, there will be <u>dissolved</u> constituents in the discharge water from ash ponds; for example, some trace elements removed from two types of fly ash by a three-day "shake" test using distilled water are listed in Table 23.



Figure 15. Flow Diagram for Power Plant Ash and Scrubber Sludge Waste Disposal.

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	Concentrat	ion (mg/L)	
Metal	Fly ash 1 (pH 11)	Fly ash (pH 4)	
Zinc	0.06	0.59	
Cadmium	0.035	0.05	
Copper	0.030	0.30	
Chromium ·	0.21	0.04	
Lead	0.75	0.25	

0.5

<0.0001

< 0.2

0.0007

Table 23. Trace Elements Released from Fly Ash Samples after a 3-day Shake Test with Distilled Water (200 grams fly ash/liter)<sup>a</sup>

<sup>a</sup>Data from Frascino and Vail (1976).

Arsenic

Mercury

A laboratory leaching study with fly ash indicated that after one month equilibration in water, there was little change in the concentrations of aluminum, calcium, cadmium, iron, phosphorus, and silicon, whereas potassium, magnesium, and sodium concentrations steadily increased. Solubilities of iron and aluminum, as expected, increased as pH decreased below pH 5 (Clapp et al. 1977).

Effluent from ash settling ponds is often at temperatures above the ambient temperature of the receiving water, particularly if blowdown from cooling towers is used for sluicing of the ash. The excess temperature over ambient will depend on a number of factors such as sluice water temperature, retention time in the ash pond before discharge to natural waters, season of the year, and meteorological conditions.

After further dewatering by natural evaporation, the fly ash is excavated and hauled offsite to a landfill area, or covered in situ with a layer of earth.

Fly ash and bottom ash combined in impoundments. Another common disposal method is to convey the fly ash pneumatically to a tank where it is mixed with bottom ash, then slurried to ash settling ponds as above. The combined ash is allowed to dewater by evaporation and/or withdrawal of supernatant liquid, and either covered in situ or excavated and hauled to an offsite landfill area.

A less common (but often more desirable) method is to collect the bottom ash separately from the fly ash. The bottom ash is then layered over the compacted fly ash. As mentioned above, bottom ash has a larger grain size than fly ash and is thus more permeable to water. When placed as a cover on compacted fly ash, it reduces runoff and wind dispersal of the fly ash.

Bottom ash separate disposal. At power plants where a large amount of bottom ash is produced, separate disposal is practiced. For example, at one operating station in Kentucky, bottom ash is continually removed and transported by a 1.6-km-long (one-mile-long) conveyor to an abandoned surface mine pit (Stainer and Jahnig 1977).

Ash disposal at mine-mouth plants. At mine-mouth power plants (and occasionally at other plants), it is convenient to deposit the ash within the mine (Ariz. Public Serv. Co. and Utah Int. Inc. 1975). The dry or dewatered ash is hauled by truck and deposited into (1) the active mine pit after the coal is removed but before the spoil from the adjacent cut is deposited, or (2) the trough areas between the rows of spoil piles. In either case, the ash is covered by spoil and revegetated.

Fly ash combined with scrubber sludge. At sites where flue-gas desulfurization is employed, the fly ash is often mixed with the lime or limestone scrubber sludge before disposal (bottom ash is either combined with the fly ash or disposed of separately). Variations of this general procedure are described below in the section on Scrubber Sludge Disposal.

Ash utilization. In 1974, 8.4% of fly ash, 20.3% of bottom ash, and 50.0% of boiler slag generated in the United States were utilized--primarily in cement mixtures, asphalt mixes, road surfacing, and miscellaneous products (Faber 1976). The use of fly ash as fertilizer has also been suggested. Coal ash can be viewed as a mineral resource, and efforts to utilize this resource are intensifying, as indicated in several references (Usmen and Anderson 1976; Hecht and Duvall 1975; Faber 1976).

#### Scrubber Sludge Disposal

<u>Sludge aeration prior to disposal</u>. The scrubber sludge may be aerated by bubbling air through the reaction tank, thereby oxidizing the sulfite to sulfate [calcium sulfite tends to form small particles that settle slowly, whereas calcium sulfate forms larger particles that settle rapidly; aeration also reduces the BOD of the effluent (Cooper 1975)]. The calcium sulfate is then precipitated by the addition of gypsum seed crystals. The solids are removed through a bleed line to a clarifier. In the clarifier, the waste solids (consisting of calcium sulfate, calcium carbonate, and some fly ash) settle out and the clarified water is returned to the process. The clarifier underflow (the waste solids) is pumped to a settling pond that may or may not be lined. At one operating station, for example, the settling pond is lined with 45.7 cm (18 inches) of clay (U. S. Dep. Army 1974).

<u>Permanent onsite pond disposal</u>. The scrubber sludge is conveyed by pipeline to an onsite pond, usually about 3 m (10 ft) deep. The sludge is allowed to settle, and the supernatant liquid is pumped back to the limestone preparation and slurry recycle tanks. The ponds may or may not be lined. As one pond fills up, another is constructed.

Temporary onsite pond disposal. The sludge is separated from the spent scrubbing liquor in large clarifiers, treated with a hardening agent, and deposited in onsite ponds. When the sludge is firm, it is excavated and hauled by truck to a permanent landfill area. At one operating power plant, for example, the permanent site for disposal is a small valley that has been used for many years for disposal of bottom ash. The hardened sludge and ash are layered by bulldozers. As portions of the valley are filled up, they are covered with earth (Herlihy 1977).

<u>Scrubber sludge combined with fly ash</u>. Scrubber sludge is combined with a fly ash slurry from the boiler and pumped to a thickener. Sludge from the thickener is mixed with a stabilizing agent and pumped to a landfill area. For example, at one operating power plant, the disposal site is a ravine, 11.3 km (7 mi) away (Herlihy 1977).

Combining fly ash or bottom ash with flue-gas desulfurization sludge is one method for improving the physical and chemical properties of the sludge for land disposal. The ash acts as a hardener and also serves to neutralize the acidity of the sludge effluent (Cooper 1975). Lime can also be added to the sludge and fly ash mixtures to promote hardening.

Sludge and fly ash combined disposal at mine-mouth plants. At mine-mouth power plants, scrubber sludge may be mixed with fly ash to produce a mixture containing 27% moisture. The mixture is then trucked to an onsite landfill area (e.g., a mine pit) and layered over previously placed ash layers. When the pit is filled, a 0.3-m (one-foot) thick overburden of earth is placed over it and graded (U.S. Bur. Land Manage. 1976).

<u>Utilization</u>. The current application of lime and limestone scrubber sludge from flue-gas desulfurization is primarily as landfill; due to the physical nature of the sludge, however, the material furnishes poor support for buildings or road foundations. New utilization methods under investigation include conversion to sulfur and calcium carbonate, as a filler and source of sulfur in fertilizers, as a source of gypsum in portland cement manufacture, and as a source of sulfur, alumina, and dicalcium silicate (Leo and Rosoff 1976).

## REFERENCES

American Society of Mechanical Engineers. 1973. Recommended Guide for the Prediction of the Dispersion of Airborne Effluents, 2nd ed. New York. 85 pp.

Anderson, J. C., J. W. Leonard, and C. T. Holland. 1968. Raw coal preparation, pp. 6-1 to 6-38. <u>In</u> J. W. Leonard and D. R. Mitchell (eds.), Coal Preparation. American Institute of Mining, <u>Metallurgical and Petroleum Engineers, New York.</u>

Arizona Public Service Co. and Utah International, Inc. 1975. Four Corners Generating Plant and Navajo Coal Mine Environmental Report.

Aude, T. C., T. L. Thompson, and E. J. Wasp. 1974. Economics of slurry pipeline systems. Presented at Hydrotransport 3, Colorado School of Mines, Golden, May 15-17, 1974. 17 pp.

Babcock and Wilcox Co. 1972. Steam, Its Generation and Use, 38th ed. New York. 1 v. (various pagings).

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- Bechtel Corporation. 1974. Draft Environmental Impact Report, Coal Slurry Pipeline. Prepared for Energy Transportation Systems, Inc.
- Bisselle, A., et al. 1975. Resource and Land Investigations (RALI) Program: An Approach to Environmental Assessment with Application to Western Coal Development. MTR-6988. Mitre Corporation.
- Brown, R. A., H. B. Mason, and R. J. Schreiber. 1974. Systems analysis requirements for nitrogen oxide control of stationary sources. EPA-650-2-74-091; PB 237367. Prepared by Aerotherm/Acurex Corp. for the U.S. Environmental Protection Agency, Office of Research and Development. 165 pp.
- Butler, P. E. 1974. Utilization of coal mine refuse in the construction of highway embankments, pp. 237-255. <u>In</u> First Symposium on Mine and Preparation Plant Refuse Disposal. National Coal Association, Washington, D.C.
- Campbell, T. C., and S. Katell. 1975. Long-distance coal transport: unit trains or slurry pipelines. U.S. Bur. Mines Inf. Circ. 8690. 31 pp.
- Cavallaro, J. A., M. T. Johnston, and A. W. Deurbrouck. 1976. Sulfur reduction potential of the coals of the United States. U.S. Bur. Mines Rep. Invest. 8118. 323 pp.
- Clapp, J. L., B. H. Murray, D. E. Willard, and O. L. Loucks. 1977. Documentation of Environmental Change Related to the Columbia Generating Station, Tenth Semi-Annual Report, Winter-Spring 1977. IES Report 82. Institute for Environmental Studies, University of Wisconsin--Madison. 348 pp.
- Cooper, H. B. 1975. The ultimate disposal of ash and other solids from electric power generation, pp. 183-195. <u>In</u> E. F. Gloyna, H. H. Woodson, and H. R. Drew (eds.), Water Management by the Electric Power Industry. Water Resources Symposium No. 8, Center for Research in Water Resources, University of Texas at Austin.
- Cowper, N. T., et al. 1972. Processing steps: keys to successful slurry pipeline system. Chem. Eng. 79(3):58-67.

Deurbrouck, A. W. 1974. Coal preparation 1973. Min. Congr. J. 60:65-67.

- Dvorak, A. J., et al. 1977. The Environmental Effects of Using Coal for Generating Electricity. NUREG-0252. Prepared by Argonne National Laboratory, Argonne, Ill., for the U.S. Nuclear Regulatory Commission. 221 pp.
- Faber, J. H. 1976. U.S. Overview of Ash Production and Utilization, pp. 5-13. <u>In</u> Ash Utilization. Proceedings of the Fourth International Ash Utilization Symposium, St. Louis, Mo., March 24-25. MERC/SP-76/4. U.S. Energy Research and Development Administration, Morgantown Energy Research Center, Morgantown, W. Va.
- Falkie, T. V., J. E. Gilley, and A. S. Allen. 1974. Overview of underground refuse disposal, pp. 128-144. <u>In</u> First Symposium on Mine and Preparation Plant Refuse Disposal. National Coal Association, Washington, D.C.
- Frascino, P. J., and D. L. Vail. 1976. Utility ash disposal: state of the art, pp. 345-368. <u>In</u> Ash Utilization. Proceedings of the Fourth International Ash Utilization Symposium, St. Louis, Mo., March 24-25. MERC/SP-76/4. U.S. Energy Research and Development Administration, Morgantown Energy Research Center, Morgantown, W. Va.
- Freudenthel, D., et al. 1974. Coal Development Alternatives, an Assessment of Water Use and Economic Implications. Prepared by the Wyoming Department of Economic Planning and Development for the Wyoming Legislative Special Subcommittee on Consumptive Water Use.
- Gluskoter, H. J., and P. C. Lindahl. 1973. Cadmium: mode of occurrence in Illinois coals. Science 181:264-266.
- Gold, H., D. J. Goldstein, R. F. Probstein, J. S. Shen, and D. Yung. 1977. Water Requirements for Steam-Electric Power Generation and Synthetic Fuel Plants in the western United States. EPA 600/7-77-037. U.S. Environmental Protection Agency, Washington, D.C.
- Gorman, P., J. Nebgen, I. Smith, E. Trompeter, and J. Galeski. 1976. Evaluation of the Magnitude of Potentially Hazardous Pollutant Emissions from Coal and Oil-fired Utility Boilers. Prepared by Midwest Research Institute, Kansas City, Mo., for Industrial Environmental Research Laboratory, Environmental Protection Agency, Research Triangle Park, N. C. 99 pp.

- Hecht, N. L., and D. S. Duvall. 1975. Characterization and Utilization of Municipal and Utility Sludges and Ashes. Vol. III, Utility Coal Ash. EPA-670/2-75-033C. U.S. Environmental Protection Agency, National Environmental Research Center, Office of Research and Development, Cincinnati, Ohio. 65 pp.
- Herlihy, J. 1977. Flue Gas Desulfurization in Power Plants, Status Report. U.S. Environmental Protection Agency, Division of Stationary Source Enforcement, Office of Enforcement, Washington, D.C. 1 v. (various pagings).
- Holland, W. F., K. A. Wilde, J. L. Parr, P. S. Lowell, and R. F. Pohler. 1975. The Environmental Effects of Trace Elements in the Pond Disposal of Ash and Flue Gas Desulfurization Sludge. Research Project 202, Final Report. Prepared by Radian Corporation, Austin, Texas, for Electric Power Research Institute, Palo Alto, California. 49 pp. + App.
- Huber, A. H., and W. H. Snyder. 1976. Building wake effects on short stack effluents. Presented at Third Symposium on Atmospheric Turbulence, Diffusion, and Air Quality, Raleigh, N.C., October. [As cited in USEPA (1976).]
- Johnson, W. B., D. E. Wolf, and R. L. Mancuso. 1977. Seasonal and annual patterns and international exchanges of SO<sub>2</sub> and SO<sub>4</sub><sup>=</sup> concentrations and deposition in Europe as simulated by the <u>EURMAP</u> model, pp. 52-63. <u>In</u> Joint Conference on Applications of Air Pollution Meteorology, Salt Lake City, Nov. 29-Dec. 2, 1977 (preprints).
- Klein, D. H., A. W. Andren, and N. E. Bolton. 1975a. Trace element discharges from coal combustion for power production. Water Air Soil Pollut. 5:71-77.
- Klein, D. H., et al. 1975b. Pathways of thirty-seven trace elements through a coal-fired power plant. Environ. Sci. Technol. 9(10):973-979.
- Leo, P. P., and J. Rossoff. 1976. Control of Waste and Water Pollution from Power Plant Flue Gas Cleaning Systems: First Annual R and D Report. EPA-600-7-76-018; PB-259 211. Aerospace Corp., Los Angeles. Prepared for U.S. Environmental Protection Agency, Industrial Environmental Research Lab, Research Triangle Park, N. C. 165 pp.

Lucas, D. 1974. Pollution control by tall chimneys. New Sci. 63(916):790-791.

- Manz, O. E. 1976. Lignite production and utilization, pp. 39-57. <u>In</u> Ash Utilization. Proceedings of the Fourth International Ash Utilization Symposium, St. Louis, Mo., March 24-25. MERC/SP-76/4. U.S. Energy Research and Development Administration, Morgantown Energy Research Center, Morgantown, W. Va.
- McBride, J. P., R. E. Moore, J. P. Witherspoon, and R. E. Blanco. 1977. Radiological Impact of Airborne Effluents of Coal-Fired and Nuclear Power Plants. ORNL-5315. Oak Ridge National Laboratory, Oak Ridge, Tenn. 43 pp.
- Montfort, J. G. 1972. Operation of the Black Mesa pipeline system. Presented at the 23rd Annual Pipe Line Conference, Dallas, April 10-12, 1972. 7 pp.
- Montgomery, T. L., and J. H. Coleman. 1975. Empirical relationships between time-averaged SO<sub>2</sub> concentrations. Environ. Sci. Technol. 9(11):953-957.
- Moses, H., and J. E. Carson. 1968. Stack design parameters influencing plume rise. J. Air Pollut. Control Assoc. 18(7):454-457.
- Palowitch, E. R., and A. W. Deurbrouck. 1968. Wet concentration of coarse coal. Part 1: dense medium separation, pp. 9-1 to 9-37. <u>In</u> J. W. Leonard and D. R. Mitchell (eds.), Coal Preparation. American Institute of Mining, Metallurgical and Petroleum Engineers, New York.
- Research and Education Association. 1975. Sulfur reduction potential of U.S. coals, pp. 1413-1422. In Modern Energy Technology, Vol. 2. New York.
- Roffman, H. K., R. E. Kary, and T. Hudgins. 1977. Ecological distribution of trace elements emitted by coal-burning power generating units employing scrubbers and electrostatic precipitators, pp. 192-215. <u>In</u> Fourth Symposium on Coal Utilization. National Coal Association/ Bituminous Coal Research, Inc.

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- Ross, B. A., and P. D. Martinka. 1975. Western coal transportation a challenge. Min. Congr. J. 61(4):40-45.
- Ruch, R. R., H. J. Gluskoter, and E. J. Kennedy. 1971. Mercury content of Illinois coals. Ill. State Geol. Surv. Environ. Geol. Notes No. 43. 15 pp.

- Ruch, R. R., H. J. Gluskoter, and N. F. Shimp. 1974. Occurrence and distribution of potentially volatile trace elements in coal. Ill. State Geol. Surv. Environ. Geol. Notes No. 72. 96 pp.
- Schmidt, R. A. 1975. Current trends in coal preparation. Coal Min. Process. 12(9):74-76.
- Slade, D. H. (ed.). 1968. Meteorology and Atomic Energy 1968. TID-24190. U.S. Atomic Energy Commission, Oak Ridge, Tenn. 445 pp.
- Snyder, W. H., and R. E. Lawson, Jr. 1976. Determination of a necessary height for a stack close to a building--a wind tunnel study. Atmos. Environ. 10:683-691.
- Snyder, W. H., R. S. Thompson, and R. E. Lawson, Jr. 1976. The EPA Meteorological Wind Tunnel: Design, Construction, and Operating Details. U.S. Environmental Protection Agency, Research Triangle Park, N.C. (in preparation). [As cited in USEPA (1976).]
- Staff, C. E. 1967. Seepage prevention with impermeable membranes. Civ. Eng. 37(2):44-46.
- Stainer, G. R., and D. G. Jahnig. 1977. Role of ponds in treatment of wastewater expands at fossil-fueled TVA plants. Power 121(7):54-58.
- Strom, G. H. 1976. Transport and diffusion of stack effluents, pp. 401-501. <u>In</u> A. C. Stern (ed.), Air Pollution, 3rd ed. Vol. 1, Air Pollutants, Their Transformation and Transport. Academic Press, New York.
- Thompson, T. L., and E. J. Wasp. 1971. Coal slurry pipelining in the western United States: Presented at the National Western Mining Conference, Denver, Feb. 5, 1971. 10 pp.
- Turner, D. B. 1969. Workbook of Atmospheric Dispersion Estimates. Public Health Serv. Publ. No. 999-AP-26. U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration, Cincinnati, Ohio. 84 pp.
- U.S. Bureau of Land Management. 1974. Proposed Federal Coal Leasing Program, Draft Environmental Statement. DES 74-53. U.S. Department of the Interior, Washington, D.C.
- U.S. Bureau of Land Management. 1976. Final Environmental Impact Statement, Kaiparowits Project. U.S. Department of the Interior, Washington, D.C.
- U.S. Department of Agriculture, Rural Electrification Administration. 1977. Merom Generating Station and Associated Transmission [Facilities], Final Environmental Impact Statement. USDA-REA-ES (ADM)-76-10-F. Hoosier Energy Division of Indiana, Statewide R.E.C., Inc., Bloomington, Ind. 514 pp.
- U.S. Department of the Army. 1974. Final Environmental Impact Statement, Sherburne County Generating Plant, Sherburne County, Minnesota. U.S. Engineer District, St. Paul, Minn. 154 pp. + App.
- U.S. Energy Research and Development Administration. 1975. Baseline Data Environmental Assessment of a Large Coal Conversion Complex. R & D Report No. 101, Interim Report No. 1, Vol. 22. Report No. FE-1508-TI, Vol. 2. 128 pp.
- U.S. Environmental Protection Agency. 1971. Standards of performance of new stationary sources. Fed. Regist. 36(247):24876-24895.
- U.S. Environmental Protection Agency. 1976. Fluid Modeling Facility. Environmental Sciences Research Laboratory, Research Triangle Park, N.C. 14 pp.
- Usmen, M., and D. Anderson. 1976. Use of power plant aggregate in asphaltic concrete, pp. 151-169. <u>In</u> Ash Utilization. Proceedings of the Fourth International Ash Utilization Symposium, St. Louis, Mo., March 24-25. MERC/SP-76/4. U.S. Energy Research and Development Administration, Morgantown Energy Research Center, Morgantown, W. Va.
- Van der Hoven, I. 1976. A survey of field measurements of atmospheric diffusion under lowwind-speed inversion conditions. Nucl. Saf. 17(2):223-230.
- Walker, F. E., and F. E. Hartner. 1966. Forms of sulfur in U.S. coals. U.S. Bur. Mines Inf. Circ. 8301. 51 pp.
- Walker, J. L. 1975. Coal is upgraded in unique preparation plant. Power Eng. 79(3):62-64.
- Westerstrom, L. 1975. Coal--bituminous and lignite, pp. 317-376. <u>In</u> Minerals Yearbook 1973. Vol. I, Metals, Minerals, and Fuels. U.S. Bureau of Mines, Washington, D.C.

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- Williams, R. E., and W. B. Jackson. 1974. Semi-annual Report, Bird Hazard Monitory Contract, Davis-Besse Site, June 1974. 1. General Observations. Environmental Studies Center, Bowling Green State University. 12 pp. (mimeo).
- Wilson, E. B., and F. G. Miller. 1974. Coal dewatering some technical and economic considerations. Min. Congr. J. 60(9):116-121.
- Wolfson, D. F. 1968. Carbonization, pp. 1-19 to 1-21. <u>In</u> J. W. Leonard and D. R. Mitchell (eds.), Coal Preparation. American Institute of Mining, Metallurgical, and Petroleum Engineers, New York.
- Woodward-Clyde Consultants. 1976. Environmental Report, Sweetwater Uranium Project, Sweetwater County, Wyoming. Prepared for Minerals Exploration Company. 1 v. (various pagings).
- Yancey, H. F., and M. R. Geer. 1968. Properties of coal and impurities in relation to preparation, pp. 1-1 to 1-56. In J. W. Leonard and D. R. Mitchell (eds.), Coal Preparation. American Institute of Mining, Metallurgical, and Petroleum Engineers, New York.

# IMPACTS OF COAL-FIRED POWER STATIONS ON FISH AND WILDLIFE

# HANDLING COAL RECEIVED VIA SLURRY PIPELINES

Coal slurry received via a pipeline is agitated in storage tanks and then sent to a dewatering facility. The filter cake (product of the dewatering process) may be stored or diverted directly to the boiler feed stream. Usually, most of the water from this process is treated and used as makeup water in the power plant cooling system. The remaining water may be treated with chemical coagulants and/or sent to evaporation ponds, depending on water clarification method(s) employed by the power plant. Water treatment involves addition of chemical coagulants, and centrifugation or filtration; the supernatant or filtrate, along with clarified water from evaporation ponds, may be discharged to neighboring water bodies--according to existing water quality standards--or routed to the power plant cooling system. In arid regions, the water in the evaporation ponds may remain contained and allowed to evaporate. The coal fines carried into the power settle out and are eventually used in the power plant.

Accidental release of slurry results in the addition of solid and liquid contaminants to soil and surface waters. Such additions can cause pH changes, introduce potentially toxic material, and, in the case of surface waters, cause increased turbidity.

Adverse impacts to aquatic organisms which may result from coal slurry spills include: deprivation of food supplies, destruction of spawning habitat, scouring of algae and benthic invertebrates from substrates, reduction of primary production, clogging of fish gills, reduced growth rates and reduced resistance to disease in fish, alterations of fish movements and migrations, change in species composition to less desirable species, and creation of large oxygen demands and/or production of toxic compounds resulting from decomposition of organic debris carried to the bottom as suspended solids (Ellis 1936; Eur. Inl. Fish. Advisory Comm. 1965; McKee and Wolf 1963; Aitken 1936; Hutchinson 1957, as summarized in Dvorak et al. 1977). Toxic trace-element effects on aquatic ecosystems are discussed thoroughly on page 88 and in Appendix D.

Effects similar to those from acid mine drainage can be expected if the slurry consists of high-sulfur coal. These effects include alteration of the quantity and quality of species composition for algae, benthic invertebrates, and fish (Cairns et al. 1971; Roback and Richardson 1969; Orciari and Hummon 1975; Archibald and Gentile 1971; Jones 1964).

Additions of coal slurry to soil will reduce soil porosity, water-holding capacity, and aeration. Low-growing vegetation such as grasses and forbs will likely be killed along with small rodents. If the spill is promptly contained and corrective measures are taken, however, these adverse effects will be localized and the impacted area is expected to recover within one to three years, depending primarily on climate. Regions of high rainfall are expected to recover sooner than arid regions.

Exposed filter-cake and refuse piles which accumulate from dewatering processes are subject to runoff and erosion by wind and water. Runoff introduces coal particles and soluble material to surface waters; windblown dust reduces air quality and can deposit on vegetation, thereby reducing photosynthesis and providing a pathway for ingestion of coal particles by herbivores. Spontaneous combustion of stored filter cake also reduces air quality.

The use of evaporation ponds as drinking water sources for wildlife has the potential for adverse effects if concentrations of particular elements exceed recommended limits (see Table 30).

## COAL CLEANING AND STORAGE

# Impacts of Coal Cleaning

<u>Terrestrial</u>. Aside from the loss of habitat due to construction of the coal cleaning facilities, potential sources of impact are the coal refuse-disposal areas and noise.

Refuse slurry ponds can provide temporary habitat for wildlife when cattails and other marsh vegetation become established around the periphery of slurry ponds; however, these areas are not likely to benefit great numbers of wildlife because of the poor water quality and increasing degradation of the habitat as the ponds fill up.

Dust associated with gob can deposit on vegetation and reduce air quality, but the magnitude of gob contribution to dust is small compared to the dust generated by the mining operation and associated activities.

The impacts of noise generated by coal preparation facilities are difficult to determine. Although considerable data are available to document the health effects of noise on people (USEPA 1971a; Kryter 1970; ReVelle and ReVelle 1974), information is generally lacking on the effects of noise on wildlife (USEPA 1971b).

The noise levels produced inside coal crushing and washing facilities will most likely exceed 70 dB during normal operation. Sound intensities at varying distances from the preparation facility will be less. Studies on laboratory and farm animals indicate that the effects of noise on wildlife can be both auditory (hearing loss) or non-auditory (stress-related) (USEPA 1971b). Physiological responses to noise have been observed with sound intensities of 120 dB or more (Bond 1971).

Noise also can be expected to interfere with animal behavior of species relying on auditory stimuli for communication (USEPA 1971b). Noise levels within 100 m of the preparation facility may disrupt the normal nesting behavior of passerine birds. Territorial defense and mate attraction may be adversely affected. Many songbirds elicit alarm calls in response to the presence of potential predators. A continuous noise level > 70 dB in the immediate vicinity of preparation facilities may reduce the effectiveness of these calls.

<u>Aquatic</u>. Oxidation of the pyrite in coal-processing wastes may create acidic drainage similar to that experienced at mines for high-sulfur coal. Drainage from some coal-refuse piles has low pH and high concentrations of sulfate and metals such as iron, manganese, aluminum, and zinc (Libicki 1977; Schubert et al. 1977). Such drainage may impair the quality of surface water and groundwater (Schubert et al. 1977) and have effects similar to those discussed in relation to runoff from coal storage piles.

Runoff and erosion from waste storage areas may also contribute a large sediment load to receiving waters, causing substrate alterations which could eliminate or modify the benthic community and impact other organisms by reducing their food supply and spawning areas.

Since coal refuse is often disposed of in natural depressions or valleys, aquatic habitat such as ponds, marshes, and streambeds may be destroyed.

The magnitude of surface-water impacts of drainage from coal refuse depends upon the quality and quantity of the effluent, the discharge and quality of the receiving stream, and the sensitivity of the biotic community to any induced water quality changes. The amount of dilution of drainage and the buffering capacity of the receiving water are of particular importance in determining water quality impacts. The magnitude of impacts to groundwater will depend upon the amount of water infiltrating from the disposal area into groundwater systems and the buffering exchange capacities of soils through which the water passes.

#### Impacts of Coal Storage Piles

<u>Terrestrial</u>. The establishment of coal storage piles initially results in losses of primary productivity and small animal habitat from the storage site. As indicated in Table 4, the area lost to storage and handling ranges from 1 to 10 ha, depending on plant size. More mobile animal species will seek habitat in areas adjacent to the storage pile, but since these undisturbed areas are very likely at their carrying capacity, the total number of individuals of a given species will be permanently reduced.

Noise generated during the unloading of unit trains or barges may affect wildlife in the immediate vicinity of the railroad spur or docking facility. Depending on the size of the coal-fired station, one or more unit trains are needed each week to supply the necessary coal. The effects of intermittent noise on animals are less severe than effects of continuous noise, as determined with captive laboratory animals (USEPA 1971b). Noise effects on wildlife, which can move away from the noise source, have not been investigated to an extent that can be used for impact assessment; familiarity with wildlife response to noise indicates that the animals will either avoid the area of activity or adapt to the noise.

Windblown coal dust from the storage piles reduces air quality and deposits on vegetation. Lerman and Darley (1975) reviewed the literature on particulate ("soot") effects on vegetation and reported that soot may plug the stomates of leaves, may lower photosynthetic activity, and cause leaf necrosis. "Soot particles" are the result of coal combustion and have different chemical and physical properties than coal dust, but effects may be similar. It can also be speculated that long-term exposure to dust may cause changes in vegetation community structure.

<u>Aquatic</u>. The major potential impacts to aquatic organisms from coal storage piles result from surface-water runoff. Runoff from coal storage piles contains coal fines and various concentrations of minerals and trace elements, including heavy metals (see the section on aquatic impacts of trace elements, p. 88). Contamination of surface waters by runoff from coal storage piles can have effects similar to those from acid mine drainage (for high-sulfur coals) or alkaline mine drainage (for low-sulfur coals). Damage to aquatic life from acid mine drainage is attributed to a combination of low pH, high concentrations of metals and sulfates, and the deposition of a smothering blanket of iron hydroxide precipitates (Herricks and Cairns 1975; Parsons 1956); impacts from alkaline mine drainage include osmotic stress, due to dissolved constituents, and sedimentation and turbidity effects from additions of solids.

# LIMESTONE PREPARATION AND STORAGE

## Terrestrial Impacts

The impacts of limestone storage on terrestrial biota are related to (1) loss of primary productivity and wildlife habitat from the areas covered with the limestone, (2) noise created at the pile during unloading, (3) dust, and (4) runoff. Of these, dust and runoff merit discussion.

The effects of limestone dust on vegetation have been studied at limestone-processing plants and cement-kilns (Brandt and Rhoades 1972, 1973; Darley 1966; Lerman and Darley 1975). (Caution should be exercised in extrapolating the results of these studies in assessing the effects of limestone dust from limestone storage piles, since limestone dust contains mostly  $CaCO_3$  whereas cement-kiln dust contains trace elements and compounds such as KC1.)

In regions of the United States where dew formation occurs and the relative humidity is high (above 60%) during much of the growing season, limestone dust can form crusts on leaf surfaces. This causes lowered photosynthetic activity and leaf mortality in severe cases (Lerman and Darley 1975). Exposure of fir trees to atmospheric concentrations of limestone dust believed to be in excess of  $1.0 \text{ g/m}^2/\text{day}$  resulted in needle retardation or death of entire twigs. The net effect was a reduction in each year's growth (Lerman and Darley 1975). Other researchers have reported no harmful effects to a variety of plants tested with cement-kiln dusts ranging from 0.75 to  $1.5 \text{ g/m}^2/\text{day}$ .

Runoff from uncovered lime or limestone storage piles introduces alkaline calcium solution to soils. In arid regions where soils are generally alkaline, additions of the alkaline solution to soils may have little effect other than displacement of sodium, magnesium, and potassium from the soil exchange complex. The presence of excess calcium can also tie up phosphate ions in the soil. These reactions can lead to potassium and phosphate deficiencies in surrounding vegetation.

In humid regions where soils are generally acid, effects of alkaline solutions can be marked. For example, the buffer capacity of the soil can be exceeded, leading to increases in soil pH. If such increases exceed the pH range of tolerance of the native species, changes in vegetation species can occur. Increasing pH also changes the availability of nutritive elements such as phosphate, iron, and manganese, leading to deficiencies of these ions in vegetation.

## Aquatic Impacts

Impacts to aquatic ecosystems associated with limestone storage and preparation are primarily related to dust and runoff inputs. These inputs could result in increases in calcium concentrations with resultant increases in water hardness, alkalinity, and total dissolved solids (TDS), and/or sedimentation and turbidity increases. Quantification of impacts cannot be determined generically since the impacts will be site-specific, depending among other things upon (1) dilution capabilities and chemistry of the receiving water, (2) size of the storage and preparation facilities, (3) containment potential for runoff and dust, (4) the intermittency of inputs, and (5) the organisms present in the receiving water.

The potential deleterious impacts to aquatic biota resulting from suspended and settled solids (turbidity and sedimentation) have previously been discussed.

Significant quantities of dust or runoff from the limestone storage and preparation facilities could increase the TDS levels of the receiving water, altering the ionic balance, and thus creating osmotic stress to the biota. Generally, freshwater organisms will not be able to tolerate osmotic concentrations much higher than that of their blood (Clarke 1974). External concentrations of "non-toxic" salts much higher than the concentration in their blood would alter the salt/water balance of the fish, resulting in adverse stress and possible death. Calcium has been reported to be toxic to fish in the range of 300 to 1,000 ppm, although for short periods of time fish have been known to tolerate 4,000 ppm (Doudoroff and Katz 1953). Zooplankton are apparently less tolerant of calcium with toxicity values ranging from 52 to 464 ppm for the cladoceran *Daphnia magna* (Biesinger and Christensen 1972; Dowden and Bennett 1965).

Although excessive levels of calcium may be toxic, additions from dust and runoff may prove to be more beneficial than detrimental. Calcium has been shown to affect the distribution of many aquatic organisms. For example, all other factors being equal, a minimum calcium concentration in the water appears essential to support the maximum number of mollusc species possible, i.e., waters with > 25 mg/L of calcium can support all molluscan species in a geographic region, and waters with lesser concentrations support fewer species (Hunter 1964). Additionally, certain levels of calcium are needed for primary productivity. Increased primary productivity would increase food and cover for animals such as snails (Harman 1974).

Water hardness and alkalinity increases due to calcium in runoff from limestone storage and preparation facilities would undoubtedly benefit receiving water bodies with respect to heavy metal contamination. The solubility of heavy metals decreases as water becomes more alkaline, and this could be of potential benefit, inasmuch as metals may be entering nearby water bodies from coal and/or slurry storage facilities, from stack-emission fallout, and so forth. Since greater metal uptake by organisms occurs in the soluble state, in addition to metals being more toxic when soluble, increased alkalinity near the source of metal inputs could help mitigate potential detrimental metal impacts. The toxicity of many heavy metals has been shown to be reduced in hard water (Jones 1938; Cairns and Scheier 1957; Lloyd and Herbert 1962). Additionally, increased alkalinity would serve as a buffer for acid inputs also occurring from coal storage and stack emission fallout.

## IMPACTS OF GASEOUS PRIMARY POLLUTANTS

#### Introduction

Information and data are presented in this section which may be used in the assessment of potential ecological impacts of the major gaseous primary pollutants--sulfur oxides  $(SO_X)$  and nitrogen oxides  $(NO_X)$ --emitted from coal-fired electric generating plants. Since many of the parameters which affect such assessments are site-specific, the discussion will necessarily be generic in nature with specific examples cited where appropriate.

To date, the main interest in gaseous pollutants has been focused on the detrimental effects on human health, materials, and economically important crop and ornamental plants. The effects of gaseous pollutants on the biota and other components of natural ecosystems has received relatively little scientific, governmental, or public attention. Although this lack of information makes impossible the precise evaluation of impacts of gaseous pollutants on fish, wildlife, and other natural ecosystem biota, perhaps the elucidation of these deficiencies will encourage needed research in these areas.

<u>Gaseous pollutants and their sources</u>. Gaseous pollutants resulting from coal-fired electric power generation amount to about 7% (by weight) of the total primary pollutants currently generated by human activities and emitted to the atmosphere in the United States. The two most important and abundant primary pollutants emitted by coal-fired plants are sulfur oxides and nitrogen oxides (Kozlowski and Mudd 1975).

Sulfur is introduced into the atmosphere as hydrogen sulfide  $(H_2S)$  from biological decay, as sulfates  $(SO_4)$  from sea salt, and as sulfur dioxide  $(SO_2)$  from natural sources-e.g., volcanoes--and anthropogenic sources (Dovland et al. 1976). It is the man-made emissions of sulfur that are addressed in this section, since 90% of atmospheric sulfur over the continental United States results from man-made emissions. Of the anthropogenic emissions, 62% are related to coal combustion, 11% to metal smelters, 10% to other industrial sources, 2% to gasoline and fuel combustion, and 1% to miscellaneous emitters (Greeley et al. 1975).

Nitrogen is released to the atmosphere as ammonia  $(NH_4)$  from biodecay and fertilizers and as nitrogen oxides  $(NO_X, chiefly as NO and NO_2)$  from biochemical reactions in soil and from high-temperature combustion processes (Dovland et al. 1976). On a global basis, most  $NO_X$  is produced by bacteria. Biologically produced sources produce some  $45 \times 10^7$  MT ( $50 \times 10^7$  tons) per year versus  $4.5 \times 10^7$  MT ( $5 \times 10^7$  tons) per year for man-made sources (USEPA 1971c). The USEPA (1971c) reported that coal, oil, natural gas, and motor-vehicle fuel combustion accounted for 16 million MT (18 million tons) of the estimated 18.7 million MT (20.6 million tons) of anthropogenic  $NO_X$  emissions in the United States in 1968. Power plants accounted for 3.6 million MT (4 million tons) of this.

Coal combustion in power plants accounts for about 40% of the total sulfur-compound emissions, and about 11% of the total nitrogen oxide  $(NO_X)$  emissions in the United States (USEPA 1971c; U.S. Dep. Health Educ. Welfare 1969). Sulfur oxides  $(SO_X)$  and NO<sub>X</sub> account for approximately 98% of the total gaseous pollutant emissions from a coal-fired plant. Carbon dioxide and water vapor are major emission products, but are usually not considered as primary pollutants. Carbon monoxide, hydrocarbons, and various other organic and inorganic compounds make up the remaining 2% of the emitted pollutants (Kozlowski and Mudd 1975).

Once these primary pollutants are in the atmosphere, numerous conversions and reactions can take place giving rise to secondary pollutants such as sulfate aerosols, ozone  $(0_3)$ , and peroxyacetyl nitrate (PAN). These secondary pollutants have other major sources of reactants (i.e., NO<sub>X</sub> from transportation) and may have variable reaction times (depending on the presence of catalysts, water vapor, sunlight, etc.) and thus be formed at long distances from their source. The potential effects of secondary pollutants and the long distance transport of primary pollutants thus become regional problems that are impossible to associate with a particular source. However, these secondary pollutants can injure biota and may also synergistically intensify the effects of SO<sub>2</sub> and NO<sub>X</sub>. These factors may affect the initial selection of a particular energy technology, but probably have little bearing on the selection of the best site within a local area for a coal-fired plant once the decision is made to build it. For the above reasons, secondary pollutants and the long-distance transport of pollutants are considered to be beyond the scope of this report and will not be treated in detail.

<u>Gaseous pollutant impacts on terrestrial biota</u>. Under field conditions, biota are most adversely affected by high, short-term concentrations of  $SO_2$  and  $NO_X$  that occur near the power plant, usually under adverse meteorological conditions. The meteorological conditions that would create maximum ground-level effluent concentrations from the model plants occur during an event described as plume fumigation (Neiburger et al. 1973). Plume fumigation occurs when the stack-gas plume is trapped by the bottom of an inversion layer rising above the top of the stack after sunrise or lying within several hundred meters (a few thousand feet) of the top of the stack (see Fig. 14). Under these conditions, the stack effluents mix downward rapidly, fumigating the ground within the plume sector. Upward mixing is limited by the inversion. The highest concentrations are usually reached within a few kilometers of the plant. Under actual field conditions of plume fumigation, organisms are never exposed to single pollutants. Rather, they are exposed to relatively high concentrations of all the plume constituents plus usually lesser concentrations of the pollutants present in the ambient air. It is well documented that certain combinations of pollutants cause synergistic responses in biota (USEPA 1971c; U.S. Dep. Health Educ. Welfare 1969). In these cases, two gases at concentrations too low to cause visible injury when applied alone cause injury as a mixture.

Table 14 presents calculated short-term (3-hour and 24-hour) concentrations of  $SO_2$  and  $NO_X$  from four model coal-fired plants of various generating capacities, using coal from the three major coal fields of the United States. These estimates approach worst-case conditions since the concentration and distance (plant to concentration isopleth) are the maximum for each model plant and the meteorological conditions used to calculate these values were chosen to give maximum ground-level concentrations (plume fumigation). These short-term concentrations will prevail only in the sector downwind from the plant, since the plume will follow the trajectory of the local wind.

The effects of gaseous air pollutants on plants and animals may be classified into three rather broad categories: acute, chronic, and long-term. Acute effects are those which result from relatively short (< 1 hour to 1 month) exposures to high concentrations of pollutants. Chronic effects occur when organisms are exposed for months or even years to comparatively low levels of pollutants. Long-term effects include abnormal changes in ecosystems and subtle physiological alterations in organisms which may result from the coexistence of air contaminants and living systems for decades or longer. Acute and chronic effects may be indirect or caused by secondary agents such as changes in soil pH caused by acid rain which, in turn, is formed primarily from atmospheric SO<sub>2</sub> and airborne water droplets.

The literature on the effects of air pollutants on biota is characterized by a preponderance of studies of experimental fumigations in chambers that utilize doses of pollutant sufficient to induce symptoms of acute injury. Information obtained from natural conditions, field Conditions, and studies dealing with chronic levels of injury is limited, although in general, pollutants reach levels associated with chronic injury more frequently than they reach levels which cause acute injury. Environmental exposures will mostly be of an intermittent nature whereas most laboratory studies have involved continuous or nearly continuous periods of exposure. Pathological conditions are more likely to appear sooner under the latter circumstances than when exposure is intermittent. Studies of long-term effects of pollutants are virtually nonexistent. This situation is partly due to the fact that acute injury symptoms in sensitive species are frequently easily recognized and lend themselves to quantitative assessment, in contrast to the more subtle effects of lower dosages. In assessing pollutant effects on biota, the concept of dose (concentration per unit time) is extremely important. For example, a brief (several minutes to hours) exposure to a relatively high concentration of a pollutant may have no measurable adverse effect on an organism, but if exposed to the same (or lower) concentration for a longer period of time, severe injury could result.

Effects of predicted model power-plant pollutant doses on terrestrial ecosystems. Of the two primary gaseous pollutants  $(SO_2 \text{ and } NO_X)$  emitted by coal-fired plants being considered here,  $SO_2$  is likely to have the greater impact on terrestrial ecosystems. Sulfur dioxide  $(SO_2)$  is the most abundant pollutant produced by any of the model plants (Table 14). Most of the 3-hour and 24-hour dose levels fall within the acute  $SO_2$  injury range for sensitive vegetation ( $\sim$  131 to 4000 µg/m<sup>3</sup>) and approach the threshold injury level for plants of intermediate sensitivity (USEPA 1973a). However, these doses are well below the acute injury threshold ( $\sim$  13,100 µg/m<sup>3</sup>) for vertebrate animals (U.S. Dep. Health Educ. Welfare 1969; Alarie 1975). Only one toxicological or epidemiological study of these emissions upon animals other than domestic or laboratory animals and man (Lewis et al. 1976) was found in the literature, and this study has not progressed sufficiently to derive pertinent conclusions from it.

It must be kept in mind that very conservative meteorological assumptions were used to develop Table 14 and the values represent worst-case conditions. These values only indicate that  $SO_2$  injury to vegetation is possible. The actual likelihood of significant acute injury to biota is small because of the infrequency of occurrence of the conditions used to calculate the values in Table 14 and the simultaneous occurrence of maximum sensitivity in biota, upon which their sensitivity ranges are based.

Nitrogen oxides are the next most abundant pollutant produced by coal-fired plants. Both animals and plants can be directly affected by  $NO_X$ , but acute and chronic threshold injury levels are at higher doses ( $\sim 2000 \ \mu g/m^3$ ) than any of the doses predicted in the vicinity of the model plants (USEPA 1971c).

Perhaps the most important problem associated with  $NO_X$  is not the toxicity of such gases themselves but the secondary pollutants ( $O_3$  and PAN) that are produced when  $NO_X$  reacts with airborne hydrocarbons. Very small amounts (relative to  $SO_2$  and  $NO_X$ ) of carbon monoxide (CO) and hydrocarbons are emitted by coal-fired power plants (USEPA 1973b). The expected short-term maximum concentrations of neither CO nor hydrocarbons are sufficient to cause measurable direct impacts to ecosystems in the vicinity of any of the four model plants. However, the power-plant emissions will cause increases in the local ambient levels of both pollutants (mainly from transportation sources) and, like  $NO_X$ , contribute to the formation of secondary pollutants.

As indicated above, plants in general are considerably more sensitive than animals to the direct effects of  $SO_2$  and about equally sensitive to  $NO_X$  when considering levels that cause threshold acute injury. Thus, it seems probable that in natural ecosystems exposed to  $SO_2$  and  $NO_X$  from a coal-fired power plant, vegetation would be the first major biotic component to exhibit  $SO_2$  injury symptoms, if they occur. The animal component may be impacted primarily by secondary effects due to habitat changes or food species changes caused by pollutant effects on vegetation. Herbivores are likely to be the first trophic level affected since they are dependent on vegetation for both food and habitat. Depending on the severity of the impacts to vegetation, gaseous pollutant effects could, through ecosystem component interactions, elicit changes in higher trophic levels as well. Thus, to understand and begin to evaluate the total ecosystem impacts likely to occur in real-world pollution episodes due to coal combustion effluents, impacts on plants must first be examined. Since predicted model power-plant  $NO_X$  levels are well below those for which reliable data are available, the following sections on vegetation impacts are limited to  $SO_2$  effects.

## Effects of SO<sub>2</sub> on Vegetation

Acute injury to vegetation, usually associated with short-term exposure to high  $SO_2$  concentrations, is characterized by collapsed marginal or intercostal leaf areas that first have a water-soaked appearance. Later, these dead areas dry and bleach to an ivory color in most species, but in some they become brown or brownish red. Chronic  $SO_2$  injury results in light to severe damage and is characterized by leaf yellowing (chlorosis), proceeding from the margins to the intercostal areas, that develops from exposure to sublethal concentrations of the gas over a long period of time (USEPA 1973a).

Acute and chronic  $SO_2$  injury can result in death of the plant or in transient reductions of live plant biomass. If the fumigations occur intermittently, affected plants may recover by continued or increased growth and replacement of damaged tissue during periods when conditions are favorable. However, if the amount of damaged tissue exceeds 5-30% of the total amount of foliar tissue (depending on species), productivity or yield may be decreased (Davis 1972; Anon. 1974). Subtle long-term effects are also possible, in which the  $SO_2$  interferes with physio-logical or biochemical processes without visible symptoms but which result in effects on growth and possibly on yield (USEPA 1973a).

Plant species and varieties show a considerable range of sensitivity to  $SO_2$ . This range is the result of complex interactions among microclimatic (temperature, humidity, light, etc.), edaphic, phenological, morphological, and genetic factors that influence plant response. Threshold acute injury in various plants may be caused by short-term  $SO_2$  concentrations ranging from <1 ppm to > 10 ppm (USEPA 1973a). In other words, a level of  $SO_2$  that may kill one species may not affect another species. Figures 16 to 18 give the  $SO_2$  dose-injury curves for plants in the sensitive, intermediate, and resistant classes, respectively. The concentrations and exposure times (doses) shown for each susceptibility grouping are applicable only when the plants are growing under the most sensitive environmental conditions and stage of plant maturity (USEPA 1973a). Thresholds for chronic plant injury by  $SO_2$  have been estimated at about 130 µg/m<sup>3</sup> on a seasonal or annual average (Mukammal 1976).

Appendix C presents lists of plant species for which  $SO_2$  sensitivity has been determined. The plants are grouped into the  $SO_2$  sensitive, intermediate, and resistant categories as well as by herbaceous native plants/weeds; woody trees, shrubs, and ornamentals; crop plants; garden plants; and herbaceous flowers and ornamentals. These lists can be used in conjunction with the dose response curves (Figs. 16 to 18) to determine the likelihood of injury to any plant listed for a specific  $SO_2$  dose up to 8 hours.

Interactions and synergistic effects of  $SO_2$  and other pollutants have been reported (USEPA 1973a). These preliminary studies have shown injury to several species resulting from the interaction of  $NO_X$  and  $SO_2$ . In most cases, the injury resulting from  $NO_X$  and  $SO_2$  applied together is greater than the injury caused by the same concentrations of either gas alone.



Figure 16. Dose-Injury Curves for SO<sub>2</sub>-Sensitive Plant Species. Adapted from USEPA (1973a).

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Figure 18. Dose-Injury Curve for  $SO_2$ -Resistant Plant Species. Adapted from USEPA (1973a).
<u>Mechanism of SO<sub>2</sub> injury</u>. Sulfur dioxide (SO<sub>2</sub>) enters the plant principally through the leaf stomata and passes into the intercellular spaces of the mesophyll, where it is absorbed on the moist cell walls and combined with water to form sulfurous acid and sulfite salts (Treshow 1970). The sulfites are presumably oxidized to sulfates which can be metabolized normally by the plant. These sulfates can actually stimulate growth if the plant is deficient in sulfur (Grennard and Ross 1974). However, if plant tissues accumulate SO<sub>2</sub> faster than it can be oxidized and assimilated, concentrations of sulfite become toxic and damage occurs as a result of chlorophyll destruction and cell collapse (Treshow 1970).

<u>Factors affecting SO<sub>2</sub> sensitivity in plants</u>. Various environmental factors can have a profound effect on the response of plants to SO<sub>2</sub>. For example, a turgid plant growing under conditions of adequate soil moisture may be severely damaged by a given concentration of SO<sub>2</sub>, whereas a plant of the same species which is near the wilting point due to low soil moisture may be unaffected by the same exposure. In this case, the difference in response is probably due to open stomata in the turgid plant and closed stomata in the wilting plant. Sensitivity to SO<sub>2</sub> can be considered as a function of morphological and biochemical characteristics controlled by the genetic diversity of plants within a population. Thus, two varieties of the same species may exhibit marked differences in SO<sub>2</sub> tolerance.

Practically every environmental, genetic, and plant development factor that has been studied in relation to  $SO_2$  effects has been found to interact with these effects. No one factor may be considered independently of the other factors. Sulfur dioxide tolerance levels are low under the following conditions (Loman et al. 1972; USEPA 1973a): (1) high light intensity before and/or during fumigation, (2) high temperature, (3) daylight, (4) morning hours, (5) high relative humidity, (6) water on leaves, (7) high soil moisture, (8) old plants, (9) young (but not expanding) leaves, (10) developing conifer needles, (11) high physiological activity (flowering, seed set), (12) low vigor due to insects or disease, and (13) low nutrition levels.

<u>S02 effects on native plant species</u>. Native species seem less sensitive to  $S0_2$  than introduced species, ornamentals, or crop plants. Hill et al. (1974) exposed 87 species of plants native to the Arizona desert in their natural habitat to from 1,300 to 26,000 µg/m<sup>3</sup> S0<sub>2</sub> for two hours and found that 5,200 µg/m<sup>3</sup> was needed to damage all but a few of the species. Only one species was damaged by 1,300 µg/m<sup>3</sup> S0<sub>2</sub>. The resistance of these plants may have been due to low levels of sulfur in the soil and the relatively short fumigation time.

In Montana, Heitschmidt et al. (1976) studied 10 species at a native grassland site that were exposed to four levels of  $SO_2$  [ $\sim 10$  (ambient), 52, 130, and 260 µg/m<sup>3</sup>] applied continuously through a network of perforated aluminum pipe from early June through late October. In this initial experiment, there were no significant treatment differences in phenological development, plant size, and total leaf area damaged. There were also no clear differences in seasonal biomass dynamics or peak biomass by species in response to the  $SO_2$  treatments.

<u>S02 effects on lower plants</u>. The effects of S0<sub>2</sub> on nonvascular plants have been studied by many investigators. The loss or absence of species of lichens and mosses have been correlated with annual average S0<sub>2</sub> concentrations as low as 39  $\mu$ g/m<sup>3</sup> (USEPA 1973a). However, annual averages may not be meaningful in this context since one or several short-term, high-concentration S0<sub>2</sub> episodes that would not be reflected in the annual average could be responsible for the effect on the plants.

The extreme sensitivity of lichens to  $SO_2$  appears to be due to the destruction of the algal component (USEPA 1973a). In many areas of the West, surface stability and soil nitrogen levels are enhanced by nitrogen-fixing lichens which grow on the soil surface and have rhizines that extend into the soil (Sheridan 1976). Relatively low concentrations of  $SO_2$  or its oxidation products may adversely affect these lichens and lead to increased erosion by wind and water.

<u>S02 effects on crop plants</u>. Until recently, some investigators had supported the theory that  $\overline{S0_2}$  injury had not occurred in the absence of visible symptoms. However, research on crop plants (USEPA 1973a) has indicated that exposure to low levels of  $S0_2$  that are insufficient to cause visible injury may produce reductions in growth, yield, and photosynthesis, and adversely affect other physiological reactions. Reductions of yield, even when accompanied by moderate visible injury, are difficult to demonstrate under field conditions because of interacting factors.

In one study (Jones et al. 1973), soybeans (SO<sub>2</sub>-sensitive plants) distributed among 62 fields (a total of 456 ha or 1127 acres) were exposed to  $SO_2$  from a large coal-fired electric generating station at levels which caused some severe leaf injury on 0.5-m tall plants at an early preblooming stage. Eighteen variables, including leaf injury (chlorosis and necrosis) by SO<sub>2</sub>, were examined to determine if possible yield losses were attributable to SO<sub>2</sub>. The SO<sub>2</sub>-induced leaf injury was not a significant factor in accounting for yield variation from most of the 110 fields studied. Factors contributing to poor yields were low soil fertility, soybean cyst nematode infestation, continuous soybean cropping, and late planting, rather than SO<sub>2</sub> injury. Apparently, most of the affected plants attained near-normal growth after the SO<sub>2</sub> injury episode. In several other studies on soybeans (Jones 1975, personal communication), it was found that if the SO<sub>2</sub> exposure occurs between 15 August and the first week in September (the flowering period) and if leaf chlorosis is greater than about 5%, some yield reduction can be expected. Exposures before or after these dates probably will not result in yield reduction unless chlorosis is severe. Sheridan (1976) reported that SO<sub>2</sub> fumigation of soybean plants under laboratory conditions caused a reduction in nitrogen fixation at concentrations of 130  $\mu$ g/m<sup>3</sup> or higher when exposed for 14 days.

Grain, vegetable, pasture, and forage crops--most of which are also in the sensitive class--are probably susceptible to  $SO_2$  injury for most of the growing season. Corn, on the other hand, is one of the most resistant crop species and has rarely been injured by  $SO_2$  under field conditions (USEPA 1973a). In areas where pollutant fumigation is known to be a problem, resistant agricultural varieties or entirely different, more resistant crops may be planted.

### Effects of Sulfur Oxides on Animals

Most of the data on the biological effects of sulfur oxides are derived from toxicological studies of laboratory animals and epidemiological studies of human populations. There is considerable variability in the sensitivity of the test animals and among the methods and results of the different studies. Thus, clearcut threshold levels for injury or death are not available. Sulfur oxides usually irritate or injure the respiratory passageways and other mucosal tissues with which they come in contact. It seems likely that animals with higher rates of ventilation or more exposed mucosal tissues relative to their body size would be more sensitive to exposure than others. At lower concentrations, the derivatives of  $SO_2$  seem to be more injurious than  $SO_2$  itself (Colucci 1976), and  $SO_2$  has some synergistic reactions with other pollutants although the quantitative relationships are not clear (Colucci 1976).

Emission modeling for a 2100-MWe coal-burning generating station has resulted in an estimate that maximum short-term (3-hour) concentrations of  $SO_2$  near the ground surface may exceed 3,000 µg/m<sup>3</sup> within a radius of 1 km from the plant (see Table 14). The highest levels of exposure would be expected in the western United States, where scrubbers are not used. Short-term fumigation with high levels of  $SO_2$  may occur more often in the eastern states where atmospheric inversions are more common and wind dispersal less. Predicted concentrations may reach 850 µg/m<sup>3</sup> for a 24-hour period, and annual averages may range up to 350 µg/m<sup>3</sup>. Significant mortality in laboratory animals has not been shown during exposure to concentrations from about 65,000 to 3.1 million µg/m<sup>3</sup> for less than 90 hours (Colucci 1976). Acute exposures (2-3 hours) of some laboratory animals to  $SO_2$  have resulted in deleterious effects to pulmonary function at concentrations as low as 13,000 µg/m<sup>3</sup> may produce pulmonary problems that are reversible after exposure is terminated (Colucci 1976). It may be interpreted from epidemiological studies that chronic exposure to concentrations of about 100 µg/m<sup>3</sup> can adversely affected by low levels of SO<sub>2</sub>, but threshold levels are unclear (Lewis et al. 1976).

The maximum concentrations of  $SO_2$  in a 3-hour interval that are predicted for the model plants (Table 14) are one-sixth of the lower levels for which deleterious effects have been found in laboratory animals during acute exposures. Chronic exposures are predicted to be from 10 to 25 times lower than the lowest limit for reversible pulmonary dysfunction in laboratory animals; the predicted concentrations are well below levels eliciting irreversible damage in laboratory animals. However, concentrations may exceed levels for which adverse effects upon human health are indicated from epidemiological studies. Should there be a failure of the scrubber in plants using high-sulfur coal,  $SO_2$  concentrations may approach levels deleterious to laboratory animals. It is unlikely that this condition would persist for more than an hour.

Extrapolation of these data to wildlife in the vicinity of an  $SO_2$  source is confounded by the variability of results in the toxicological studies, variability of sensitivity of individual species to  $SO_2$ , duration of exposure, concentrations of emissions from the power plant, and the accuracy of laboratory animals as models for wildlife. Sulfur oxides may affect wildlife more indirectly than directly, because impacts upon vegetation may lead to habitat modification or loss of important foods.

#### Effects of Nitrogen Oxides on Animals

Information on effects of nitrogen oxides also comes predominantly from toxicological studies of laboratory animals and epidemiological studies of human populations. These pollutants affect primarily the lower respiratory tract. Under worst-case conditions, predicted maximum NO<sub>X</sub> concentrations within 1 km of a 2100-MWe generating station exceed 1,000  $\mu$ g/m<sup>3</sup> for short periods (3 hours) (see Table 14). Nitrogen oxide emissions are influenced primarily by the manner of burning the coal and the amount of atmospheric nitrogen that is oxidized. Areas subject to frequent inversions would be subjected to higher concentrations more often.

Table 24.	Summary of	f Toxicological	Experiments	with	Sulfur	Dioxide	$(S0_{2})^{a}$

Species	$\begin{array}{c} \text{Concentration} \\ (10^5 \ \mu\text{g/m}^3) \end{array}$	Duration	Effects
Monkey	<0.034	78 weeks	None
Donkey	<0.078 <0.78		None Impaired bronchial clearance
Dog	0.13	21 hours/day for 620 days	None
Monkey	0.13	78 weeks	None
Guinea pig	<0.13	22 hours/day for 365 days	None
Dog	0.13	21 hours/day for 225 days	Increased pulmonary resistance
Rat	0.026-0.079	12 hours/day for 4 months	None
Mouse	0.18 -0.26	7 days	Increased sensitivity to pneumonia infection
Rabbit	0.26	3-10 days	Increased S-sulfonate clearance
Mouse	0.26	Up to 72 hours	Lesions in respiratory tract
Rat	0.26	6 hours/day, 5 days/week for 113 days	None
	2.6	6 hours/day, 5 days/week, for 22 days	40% mortality
	∿15	6 hours/day, 5 days/week, for 12 days	$\sim 90\%$ mortality
Guinea pig	0.26	6 hours/day for 20 days	None
Cat	0.52		Increase in pulmonary flow resistance
Rabbit	∿0.52	14 and 62 hours	Formation of S-sulfonate
Mouse	13	5 min/day, 5 days/week for 300 days	Accelerated onset of neoplasia
Hamster	14	3 hours/day for 75 days	Increased pulmonary infection
Dog	13-14	<pre>2 hours/2 times/week for 4 to 5 months</pre>	Change in goblet cells of bronchi and bronchioles
Rat	13-78		Change in goblet cell release
Rat	26 52 104	Up to 6 weeks Up to 6 weeks Up to 6 weeks	None Bronchial damage Death within 22 days
Rat	78	6 hours/day for 10 days	Increased acid phosphatase activity
Rat	78	2 hours	Gastric inhibition
Mouse	≤78	<pre>10 exposures of 10 min- utes, with 3 or 7 min- utes recovery between exposures</pre>	Initial decrease in respiratory rate, then progressive return to preexposure rate; desensitization to successive exposures.
Mouse	Various		Sensitized mice to pneumonia infection

<sup>a</sup>Data extracted from summary of Colluci (1976) and presented in order of increasing concentration, except where there is more than one entry for a single experiment. Predicted maximum 24-hour averages approach 300  $\mu$ g/m<sup>3</sup>, and annual averages may surpass 100  $\mu$ g/m<sup>3</sup>. Possible effects upon guinea pigs have been noted during exposure for several days at levels as low as about 1,000  $\mu$ g/m<sup>3</sup> (Ziskind and Hausknecht 1976). More pronounced effects occur only when levels exceed 2,000  $\mu$ g/m<sup>3</sup> during several hours exposure and about 1,000  $\mu$ g/m<sup>3</sup> during chronic exposure for several months (see Table 25). From epidemiological studies of human populations, it is suggested that chronic exposure to  $\sim 100 \ \mu$ g/m<sup>3</sup> NO<sub>2</sub> may be deleterious. Predicted maximum ambient levels are one-half the concentrations at which responses appear after a few hours exposure, and well below threshold levels for longer exposures. Annual averages may surpass levels at which human populations may be adversely affected. Extrapolation of this information to wildlife in the vicinity of generating stations is, again, uncertain.

## Impacts of Gaseous Pollutants on Ecosystems

None of the factors discussed in the preceding sections that influence pollutant tolerance levels in biota can be controlled in natural or unmanaged ecosystems. Therefore, since the loss or change of even the most sensitive ecosystem component could, eventually, change the entire ecosystem, the ecosystem as a whole must be considered as sensitive as its most sensitive component. For example, the loss of  $SO_2$ -sensitive, surface-encrusting lichens from a grassland ecosystem could lead to increased erosion, and this to the loss (or invasion) of other species.

In addition to acute pollution effects, the chronic and long-term effects take on added significance in natural ecosystems because of the relative permanence of the vegetation and other components, coupled with the delicate balances that exist between all components. As a contrast, in areas supporting managed agricultural ecosystems where the existing forage or crop plants are harvested and replaced by new plants each growing season, the chronic and long-term effects of air pollutants may be virtually eliminated.

It is likely that in natural ecosystems subjected to persistent pollution levels, vegetation would be affected first and that annual and perennial plant species would be affected differently. For example, a population of annual plants would be affected sooner and perhaps more severely by factors impairing sexual reproduction and/or seed germination than would a population of perennial plants. Such chronic and/or long-term effects may result in changes in diversity (through elimination of sensitive species), community structure, productivity, stability, nutrient cycling, etc. These changes would, in turn, affect the animal components of the ecosystem via changes in habitat, food availability, population dynamics, etc. These effects would be in addition to the poorly known, direct long-term effects of air pollutants on animal species.

Smith (1974) has proposed that air pollution has three levels of effects on ecosystems. Under conditions of low dosage, the first level, the vegetation and soils function as an important sink for air contaminants. When exposed to intermediate dosages, the second level, individuals of various biota species may be adversely and subtly affected in ways discussed above. Exposure to high pollutant doses, the third level, may induce acute morbidity or mortality of individuals.

Air pollution itself is an environmental change and as such can act as a mechanism of genetic selection. Gene pools of the species in polluted areas are initially unselected for the pollution factor and have, in fact, shown a wide range of variability to pollution effects. Bradshaw (1976) has elegantly shown that in polluted ecosystems evolution does occur, can be extremely rapid, and can substantially alter the response of species to the effects of pollution.

With the recognized deficiencies in available information, it is possible to speculate on, but not quantify, the total impact of air pollutants on ecosystems.

#### IMPACTS OF ACID PRECIPITATION

Acid precipitation forms in the atmosphere from chemical conversion of sulfur and nitrogen compounds under the influence of oxygen, water, and sunlight to form sulfuric acid (for  $SO_X$ ) and nitrous and nitric acids (for  $NO_X$ ) (USEPA 1971c; Emmelin 1976). Hydrochloric acid (HCl) accounts for the third component of strong acids in precipitation, partly owing to combustion of coals containing chlorine (Gorham 1976).

Pure water in equilibrium with atmospheric carbon dioxide  $(CO_2)$  would result in a rainwater pH of  $\sim 5.7$  (Barrett and Brodin 1955). However, formation of sulfuric and nitric acids from SO<sub>X</sub> and NO<sub>X</sub> emissions have resulted in more acid rainfall in several regions of the world. Most of the major industrial sulfuric acid sources (SO<sub>2</sub> emitters) are localized within the industrial belt of the north-temperate zone. Hence, most of the acid precipitation will be concentrated into relatively limited areas downwind of these sources; eastern Canada, the northeastern United States, and northern Europe are likely to experience acid precipitation long before other

Species	Concentration (10 <sup>5</sup> µg/m <sup>3</sup> )	Duration	Effects
		Acute exposures	
Guinea pig	0.01-0.20	4 to 24 hours/day for up to 14 days	Elevated protein in urine
Guinea pig	0.04	Up to 21 days	Increased average area per alveolar wall cell
Mouse	0.02-0.30	Up to 17 hours	Impaired bacterial defense
Monkey	0.2 -1.0	2 hours	Decreased tidal volume, progressive histopathological damage
Rat	0.30-0.34	48 hours	Increase in Type II pneumocytes
Rabbit	0.16-1.2	3 hours	Impaired bacterial defense at all levels of exposure
Hamster	0.60-0.70	7 to 10 days	Bronchiolitic lesions
ан сайтаан ал		Chronic exposures	•
Mouse	0.01	Up to 12 months	Reduction of functional lung tissue
Monkey	0.02	493 days	Slight to moderate emphysema
Monkey	0.04	14 months	Hypertrophy of bronchiolar epithe- lium in bronchiole
Rat	0.02	14 months	Marginal changes in epithelium
Guinea pig	0.02	6 months	Higher mortality
Rat	∿0.06	9 months	Decrease in lung compliance
Rat	0.04	Lifetime	"Emphysema-like" injury suggested
Rat	0.04 0.34	Up to 360 days Up to 7 days	Increase in number of cells prepar- ing to divide
Rat	0.12	6 weeks	Interstitial edema, vascular congestion
Rat	0.20	90 days	Decreased body size
Rat	0.30	90 days	Decreased body size
Mouse	∿0.80	Up to 8 weeks	Epithelial damage near terminal bronchioles
Hamster	0.9-1.1	10 weeks	Respiratory rate increased, hyper- plasia and hypertrophy in termi- nal and respiratory bronchioles

Table 25. Summary of Toxicological Experiments with Nitrogen Oxides  $(NO_x)^a$ 

<sup>a</sup>Data extracted from summary of Ziskind and Hausknecht (1976) and presented in order of increasing concentration, except where there is more than one entry for a single experiment.

areas of the world (Greeley et al. 1975). Large areas of Scandinavia that are downwind of industrial complexes of England and Europe receive precipitation with a pH  $\leq$  4. Similarly, the annual acid precipitation value averages about pH 4 in the northeastern United States, and values between pH 2.1 and 5 have been recorded for individual storms (Likens and Bormann 1974).

As previously mentioned, the distribution of acid precipitation is greatest in the northeastern United States, especially in New England, New York, and Pennsylvania. This results from emission sources both within this area and from the fact that the northeastern states are downwind from the major  $SO_2$  sources in the Chicago-Pittsburgh industrialized area (Cogbill and Likens 1974). The areal extent of acid rainfall is spreading both south and west, with intensification at the center of the northeastern United States (Cogbill 1976). Cogbill (1976) stated, however, that it cannot be predicted how widespread or intense the acid precipitation problem will become. Although only the northeastern United States now experiences acid precipitation, large areas-i.e., Washington, Oregon, Idaho, and adjoining coastal areas--are sensitive to acid precipitation, due to low buffering capacities of the surface water, but are not currently experiencing it. Galloway and Cowling (1977) stated that some of these areas may be affected in the future if the geographical spread of acid precipitation continues. It should be noted that areas currently impacted or with potential to be impacted from acid rain fallout have waters characterized by low acid-neutralizing capacity and drainage systems in areas of crystalline or metamorphic bedrock with shallow, acid soils of low buffer capacity (Schofield 1976).

In the atmosphere,  $SO_2$  is converted to  $SO_3$  by the processes of photolysis and oxidation; in the presence of water vapor,  $SO_3$  is converted to  $H_2SO_4$  aerosol (Heicklen 1976). Greeley et al. (1975) reported that 80% of the sulfate in the atmosphere is removed in rainfall (wet deposition), commonly called acid rain; the remaining 20% settles out as dry fallout (dry deposition). Drv fallout from sulfate aerosols accumulates on vegetation and soil (Granat and Rodhe 1973). Overrein (1976) stated that dry fallout of sulfur and nitrogen oxides is greater near emission sources whereas wet deposition is important at distances hundreds or thousands of kilometers from their sources. Effects of acid rain do not remain localized due to the relatively long (up to 25 days) residence time of  $H_2SO_4$  in the atmosphere (Greeley et al. 1975; Emmelin 1976). Nitrogen oxides have a residence time of  $\sim$  3 days for NO<sub>2</sub> and  $\sim$  4 days for NO (USEPA 1971c). The wind can thus provide a long-range transport mechanism for sulfur and nitrogen oxides. In the past, much of the sulfate was deposited near its source in both particulate form and as neutralized salts due to interactions with particulate emissions. With the advent of tall smokestacks and precipitators, less  $SO_2$  is removed from the air as dry fallout because more time is available for conversion to sulfates which are better removed by rainfall (Cooper et al. 1976; Likens and Bormann 1974; Gorham 1976). Also, low pH rain is less effective in removing  $SO_2$  from the atmosphere and this may influence long-range transport (Dovland et al. 1976). Thus, although it has been shown that high-intensity showers may decrease the acidity of rain-water with distance (5 km) from a single power plant (Li and Landsberg 1975), combined sulfur and nitrogen oxides from many power facilities and industries can result in a regional impact from acid rain.

Hornbeck et al. (1977) reported that maximum sulfur in precipitation occurs in summer. Reasons suggested for this temporal variation are that snow may be less efficient than rain in capturing sulfur compounds from the atmosphere (Fisher et al. 1968) and/or that greater electrical power generation may occur in summer (Hornbeck et al. 1977). Increased acidity in summer can result in greater effects on both aquatic and terrestrial ecosystems than in winter, since summer is usually the time for optimum growth and reproduction.

## Impacts of Acid Precipitation on Vegetation and Soils

Acid precipitation is perhaps the most important secondary pollutant associated with the emission of a coal-fired power plant. As pointed out earlier, acid precipitation, like other secondary pollutants, is usually a regional problem that is difficult to associate with a particular point source. However, under conditions of high intensity rainfall, decreases in pH of the rain have been observed downwind in close proximity (within 5 km) to coal-fired plants (Li and Landsberg 1975).

In most natural ecosystems, the surfaces of the leaves and stems of vegetation are the initial deposition sites for rainfall and other airborne aerosols and particulates. In a mature forest, an average raindrop will be intercepted by three tiers of foliage before it reaches the soil (Dochinger and Seliga 1976). Thus, acidic precipitation can affect vegetation both by direct contact and through root interactions in the soil.

Among the many reported direct effects of natural and simulated acid rain on vegetation are: (1) changes in stomata size and frequency, (2) decreases in overall growth, (3) increased bark acidity, (4) changes in the physiology of foliar organs, (5) alterations in root function, (6) direct injury to the foliage of conifer and deciduous trees, (7) excessive adventitious budding, (8) premature abcission of mature leaves, (9) poorer germination of seeds, (10) decreased pollen germination, (11) accelerated leaching of nutrients from foliage, humus, and soil, (12) inhibition or stimulation of plant diseases, (13) inhibition of free-living nitrogen-fixing bacteria in the soil, and (14) inhibition of nodule formation in legumes (Dochinger and Seliga 1976; Sheridan 1976; Carrier 1977).

Acid precipitation impacts the terrestrial ecosystem by effecting changes in the chemical properties of the soil and affecting aboveground portions of the plants intercepting the precipitation. The degree to which soils are altered is dependent on the buffering capacity of the soil. The buffering capacity of soils originating from carbonaceous sedimentary parent materials is high, but it is low for noncalcareous soils formed from granites and quartzites. A lowering of the soil pH causes a decrease in the cation exchange capacity of the soil and cations such as  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Fe^{3+}$ , and  $Ca^{2+}$  are leached from the soil profile. The leaching of cations, notable when the pH of rainwater is approximately 4.0, increases markedly as the pH decreases below 3.0 (Fairfay and Lepp 1975; Biddings and Galloway 1976; Farenbaugh 1976). A reduced soil pH (below 5.0) results in increased availability of phosphorus. The effects of acid precipitation on the soil can be ameliorated by applications of lime.

### Impacts of Acid Precipitation on Terrestrial Animals

It is unlikely that most terrestrial vertebrates are affected directly by acid precipitation because of the protection afforded the body surface by scales, feathers, or hair. During preening or grooming, birds or mammals may ingest small amounts of precipitation that have fallen upon them. However, since these animals are capable of avoiding direct rain or snow, the amount of precipitation that they contact will probably be low. Most of the effects of acid precipitation upon terrestrial vertebrates will be indirect, through effects upon the soil and vegetation which may modify the critical habitat of a species.

#### Impacts of Acid Precipitation on Aquatic Biota

Impacts to aquatic ecosystems from acid precipitation can result from direct precipitation (both wet and dry fallout) and from runoff of acidic water. The effects of acid entering the system depend on the surface area and volume of the water body, size of the watershed, and type of soil, vegetation, and topography (Galloway and Cowling 1977). It should be noted that the deleterious impacts to aquatic ecosystems from acid precipitation are not solely due to the acid. Other agents from urban and industrial sources, especially toxic heavy metals and organic toxins, may accompany acidic inputs (Gorham 1976). Also, a reduced pH can mobilize trace elements from binding sites on organic and inorganic complexes (Eur. Inl. Fish. Advisory Comm. 1969). Beamish (1976) stated that synergistic or additive effects of heavy metals and acid may have caused reproductive failure of fish in acidified Canadian lakes. The following discussion will be limited primarily to direct effects of lowered pH to aquatic organisms.

Under certain conditions, a moderate degree of acid precipitation may supply beneficial nutrients (sulfur and nitrogen) either directly or through their mobilization from soils or aquatic sediments. Gorham (1976) cautions, however, that this is a very inefficient method of enriching systems, as harmful components (e.g., toxic metals) are always associated with beneficial components. Since dilution always occurs with dispersion, highly toxic compounds occur near sources of emissions whereas marginal benefit may occur to areas away from sources.

The effects of chemicals from acid precipitation are varied, ranging from fertilization-due to sulfate, nitrogen, phosphorus, and potassium--to toxification--due to  $[H^+]$ , pesticides, and toxic metal ions (Galloway and Cowling 1977). In most cases, deleterious impacts to aquatic systems are associated with acid precipitation. Reports generally show that organisms of all trophic levels are affected, resulting in reduction of productivity, disruption of natural cycles, and simplification of food webs (Grahn et al. 1974; Leivestad et al. 1976). Impacts to specific groups of organisms will be discussed below.

<u>Aquatic plants</u>. Studies by Moss (1973a, 1973b) revealed that the lower limit for growth of most algal species ranged between pH 4.5 and 5.1. Lowe (1974) stated that acidification of lakes and streams may preclude growth of most diatom species, except for acidophilous species, since the majority of diatoms require either a neutral or slightly alkaline environment. Phytoplankton studies of Canadian lakes variously impacted by acid precipitation from smelters showed that numbers of both species and organisms per unit volume were reduced in acidic waters, with the decrease starting around pH 5.7 (Kwiatkowski and Roff 1976). Kwiatkowski and Roff (1976) observed, however, that as the pH dropped, the depth of light penetration increased so that the reduced standing crop of algae (as measured by chlorophyll  $\alpha$  concentration) was offset by a deepening of the euphotic zone (upper layers of a water body into which sufficient light penetrates to permit growth of green plants). High areal algal production was noted as low as pH 4.5.

Acidification of lakes decreases biotic productivity and can lead to induced oligotrophy (deficient in plant nutrients and usually having abundant dissolved oxygen with no marked stratification). Grahn et al. (1974) and Grahn (1976) reported that this can lead to increasing

coverage of the lake bottom with dense mats of sphagnum moss. The moss has strong cationexchange properties, and therefore can take up metal cations important to aquatic ecosystems and retard recycling of these elements from sediments; it also takes up anions such as phosphate (Coffin et al. 1949; Gorham 1976). Because phosphates are often a major factor limiting aquatic productivity, acidification can decrease biotic productivity of waters by limiting algal production at the base of the food chain both by producing pH ranges that algal species cannot tolerate and by limiting nutrients available for algal production.

Species diversity of the macrophyte community may be decreased due to elimination of some macrophyte species in acidic environments (Gorham and Gordon 1963). Macrophytes did not exist in acid strip mine lakes in Missouri, where the pH ranged from 3.2 to 4.1 (Lind and Campbell 1970).

<u>Zooplankton</u>. The tolerance of zooplankton to acidic conditions is variable. Giddings and Galloway (1976), reporting results of Bick and Kunze (1971), stated that although most freshwater ciliates can tolerate pH as low as 6, some species have a broad tolerance, e.g., one species tested had a tolerance to pH 3.8. The cladoceran, *Daphnia pulex*, can tolerate a pH as low as 4.3, although it does not reproduce successfully below pH 7.0, thus exhibiting the difference between an organism vs. a population response (Davis and Ozburn 1969). It should be noted that regardless of the tolerance of zooplankton for acidic conditions, limitations will still be imposed on them if acidity precludes the development of their phytoplankton food supply (Dvorak et al. 1977).

In a study of acid-stressed lakes, Sprules (1975) found that many zooplankton species did not occur below pH 5. At this point, an abrupt change from complex to simple zooplankton communities occurred--i.e., lakes with a pH > 5 had 9 to 16 zooplankton species, whereas lakes with a pH < 5 had fewer than 7 species, and some lakes had only a single species. This phenomenon of lower zooplankton diversity as pH decreases has also been found by Carter (1971) and Salazkin (1971).

Sprules (1975)--based upon implications of Kerr (1971), Brooks and Dodson (1965), and Hrbacek et al. (1961)--stated that increased acidity resulting in reduced zooplankton diversity could have serious repercussions to both the zooplankton community and other biotic groups. Reduced zooplankton diversity would reduce the size range of primary consumers and thus reduce the feeding efficiency of the secondary consumers, affecting community structure at that level. The phytoplankton and bacterial communities can also be affected, since limited zooplankton diversity will limit the particle size ingested by them. Additionally, because pH affects fish that feed on zooplankton, the normal competitive interactions of zooplankton could be disrupted, leading to accelerated changes in zooplankton communities.

<u>Macroinvertebrates</u>. Although extensive literature does not exist concerning acid precipitation effects to aquatic macroinvertebrates, impacts would be similar to those experienced from acid mine drainage. Studies have shown that most orders of aquatic insects, as well as molluscs and worms, are eliminated or reduced under acidic conditions (Roback and Richardson 1969; Orciari and Hummon 1975; Simmons 1973; Dills and Rogers 1974). Bell (1971) found that 50% emergence for aquatic insects occurred at  $pH \ge 5$ , implying that insect emergence is seriously affected in many lakes and streams in acid precipitation regions.

<u>Fish.</u> The most extensive studies on aquatic impacts from acid precipitation have been on fish. The most noted investigations, from which much of the following discussion comes, are of lakes in the La Cloche Mountains in Canada, lakes in the Adirondack Mountains in New York, and lakes and streams in Scandinavia. In all of these areas, increased acidity has been shown to reduce or eliminate fish species, with some of the more desirable species being eliminated at a pH range as high as 5.5 to 6.0 and other species showing tolerance to a pH range as low as 4.5 to 4.7.

A survey of higher-elevation lakes (217 lakes with elevations > 600 m) in the Adirondack Mountains, New York, revealed that 51% of them have a pH < 5, with 90% of those devoid of fish (Schofield 1976). Schofield (1976) stated that comparable data from 1929 to 1937 indicated that only 4% of the lakes had a pH < 5 and were devoid of fish. Similarly, extensive fishing operations in the acidic lakes of the La Cloche Mountains in Canada have documented the absence or reduction of fish communities (Beamish and Harvey 1972; Beamish 1974a; Beamish et al. 1975).

As previously mentioned, acidic conditions can reduce the diversity of fish food organisms. However, the extinction of fishes in the Canadian lakes affected by acidity did not seem to be due primarily to the indirect losses of food items. Alteration of the plankton composition in acidic lakes of the La Cloche Mountains (Sprules 1975) did not appear to be important to the fish species present because the species most dependent upon plankton for food (e.g., lake herring) were the last species to become extirpated (Beamish 1974b). Conversely, Beamish (1974b) found predatory smallmouth bass, walleye, lake trout, and northern pike became locally extirpated although their major prey species (lake herring, yellow perch, and cyprinid species) were still abundant. Beamish (1974b) also found that white suckers became extirpated in one lake even though  $\sim$  10 times the biomass of preferred benthic food items were present. Beamish (1972) did find a decrease in feeding intensity of white suckers held for several months in sublethal acid concentrations. Beamish (1976) postulated that in natural systems, fish may respond to acid stress by reduced feeding and/or food utilization.

Perhaps the major cause for local extirpation of fish species in acidified waters is due to the impact of increased acidity on fish reproduction. Decreased recruitment of young has been cited as the primary factor leading to gradual extirpation of fish populations in all areas experiencing acid precipitation. Summarizing the literature, Schofield (1976) stated that recruitment failure may occur as a result of acid-induced mortality of fish eggs and/or larvae or because of a reduction in egg deposition as a result of either disrupted spawning behavior (Johnson 1975; Mount 1973) or effects on the reproductive physiology in maturing adults (Conroy et al. 1974). Beamish et al. (1975) found that most fish species ceased reproducing before major acid "fish kills" occurred, as observed by females not releasing ova. Beamish (1974a) defined as "critically acidic" the pH at which reproduction of a particular species ceases. Beamish et al. (1975) found the following pH ranges to be adversely acidic to various fish species in the lakes of the La Cloche Mountains:

pH	Species
6.0+ to 5.5	Smallmouth bass, walleye, burbot
5.5 to 5.2	Lake trout, troutperch
5.2 to 4.7	Brown bullheads, white sucker, rock bass
4.7 to 4.5	Lake herring, yellow perch, lake chub

In natural systems, recruitment failures could be noted by the following field observations: (1) decreased population density, (2) a shift in size and age structure to larger and older fish, and (3) a possible increased growth rate owing to decreased competition for food at lower population densities (Schofield 1976). Beamish (1976) cautioned that different studies have shown fish growth to increase or decrease depending on species, site, and pH range, so growth alone is not a good parameter to study. Jensen (1971) has shown that an increase (5 to 50%) in mortality of age 0 fish (eggs and fry) can decrease yield sufficiently to eventually bring about population extinction. Schofield (1976) stated that this reduction in recruitment may be imperceptible until the population is close to extirpation, especially in the case of late maturing species with great longevity.

Seasonality of acid precipitation, as previously mentioned, can have an overriding influence on fish populations. Since the greatest acidic inputs normally occur in summer, spawning fish and/or eggs and fry (the most sensitive stages) will be exposed to the lowest pH conditions encountered throughout the year. At pH levels higher than those causing recruitment failure, the numbers in a population may decrease in response to natural mortality rates which may increase due to added stress of low pH (Beamish 1974a).

Increased acidity also can be directly toxic to fish (acute or chronic) in ways other than affecting reproduction. The mechanisms involved in acid-induced toxicity to fish will vary depending upon levels of acidity and interactions with other components, e.g., metals and  $CO_2$  (Schofield 1976). Although a pH < 3 is rarely encountered in natural systems, this level of acidity causes coagulation of mucous on fish gill surfaces, resulting in subsequent anoxia (Robinson et al. 1976). In the pH range of 4 to 5, more often encountered in waterways affected by acid rain, fish mortality occurs due to disturbance of normal ion and acid-base balance (Leivestad et al. 1976). Failure of body salt regulation was suggested as the reason for massive kills of salmon and trout observed after snowmelt and heavy rains in Norway (Leivestad et al. 1976). Smaller fishes are more susceptible to detrimental ion fluxes than larger fish, due to greater body and gill surface area per unit weight which results in a greater exchange area in contact with water (Robinson et al. 1976). Laboratory acid toxicity tests have shown that fish exposed to periods of sublethal acid stresses developed deformities (Mount 1973; Beamish 1972). Formation of deformities could potentially decrease the fishes' ability to avoid predation, obtain prey, and so forth.

Schofield (1976) suggested that the rate of extinction of fishes from acidified lakes indicates that acidification is occurring too fast for natural selection processes to be effective in maintenance of populations. Marked differences in acid tolerance have been observed in fish (Beamish et al. 1975), in part genetically inherent to the species and related to fundamental differences in metabolism and physiology. Some promise does exist for selective breeding of salmonids with superior acid tolerance under hatchery conditions (Schofield 1976).

<u>Amphibians</u>. Amphibians, having more permeable skins than other tetrapods, may be more susceptible to the direct effects of acid precipitation. Also, since amphibians require water for reproduction, acidification of water bodies plays an important aspect in their survival.

Abnormal development of frog embryos has been observed in the pH range of 3.7 to 4.6, with lethal levels generally observed at a pH < 4.0 (Gosner and Black 1957). In a study of pH effects on salamanders, Pough and Wilson (1976) found that the spotted and Jefferson salamanders tolerated pH's of 5 to 10 and 4 to 6, respectively, but best hatching of young were in the pH range of 7 to 9 and 5 to 6, respectively. Pough (1976) demonstrated that a drop in pH below 6.0 can inhibit the development and increase the egg mortality of spotted salamanders. Although extensive studies have not been conducted, studies indicate that acid effects on amphibians seem to be similar to those on fish in that reproductive impairment may be the first symptom of acid rain effects, with direct toxicity occurring as the pH is lowered.

## IMPACTS OF TRACE-ELEMENT (PARTICULATE) EMISSIONS

#### Introduction

Particulates are defined as dispersed matter existing in the condensed phase (either solid or liquid) in which individual particle units range in size from 0.005 to 500  $\mu m$  in diameter (Fennelly 1975). The combustion of coal in conventional power plants generally produces particulates in the size range of 0.01 to 100  $\mu$ m. Particulate emission control devices, particularly electrostatic precipitators, are extremely efficient (up to > 99%) in removing particulates from the stack gases. However, the percent efficiency ratings of particulate emission-control devices are misleading because they are based on particulate mass. In reality, the larger particles are efficiently removed, whereas the finer particles and vapors are much less efficiently removed. In a study of one power plant, Lee et al. (1975) indicated that about 76% of the particulates entering the precipitator were  $\leq$  30  $\mu m$ , but only about 17% were  $\leq$  10  $\mu m$ ; in contrast, about 72% of the particulates released from the precipitator were  $\leq$  10  $\mu m$  and about 14% were  $\leq$  1  $\mu$ m. For another plant, Schulz et al. (1975) reported that 50% of the particulates leaving the precipitator were about 2  $\mu$ m or less, and that 15% were <1  $\mu$ m. The USEPA (1973b) has found that electrostatic precipitators generally have a 72% collection efficiency for particles in the range of 0-5 µm, 95% efficiency for particles 5-10 µm, and 97% efficiency for particles 10-20  $\mu$ m. Unfortunately, it is the smaller particulates which can be transported the greatest distances in the atmosphere and which, potentially, could cause the greatest impacts to the environment.

Particulate matter released from the stacks of coal-fired power plants can potentially affect vegetation in several ways. Ricks and Williams (1974) observed that particles from an industrial source can block stomates of oak leaves (*Quercus petraea*) and prevent them from closing during the dark period, and can interfere with the normal gaseous diffusion of  $CO_2$ ,  $O_2$ , and water vapor between the leaf air spaces and the air. Additionally, the open stomates appeared to be the cause of enhanced  $SO_2$  uptake rates in the affected trees, as measured by total leaf sulfur. The authors also postulated that particulates can have additional adverse effects on plants by affecting the leaf adsorption and reflectance of incident solar radiation-thereby affecting heat exchange and photosynthesis--and by partially occluding the stomates which may allow easier entrance of pathogenic fungal hyphae. Little and Martin (1972) have shown that relatively coarse and hispid or pubescent leaves, such as elm, retain more particulates than smoother, shinier leaves.

Studies dealing with cement-kiln dust (Treshow 1970; Lerman and Darley 1975; Linzon 1973; Darley 1966) and limestone dust (Brandt and Rhoades 1972, 1973) comprise much of the literature on the effects of particulates on vegetation. Extrapolation from these data to an assessment of the effects of coal combustion particulates requires some caution because of the difference in chemical composition (e.g., combustion particulates are not as high in lime). However, extrapolation may give some insight into the potential effects.

Based on conservative assumptions of particle size and deposition velocity, the annual particulate deposition rate was estimated for the area surrounding a 3000-MWe model power plant [meeting New Source Performance Standards (USEPA 1971d), 0.1 1b/10<sup>6</sup> Btu heat input] hypothetically sited in southern Illinois (Dvorak and Pentecost et al. 1977). The maximum annual deposition rate was approximately 0.02 g/m<sup>2</sup>/year, which is far below the rates of cement-kiln dust deposition that have been reported to cause damage in vegetation. Deposition rates of 365 g/m<sup>2</sup>/year caused damage to fir trees, but rates of 274 g/m<sup>2</sup>/year and 400-600 g/m<sup>2</sup>/year did not damage vegetation at other sites (Lerman and Darley 1975).

Particulate emissions may affect terrestrial vertebrates either directly through inhalation or indirectly through ingestion of contaminated vegetation. It is the smallest particulates  $(\leq 1 \mu m)$  that are of most concern since these particulates can bypass respiratory filters and can be deposited deep in the pulmonary regions of the lung (Natusch et al. 1974; Davidson et al. 1974; Fennelly 1975). Fennelly (1975) indicated that there is increasing evidence that a consistent relationship exists between combined exposure to SO<sub>2</sub> and particulates, and impaired ventilatory function in young children; the incidence of diseases such as chronic bronchitis, bronchial asthma, and pulmonary edema have been linked with sulfuric acid mist and suspended dust particles. Also, exposure to particulate polycyclic organic matter may result in cancer of the skin and lungs, nonallergic contact dermatitis, hyperpigmentation of the skin, folliculitis, and acne (Fennelly 1975). It is primarily the chemical nature of the inhaled particulates which determines their toxicity. Potentially toxic trace elements adsorbed to the surfaces of inhaled particulates can, therefore, also have adverse effects on animals and man (for more information on this mechanism, see page 78). Finally relatively inert materials (such as silicones) in particulates can impair oxygen transfer in the lungs and can cause physical irritation of lung tissue leading to diseases such as silicosis (Fennelly 1975). The effects on animals of ingestion of particulates and trace elements will be discussed in the section on terrestrial impacts to animals (see p. 80).

It is well established that certain potentially toxic trace elements present in coal are preferentially concentrated on the smaller particulates due to the larger surface area per unit mass (Natusch et al. 1974; Davidson et al. 1974; Klein et al. 1975a; Lee et al. 1975; Linton et al. 1976). Initial studies of Linton et al. (1976) have indicated that the elements contained in a shell approximately 1000 A° in depth below the surface of the particle are the elements which are accessible or extractable and can interact with body fluids, water, or other reactants. Thus, in the smaller particulates a greater fraction of the trace elements (as much as 80% of a 1  $\mu$ m particle) is more readily available for interaction than in the larger particulates. Certain trace elements-notably mercury, selenium, arsenic, bromine, and chlorine--are emitted from coal-fired power plants partly, and in some cases primarily, as a vapor. Since it is the smaller particulates and the vapors which escape the emission control equipment, the environmental effects of trace elements adsorbed to particulate emissions must be examined.

## Terrestrial Impacts--Soils and Vegetation

Many factors which modify or affect the pathways and behavior of trace elements in terrestrial systems are site-specific--including temperature, precipitation, soil type, and plant and animal species. Much of the information on trace-element toxicity to both plants and animals is based on short-term, acute-exposure laboratory studies which may not give a good indication of the effects of low-level, long-term exposures to trace-element emissions from coal-fired power plants. This section contains a discussion on (1) trace-element behavior in soils, (2) the toxicity of trace elements to plants, (3) the conditions under which adverse effects are most likely to occur, (4) the conditions under which trace-element emissions may have little measurable effect in the near future (30-40 years), and (5) the complexities of trace-element pathways and interactions. Specific information on the behavior and toxicity of selected trace elements in soils, plants, and animals can be found in Appendix D.

<u>Trace elements in soils</u>. Impact assessment of the effects of trace elements in terrestrial ecosystems is dependent, in part, on knowledge of transformations and endogenous levels of trace elements in soils.

<u>Trace-element transformations</u>. Trace elements adsorbed to particulates emitted from coalfired power plants reach the soil mainly through direct deposition, the washing of plant or other particulate-intercepting surfaces by rainfall, and the decomposition of plant litter. Whatever the source, trace elements in the soil may be fixed (conversion from readily available to less available forms) in the surface layers or leached (removal of materials in solution) to lower soil horizons, perhaps reaching groundwater and thus affecting aquatic systems. (For factors affecting trace-element movement through soils, see the section Runoff and Seepage from Waste-Disposal Sites, p.110). Trace elements can also be lost from soils by surface runoff, and wind and water erosion. Ultimately, the potential toxicity of trace elements remaining within the rooting zone depends largely on whether or not the element is available (present in the soil in a form that can be readily absorbed and assimilated by growing plants). Availability is dependent upon the interactions of a complex web of factors including physicochemical properties of the trace elements, the soil, and the plant roots; biological characteristics of the soil; and environmental parameters such as temperature and precipitation (Vaughan et al. 1975). All of the interrelationships of these factors are not known, but some possibilities can be considered.

Availability is dependent in part upon the solubility of the elements in the soil solution. Soluble forms may be simple ions, complex inorganic ions or ion pairs, and chelated or soluble organic complexes (Vaughan et al. 1975). The elements Al, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Sn, V, and Zn occur most often as cations in the soil (Berry and Wallace 1974; Pratt 1966; Romney and Childress 1965; USEPA 1975b). The availability of these elements is controlled in part by the cation exchange capacity (CEC) of the soil (sum total of the exchangeable cations that a soil can adsorb), which is determined by soil texture, organic matter content, the amount and kind of clay present, and ultimately the amount of surface area of the soil colloids (Brady 1974). Heavier, clayey soils generally have higher exchange capacities than light, sandy soils low in organic matter, and thus cations are usually less available in heavy soils. Certain trace elements such as beryllium (Lisk 1972) and copper (Baker 1974; Leeper 1952) are held more strongly than most cations by the cation exchange complex and, therefore, are less mobile in the soil solution. Cations are generally bound more tightly in neutral or slightly alkaline soils. In acidic soils they become more available due to increased solubility and their replacement on the cation exchange sites by hydrogen (Brady 1974). Soil pH also affects the reduction-oxidation conditions of the soil. In acidic soils, the more mobile, lower-valency forms of trace metals usually predominate over the less mobile, higher-valency forms. Therefore, soils with a pH exceeding 6.5 may have less potential cation toxicity problems (Lagerwerff 1972).

The elements arsenic, molybdenum, and selenium usually occur as divalent anions in the soil solution. They react somewhat similarly to phosphate and are more soluble in neutral to alkaline soils (Allaway 1968; Berry and Wallace 1974; Johnson 1966; Prince 1957).

Other factors which affect the fate of trace elements in soils include precipitation by other ions, organic matter reactions, soil drainage, soil microorganisms, and plant roots. Solubilities of cations are often limited by precipitation with phosphates, carbonates, hydroxides, or sometimes sulfates. Aluminum (Pratt 1966), beryllium (Romney and Childress 1965), and lead (Miller and Koeppe 1971), for example, are precipitated by phosphate. Barium sulfate (Vanselow 1966) and cadmium carbonate (Hiatt and Huff 1975) are both insoluble. Reactions with organic matter render some elements insoluble. For example, zinc humates are quite unavailable (Ermolenko 1966). The mobility of some elements may increase in poorly drained or flooded soils, probably because of the reduction of the elements to lower valence states in the absence of good aeration (Leeper 1947; Piper 1931). Chromium (Lisk 1972), manganese (Bradfield et al. 1934; Adams and Pearson 1967), molybdenum (Johnson 1966), and nickel (Lisk 1972) all have increased mobility under flooded or poorly drained conditions. The effects of soil microorganisms and their processes on trace-element mobility and availability (and vice versa) are beyond the scope of this discussion. Soil microbiota are also responsible for trace-element cycling through organic matter decomposition. Plant roots may affect trace-element availability and uptake by causing changes in the soil immediately adjacent to the roots. Tiffin (1977) states that some plants can modify the pH of the rhizosphere, release organic agents into substrates, and in other ways change the soil environment adjacent to the roots, thereby causing an increase or decrease in trace-element or nutrient uptake.

Overall, much of the trace-element deposition, particularly the cationic forms, is probably retained in the surface layers of the soil<sup>1</sup> and is not readily leached to lower horizons, except in very acid or sandy soils. In general, trace anions are more leachable than cations (Berry and Wallace 1974). At soil pH's less than 8.5, boron exists as undissociated boric acid, which is quite leachable (Berry and Wallace 1974; Bingham et al. 1972). Retention of trace elements in the soil surface layers protects groundwater from contamination. Nevertheless, surface runoff, erosion, and windblown dust may still contaminate aquatic systems (Berry and Wallace 1974). Surface soil accumulation of trace elements from low-level deposition over long periods of time might, however, approach levels toxic to some plants. This is particularly apt to occur in areas where endogenous trace-element concentrations in soil are already close to toxic ranges.

This brings up an interesting paradox with regard to the effect of soil on trace-element impacts. For example, in the near future (30-40 years), soils which can sorb and fix large quantities of cationic trace elements in an unavailable form (i.e., soils with high CEC, high organic matter, neutral to alkaline pH, etc.) may protect groundwater from contamination and also protect plants from exposure to toxic levels of available trace elements. However, in acidic, sandy, or low organic-matter soils (especially in areas of high rainfall), cationic trace elements will be more soluble and exchangeable and thus more readily available to plants or leachable to groundwater. Nevertheless, because of each soil's finite capacity to sorb cations, the soil eventually will no longer be able to serve as a "sink" for deposited trace elements, and previously unavailable trace elements may become available. Thus, soils which in the near future may be considered safe from trace-element-toxicity effects to vegetation could, in the long run, be the greatest source of trace-element problems, due to long-term accumulations of temporarily unavailable but potentially toxic concentrations of trace elements.

Information concerning soil types for a given site and possibly typical analyses or at least characteristics of these soils may be obtained from such sources as County Soil Survey Reports, the Soil Conservation Service, University Agricultural Experiment Stations, and University Agriculture Cooperative Extension Services.

<u>Endogenous levels</u>. Perhaps one of the most important factors which influences the effects of trace elements added to the soil as a result of coal combustion is the concentration of endogenous trace elements that may be naturally occurring or the result of human activities. Regardless

<sup>&</sup>lt;sup>1</sup>Little and Martin (1972) found most of the acetic-acid-soluble lead, cadmium, and zinc in the upper 3 cm of polluted soils near a large lead and zinc smelting complex. Hutchinson and Whitby (1974) found the highest concentrations of nickel, copper, and cobalt in the surface soils surrounding a smelting complex producing these elements. In a study measuring the enrichment of trace elements in soils around a coal-fired power plant, Klein and Russell (1973) assumed that enrichment was confined to the upper 2 cm of the soil.

of the source, the addition of trace elements to soils from coal-combustion emissions or effluents will have a greater impact in areas where endogenous trace-element concentrations are already close to the tolerance limit for any of the biota living there than in areas of lower endogenous concentrations. Conversely, areas suffering from deficiencies of essential trace elements (e.g., copper, molybdenum, boron, zinc, and manganese) may benefit from the addition of these elements to the soil as a result of coal combustion.

The importance of endogenous concentrations of trace elements in soil is revealed by several studies which assess the effects on biota of coal-combustion emissions from model coal-fired power plants (Dvorak et al. 1977, Dvorak and Pentecost et al. 1977; Vaughan et al. 1975). In these studies, the predicted levels of particulate deposition for the area surrounding the model plants resulted in additions of trace elements to the soil, over the operating life of the plant, which were in most cases < 10% of the total endogenous concentrations. Therefore, uptake by vegetation could not increase dramatically unless the forms of deposited trace elements were considerably more available than the endogenous forms. However, all three studies assumed average, world-wide values for the total endogenous trace-element concentrations in the soils surrounding the model plants. Thus, trace elements added to soils as a result of coal combustion are likely to have a greater impact to terrestrial systems if the power plant is sited in an average. Additionally, impacts may be greater if the availability of the endogenous trace elements is high due to the characteristics of the area soils. The range and average total endogenous soil concentrations in Tace elements are presented in Table 26. For information on the sources and regional distributions of trace elements in U.S. soils, see Appendix E.

Element	Soil Ran	ge (µg/g)	Average Soil Concentration (µg/g)	•	Reference
Arsenic	 0.1	- 40	6.0		Allaway (1968)
Barium	100	- 3000	500		Swaine (1955); Bowen (1966)
Beryllium	1	- 40	6.0		Allaway (1968)
Boron	2	- 100	10.0		Allaway (1968)
Cadmium	0.01	- 7.0	0.06		Allaway (1968)
Chromium	5	- 3000	100		Allaway (1968)
Cobalt	1.	- 40	8		Allaway (1968)
Copper	2	- 100	20		Allaway (1968)
Fluorine	30	- 300	200		Allaway (1968)
Lead	2	- 100	10		Allaway (1968)
Manganese	100	- 4000	850		Allaway (1968)
Mercury	0.01	- 4(?)			Lisk (1972)
Molybdenum	0.2	- 5	2		Allaway (1968)
Nickel	10	- 1000	40		Allaway (1968)
Selenium	0.01	- 80	0.5		Trelease (1945)
Vanadium	20	- 500	100		Allaway (1968)
Zinc	10	- 300	50		Allaway (1968)

Table 26. Total Endogenous Soil Concentrations of Selected Elements

<u>Trace elements and vegetation</u>. In addition to information on trace elements in soils, impact assessment of trace-element effects on terrestrial ecosystems is also dependent on knowledge of such things as the effects of trace elements on aerial plant parts, plant uptake and accumulation of trace elements, plant tolerance to toxic trace elements, and the relationship of vegetative community type to trace-element effects.

<u>Effects on aerial plant parts</u>. Trace-element emissions may directly affect the aerial portions of plants. The vapor form of some elements, such as mercury and fluorine, can be absorbed by aerial plant parts in the same manner as other gaseous pollutants (e.g.,  $SO_2$ ) (Huckabee 1973; Stahl 1969; Hitchcock and Zimmerman 1957; Zimmerman and Crocker 1934; Treshow 1970; Hill 1969). Toxic concentrations of trace elements such as lead and arsenic, which are

not normally translocated in large quantities from the roots to the tops of plants (Zimdahl and Arvik 1973; Allaway 1968; Berry and Wallace 1974; Natl. Res. Counc. 1972; Liebig 1966), may be ingested by livestock or wild herbivores feeding on surface-contaminated plants (Arvik and Zimdahl 1974). However, there is some dispute as to whether or not trace elements adsorbed to particulates and deposited directly onto leaf surfaces can penetrate the cuticle, be taken into the plant, and translocated (Zimdahl and Arvik 1973). Trace elements adsorbed to particulates originally deposited on plant surfaces may reach the soil through leaf and other plant litter incorporated into the soil or through washing of plant surfaces by rainfall (Little and Martin 1972).

Plant uptake and accumulation of trace elements in soil. The uptake of trace elements in the soil by plant roots is dependent upon the elements' availability to the plant as discussed in the previous section on soils. The mechanisms of trace-element uptake are not totally understood and apparently vary--with the element, plant species, and environmental conditions--from simple diffusion to active uptake. For example, Cutler and Rains (1974) have investigated the mechanism of cadmium uptake in solution culture with excised barley roots. Based on their experiments, cadmium uptake by barley roots appears to involve three mechanisms. The first is exchange adsorption; cadmium is reversibly bound to exchange sites on the roots and can be readily exchanged by desorption solutions (solutions containing a large excess of another transition-type metal cation--e.g., zinc, copper, mercury). Calcium also apparently inhibits cadmium exchange adsorption. The second mechanism appears to be an irreversible binding or sequestering to a limited number of sites, perhaps on the root cell walls or on macromolecules within the cell. The third mechanism, diffusion, accounts for movement across cell membranes and thus translocation to the shoot. Cutler and Rains (1974) concluded that the third mechanism was diffusion and not a metabolic process because cadmium sorption responded linearly to temperature changes and was not destroyed by metabolically disturbing high temperatures. Although cadmium uptake was inhibited by anaerobic conditions and the presence of a metabolic inhibitor, 2,4-dinitrophenol, these results were explained by the fact that both are known to reduce membrane permeability.

Tiffin (1977) provided evidence for an active mechanism in iron uptake. Tomato roots in solution culture exclude intact, highly stable (slowly exchanging)  $Fe^{3+}$  chelates and  $Fe^{3+}$  ions. However,  $Fe^{3+}$  chelates apparently diffuse to sites on the tomato root where the  $Fe^{3+}$  is reduced to  $Fe^{2+}$  and absorbed by the root. The iron chelate is not absorbed intact; rather the ligand is excluded and the  $Fe^{2+}$  ion is picked up by another carrier, probably citrate, in the xylem.

Plants possess the ability to take up sufficient quantities of essential micronutrient trace elements such as zinc, copper, molybdenum, and boron from rather dilute soil solutions (bioaccumulation: accumulation to concentrations greater than in the substrate). If soil concentrations of these nutrients are increased, plants will continue to accumulate the elements, and concentrations toxic to the plant or its consumers may be reached. By similar mechanisms, plants can also bioaccumulate unessential trace elements such as cadmium and nickel.

Plant uptake and accumulation of trace elements may be affected by any number of factors, including fertility of the soil and ultimately the general nutrition of the plant. In sand culture experiments, Miller and Koeppe (1971) observed that corn plants grown with insufficient levels of phosphate accumulated 5-10 times more added lead (as lead nitrate) than plants provided with sufficient phosphate levels. Phosphate-sufficient plants were also less sensitive to the lead that was accumulated. Lead was added in quantities high enough to ensure that decreased accumulation was not just the effect of lead precipitation by phosphate. Water stress, plant age, plant growth period, and plant rooting characteristics can also affect uptake and accumulation of trace elements. For example, Little and Martin (1972) found most of the acetic-acid-soluble lead, cadmium, and zinc in the upper 3 cm of heavily polluted soils near a large lead and zinc smelting complex. Hutchinson and Whitby (1974) found the highest concentrations of nickel, copper, and cobalt in the surface soils surrounding a smelting complex producing these elements. Thus, in such soils, plants with shallow, spreading roots are probably exposed to more toxic concentrations than deeper rooting species.

Since so many factors can affect plant uptake and accumulation of trace elements, accumulation varies from species to species. The ability of each species to accumulate different elements also varies. An example of species-to-species variability in trace-element accumulation can be seen in the data of John (1973). He grew eight food crops to maturity under controlled environment conditions in cadmium-amended silt loam. Two leafy vegetables, leaf lettuce and spinach, accumulated mean concentrations of  $51.1 \ \mu g/g$  (ppm) and  $207.5 \ \mu g/g$  cadmium in the leaves, respectively, when grown on soil amended to 40  $\ \mu g/g$  cadmium. Under the same conditions, radishes accumulated mean concentrations of  $264.7 \ \mu g/g$  in the tops and  $54.6 \ \mu g/g$  in the tubers, whereas carrots accumulated only 79.3  $\ \mu g/g$  in the tops and 26.8  $\ \mu g/g$  in the tubers.

Plant species also vary in their ability to tolerate toxic trace elements. Page et al. (1972) subjected nine plant species grown in nutrient solution culture to added cadmium concentrations ranging from 0 to 10  $\mu$ g/mL (ppm). Field beans were the least tolerant of the species

tested; they suffered a 50% depression in growth when solution concentrations of cadmium were 0.2  $\mu$ g/mL, resulting in leaf tissue concentrations of 22  $\mu$ g/g. However, 9  $\mu$ g/mL of cadmium in nutrient solution and the corresponding 800  $\mu$ g/g in leaf tissue were required for a 50% growth reduction in cabbage, the most tolerant species tested. It is important to note that species which are relatively tolerant of one element may be quite intolerant of another element. There are also reports of variability in uptake among varieties of a single species (John and Van Laerhoven 1976; Pettersson 1977).

Certain species can accumulate very large quantities of a particular trace element without any apparent toxicity. These species are usually termed accumulator or indicator species. Indicator species are often found growing on soils where few or no other plants will grow due to extremely high concentrations of a trace element. In fact some species are found only on soils containing the specific element which is accumulated. The selenium accumulator-indicators, including some Astragalus species (milkvetch) and others, constitute the classic case of this phenomenon and have been the most studied. It has been suggested that Ambrosia spp. (ragweed) may be an indicator plant for high zinc concentrations (Chapman 1966b). Melilotus alba and to a lesser extent Melilotus officinalis (white and yellow sweetclover, respectively) may be accumulator species of molybdenum (Munshower and De Puit 1976). It was not clear as to whether or not sweetclover is also an indicator of high molybdenum soils. Knowledge of indicator species may be helpful in locating soils with high levels of certain trace elements.

All the variability in accumulation makes it extremely difficult to quantify the removal of trace elements from the soil by plants. In an attempt to provide at least some generalized information on plant uptake, Table 27 presents plant:soil concentration ratios (CR) determined by the method of Hodgson (1970). The CR was calculated by taking the ratio of the average concentration of each element in plants to the average concentration of each element in soils. In this case, world-wide averages from Bowen (1966) and Chapman (1966a) were employed. In reality, of course, trace-element uptake and accumulation by plants cannot be defined by single values; CR's will vary with soil type, plant species and variety, environmental conditions, and other variables.

<u>Plant tolerance and trace-element toxicity</u>. Certain plants can accumulate large quantities of an element without any apparent damage whereas another species is completely inhibited by much lower tissue concentrations of the same element. Several studies have attempted to determine some of the tolerance mechanisms by which plants moderate the effects of toxic trace elements. One mechanism appears to be exclusion of the trace element from metabolic sites within the plant cells by the binding of ions to cell walls. Turner (1969) found that this mechanism apparently accounts for the tolerance to copper and zinc in *Agrostis tenuis* (Colonial bentgrass or browntop). Malone et al. (1974) observed that lead taken up by corn roots in solution culture was concentrated in dictyosome vesicles. The vesicles (normally involved in compound secretion and cell-wall deposition) fused and migrated towards the outside of the cell. Eventually, lead deposits were concentrated in the cell wall outside the plasmalemma. Another mechanism which may or may not enable plants to tolerate trace elements in the soil (depending on species and element) is the binding of certain elements in or on plant roots so that only a small amount of the element is translocated to the plant top (Wallace and Romney 1977). This subject will be discussed in more detail in the following paragraphs.

The visible signs of trace-element toxicity in plants (e.g., chlorosis, necrosis, discoloration, and stunting or deformation) are dependent on the element, the plant species, and the exposure concentration. Since many trace elements apparently have some effect on various enzymatic reactions or metabolic processes, such as photosynthesis and respiration, toxicity is often manifested by a reduction in growth. Many trace elements such as arsenic, beryllium, chromium, lead, nickel, and vanadium are accumulated by the roots, but are not readily translocated to the aboveground plant parts, whereas other elements including cadmium, copper, and zinc are more freely translocated (Berry and Wallace 1974; Allaway 1968; Lisk 1972; Romney and Childress 1965; Wiltshire 1972). Based on the literature and their own experiments, Wallace and Romney (1977) have tentatively placed a number of trace elements into three groupings regarding element distribution between roots and shoots:

- 1. Reasonably uniformly distributed: Zn, Mn, Ni, Li, B.
- Usually more in roots than in shoots, but often moderate with sometimes large quantities in shoots: Fe, Cu, Al, Cd, Co, Mo.
- 3. Mostly in roots with very little in shoots: Pb, Sn, Ti, Ag, Cr, V, Zr, Ga.

Wallace and Romney (1977) caution that this generalization is not always true for all species under all conditions, particularly when very high levels of an element are present in the soil.

The toxicity of a particular element to plants (or animals) is often dependent upon the elemental form to which the organism is exposed. For plants, the form of an element in the soil may affect its potential for uptake or exclusion (as with the  $Fe^{3+}$  example). Additionally, the form of an element once it has been taken up by a plant may affect the degree of toxicity.

Element	Concentration ratio <sup>a</sup>
Arsenic	0.14
Barium	0.03
Beryllium	0.02
Boron	5.3
Cadmium	10.7
Chromium	0.02
Cobalt	0.11
Copper	0.47
Fluorine	0.03
Lead	0.45
Manganese	0.066
Mercury	0.02-0.5
Molybdenum	0.57
Nickel	0.045
Selenium	1.0
Vanadium	0.01
Zinc	0.64

Table 27. Plant:Soil Concentration Ratios

<sup>a</sup>This is a generalized approximation of the ability of plants to accumulate trace elements similar to the method employed by Hodgson (1970). The concentration ratio is the ratio of the average concentration of each trace element in plants to the average concentration of each trace element in soils. There are limitations to this approach as defined in the text of this report. The concentrations in plants were taken from Chapman (1966a) except for barium, beryllium, cadmium, mercury, and selenium which were taken from Bowen (1966). The concentrations in soil were taken from Bowen (1966).

For example, in the literature surveyed, the trivalent state of arsenic is believed more toxic than the pentavalent state (Allaway 1968; Berry and Wallace 1974; Lisk 1972), whereas hexavalent forms of chromium are considered more toxic than trivalent ones (Lisk 1972; Sullivan 1969b). Vanadium toxicity usually increases with increasing valence; the pentavalent state is the most toxic (Natl. Res. Counc. 1974). Elemental arsenic (Berry and Wallace 1974; Sullivan 1969a) and chromium (Sullivan 1969b) are believed relatively nontoxic. The form of a trace element depends both on chemical and biological conversions.

Location of trace-element accumulation in plants--effects on wildlife. The concentration of elements in edible plant parts directly affects herbivorous wildlife (and other grazing animals, i.e., livestock), whereas the concentrations in inedible plant parts can indirectly affect animals through habitat if concentrations are toxic to the plants. For example, consider a hypothetical situation where a specific trace element (or elements) becomes elevated in a given area. It is possible that plant species which are particularly sensitive to this element occur within the area, and therefore the growth and biomass production of these plant species could be reduced or, in an extreme case, the species could be eliminated from the area. If the diet or habitat cover of a wildlife species is dependent upon this specific plant species, then the numbers of the wildlife species in the area could be reduced or, in the extreme case, eliminated. Therefore, the location of trace-element accumulation within a plant is important. Trace elements accumulated in edible plant parts may be consumed by herbivores and thereby enter the food chain.

As discussed earlier, certain elements tend to concentrate in plant roots and are not readily translocated. The location where translocated elements accumulate within the plant top

varies with species and conditions, but research is generally beginning to indicate for at least some trace elements that the concentrations in the roots > stems and leaves > fruits or seeds. A notable exception to this appears to be in species with root storage organs, such as radish or carrot (cf. data of Page et al. 1972). A possible explanation for this is that the tuber portions of such species are not involved in ion absorption from the soil (John 1973; MacLean 1976).

Vegetative community type and trace-element effects. In considering trace-element effects on vegetation and the corresponding impacts to wildlife, the type of vegetation growing in an area becomes important in several ways. First, there are differences between areas devoted to crop production, rangeland, and areas with natural vegetation. High-value crops (particularly some vegetables) often tend to accumulate higher concentrations of trace elements than grains or forages. High-value crops are usually directly consumed by man, and because of constant cropping, trace elements are slowly removed from the soils they are grown on [thus contributing to the common micronutrient deficiency problems for these soils reported by Kubota and Allaway (1972)]. Trace elements accumulated by rangeland forages, especially in heavily-grazed or over-grazed areas, are also slowly removed from the soil and can be transmitted to man via livestock. A portion of these accumulated trace elements are also returned to the soil via animal wastes. In many natural areas, however, a much larger percentage of the vegetation is not consumed and is, therefore, recycled to the soil where concentrations could potentially build up over a period of time at a faster rate than in agricultural areas. Additionally, the soils under row crop agriculture, high-intensity grazing, and those in droughty, sparsely vegetated areas (e.g., shortgrass prairie or deserts) are more susceptible to wind and water erosion, and thus may lose larger quantities of deposited trace elements than the more densely covered tall or mixed grass prairies and forests.

Several potential effects of vegetative community type on trace-element movement and cycling can be demonstrated by comparing a forest system with a grassland system. Little and Martin (1972) observed greater deposition of trace elements on the "sheltered" side of trees downwind of smelter emissions than on the "exposed" side of the same trees. They attributed this to an increased deposition of particulates on the leeward side due to the slowing of windspeeds by the trees. Little and Martin (1972) also observed higher trace-element concentrations in the soils of a woodlot than in the soils of an adjacent open field. Thus deposition velocity can be affected by microtopography, including vegetational form. In a forest, particulates may be deposited on leaf surfaces and then reach the soil as the leaves drop. Trace elements adsorbed to leaf surfaces are tied up in the slowly decomposing litter horizon. In contrast, trace elements adsorbed to grass leaf and stem surfaces will probably be released and cycled faster because of the generally greater rate of litter decomposition in a grassland compared to a forest. (Litter decomposition is largely dependent on moisture levels and temperature; therefore a comparison of decomposition rates could be modified if large variations in these two parameters exist for the two communities being compared.) In addition, trace elements in forest systems may be tied up and rendered unavailable in wood. Also, grassland soils generally have higher organic matter contents and higher cation exchange capacities than forest soils and therefore have the capacity to sorb greater quantities of trace elements, particularly cations. Studies utilizing several soils amended with equal concentrations of certain trace elements (e.g., cadmium and lead) have indicated that plant uptake of these elements is decreased by increasing soil cation exchange capacity and organic matter (Haghiri 1974; Miller et al. 1975a, 1975b).

## Terrestrial Impacts--Animals

At least 14 trace elements are essential to animals (Table 28). [An element is considered "essential" if its deficiency consistently results in impairment of function from optimal to suboptimal (Underwood 1975).] Some of these, however, become toxic at tissue concentrations only slightly higher than the level of essentiality. Toxicity tables for some essential and nonessential trace elements are presented in Appendix D.

<u>Modes of entry of trace elements into animals</u>. Terrestrial animals are exposed to trace elements from two main sources in a coal-fired power plant: (1) emission of vapor and particulates which may subsequently be inhaled or deposited on the soil and vegetation, and (2) seepage from ash and scrubber sludge ponds and disposal sites, which provide for trace-element introduction into animal drinking water sources and vegetation. The primary modes of entry into the animal are thus inhalation and ingestion.

The effects on wildlife of trace-element inhalation and ingestion are, at present, difficult, if not impossible, to evaluate on a quantitative basis, due mainly to the absence of information on (1) concentrations of most trace elements in the diet of wildlife species, and the total amounts of food and water consumed by individual species, (2) food-chain transfers and bio-accumulation of most trace elements, (3) trace-element retention times, excretion rates, and assimilation rates in individual wildlife species, (4) physiological, biochemical, and syner-gistic effects of individual trace elements in the animal body, and (5) effects of life-time exposure to very low concentrations.

Trace element	Known function
Chromium	Involved in lipid, protein, and glucose metabolism.
Cobalt	A component of Vitamin $B_{12}$ .
Copper	A component of cytochrome oxidase and other enzymes.
Fluorine	Reduces incidence of dental caries and partially prevents osteoporosis.
Iodine	A component of thyroxine and triiodothyronine, hormones of the thyroid gland.
Iron	A component of cytochromes, succinate dehydrogenase, and catalase; functions in electron transfer, aerobic oxidation of carbohydrates, and protection against $\rm H_2O_2$ .
Manganese	A component of enzymes involved in urea formation and pyruvate metabolism.
Molybdenum	A component of enzymes involved in purine metabolism and sulfite oxidation.
Nickel	Precise role unknown.
Selenium	A component of glutathione peroxidase; protects against hemoglobin oxidation.
Silicon	Initiates mineralization process in bone, and may function as a biological cross- linking agent in connective tissue.
Tin	Precise role unknown.
Vanadium	Precise role unknown.
Zinc	A component of carbonic anhydrase and other enzymes; functions in $\rm CO_2$ formation, regulation of acidity, protein metabolism, alcohol metabolism, and superoxide dismutation.

<sup>a</sup>Compiled from information in Underwood (1975).

Most information on trace-element effects on animals has been obtained on domestic or laboratory animals using relatively high doses of a single element. Although not generally applicable to wildlife in the natural environment where trace-element concentrations are likely to be small but persistent, laboratory data can provide some insight into the toxicology of the specific element. The discussion of trace-element effects in this report draws from laboratory data to some extent, but does not include a review of laboratory studies. The general toxicological effects of trace elements in animals are described in Table 29.

Inhalation. Trace elements are emitted into the atmosphere from a coal-fired power plant as (1) vapor, (2) partially as vapor and partially adsorbed onto fly ash, or (3) totally adsorbed onto fly ash. Elements emitted as vapor (e.g., mercury, some selenium, some beryllium) are not likely to be brought to ground level except under fumigation conditions. Coal combustion emissions of beryllium and mercury, otherwise subject to stringent federal standards, are not considered hazardous by the USEPA, even under restrictive dispersion conditions (USEPA 1973c). Of most concern are the trace elements adsorbed onto fly ash particules on the order of 1  $\mu$ m or less in size. These particles can deposit in the alveolar regions of the lung (Natusch et al. 1974), thus providing trace-element access to the bloodstream and subsequent transport to various internal organs. Trace elements associated with particulates of submicron size include the more volatile elements in coal such as Be, Pb, As, Se, F, Cd, B, and Ni (see pages 42 and 70).

Particulate inhalation data for man can provide some insight into animal effects. Schroeder (1971) reported that about 25% of inhaled particles settles in lung tissue in insoluble forms, another 25% is exhaled, and 50% is swallowed. Absorption efficiencies for most trace elements in the stomach are reported to be 5-15% (Piperno 1975). The submicron particles which enter the alveolar sacs are absorbed (usually depending on solubilities) or transported to the base of the ciliated bronchiolar epithelium (Piperno 1975). Natusch et al. (1974) reported alveolar absorption efficiencies for most trace elements as 50-80%. Solubility does not necessarily

Table 29. General Manifestations of Trace Elements in Animals

Element	Target organs or characteristics of toxicity	Comments
Arsenic	Has been associated with increased incidence of lung cancer.	Non-accumulative in animals but has affinity for hair, nails, and skin.
Barium	Has strong stimulating effect on all muscles in acute poisoning.	Poorly absorbed with generally little retention in tissue.
Beryllium	Characteristic granulomatous changes of lung tissue is brought about by long- term exposure.	Via inhalation, beryllium is corre- lated with an interference in the passage of oxygen.
Cadmium	Is linked with the incidence of hyper- tension in experimental animals.	Accumulative in all animals and toxic to all systems and functions in humans and animals.
Cobalt	Causes changes in lungs typical of pneumoconiosis. Also causes induction of polycythemia in many species.	With increasing age, the body burden of cobalt diminishes.
Copper	Associated with induction of haemolytic disease, especially in certain species.	In excess, results in some accumulation in the tissue, especially in the liver
Chromium	Hexavalent compounds extremely toxic to body tissue. Insoluble forms retained in lung tissue.	In particular, the respiratory tract and fat tissue accumulate this metal.
Fluoride	Contributes to dental fluorosis in animals.	Deposits in bone tissue.
Lead	Newly absorbed lead is mostly retained in the body as lead triphosphate, espe- cially in liver, kidneys, pancreas, and aorta.	Has strong affinity to accumulate in bone tissue.
Manganese	Acute intoxication involves changes in the respiratory system, whereas chronic poisoning affects the central nervous system.	Most amounts taken into the body are retained, especially in liver and lymph nodes.
Mercury	Organic forms have effects on brain tissue. The inorganic form is more linked to damage to liver and kidneys.	Can bioaccumulate in tissues of animals.
Molybdenum	Associated with degenerative changes in liver cells.	Can accumulate in tissues.
Nickel	Associated with cancer of lungs.	Very poorly absorbed from gut.
Selenium	Associated with alkali disease in cattle.	Is converted in the body into a volatile compound which is eliminated through breath and sweat.
Vanadium	Is found to inhibit the synthesis of cholesterol and other lipids. Other complications leading to cardiovas- cular diseases are also prevalent.	Vanadium salts are poorly absorbed from the gastrointestinal tract.
Zinc	Intoxication produces either lung or intestinal tract manifestations.	Absorbed or injected zinc is incor- porated at varying rates into dif- ferent tissue, indicating varying rates of zinc turnover.

imply retention or absorption. Some examples are: AgI is rapidly absorbed from the lungs, despite its weak solubility in water; lead is insoluble in water, but is absorbed in the respiratory passages; and vanadium, assumed to accumulate in human lungs in insoluble form, is a pulmonary irritant at  $\geq$  50 µg/m<sup>3</sup> (Piperno 1975).

It thus becomes obvious that a correct evaluation of trace-element inhalation by wildlife in the vicinity of a coal-fired plant requires site-specific information on the particle size of fly ash emitted, meteorological parameters, stack height, location of the animal relative to the plume, and inhalation volume for the specific animal, in addition to animal dose-response information.

<u>Ingestion with drinking water</u>. Natural waters or surface seeps that receive leachates or surface effluent from combustion waste-disposal ponds and particulate emission fallout can introduce trace-element contaminants into the animals that drink from these water sources. The recommended limits for concentrations of elements and ions in livestock drinking water (Table 30) can serve as similar limits for wildlife, assuming that wildlife species such as ungulates have physiological tolerances to trace elements similar to livestock species. These limits may not be appropriate for wildlife species more genetically dissimilar than livestock and native ungulates.

Element or ion	Recommended limit (mg/L)
Aluminum	5
Arsenic	0.2
Boron	5.0
Cadmium	0.05
Chromium	1.0
Copper	0.5
Fluorine	2.0
Lead	0.1
Mercury	0.01
Molybdenum	uncertain <sup>b</sup>
Nitrate	100
Nitrite	10
Selenium	0.05
Vanadium	0.1
Zinc	25
Total soluble salts	5000

Table 30. Recommended Limits for Concentrations of Elements and Ions in Livestock Drinking-Water Sources Above Which Toxic Effects May Occur<sup>a</sup>

<sup>a</sup>Compiled from National Academy of Sciences-National Academy of Engineering (1974).

<sup>D</sup>Toxicity influenced by many factors. Natural surface waters rarely contain over 1 mg/L.

<u>Ingestion with food</u>. Calculation of the trace-element dose to wildlife from dietary intake requires quantitative information on the trace-element content of that diet. Much of the literature on trace-element uptake in plants is based on nutrient solution culture studies, greenhouse studies, and studies involving agricultural species. Consequently, assumptions of plant-tissue concentrations may be necessary if any estimates are to be made of biomagnification of trace elements within the food chain. In addition, it is necessary to determine the quantities of trace elements deposited and retained on the surface of vegetation. No studies are known which have examined the intake of trace elements by wildlife through ingestion of dust-coated vegetation.

When examining the potential dietary pathways of trace elements, the food habits of the species must be known. For many herbivores and granivores (e.g., small rodents, shrews, ground squirrels, and various squirrels), home range size varies from a few hundred square meters to a square kilometer (Burt and Grossenheider 1976). If these species inhabit an area immediately downwind of a coal-fired power plant, vegetation contaminated with trace elements will be consumed. Hoofed browsers such as antelope, mule deer, and white-tailed deer generally cover relatively large areas to obtain forage during the summer months. However, if during the winter months deer are found to occupy a restricted area immediately downwind of a coal-fired plant (e.g., a deer yard), the chances of trace-element ingestion will increase. Attention obviously should be given to those food items constituting the bulk of the winter diet. For white-tailed deer, the ingestion of twigs of shrubs and trees as well as acorns may represent important avenues of entry for contaminants. Large carnivores usually cover several square kilometers during their foraging activities and are less likely to ingest toxic levels of trace elements since food items consumed in highly contaminated areas may constitute only a small portion of the diet. Smaller carnivores, such as weasels and shrews, can be subject to higher exposure levels due to a much smaller home range and the consumption of prey in a smaller geographical area.

Exposure of wildlife to trace elements may vary within and among seasons, depending upon the life history stage of the animal. The chicks of some important gamebirds, such as quail and various grouse species, mainly consume insects whereas adults consume mostly grain, buds, or other vegetation. Consequently, immature individuals may be exposed to higher dietary levels of trace elements than adults because of differences in the type of food consumed. These two examples suggest that shifts in dietary habits should be considered carefully when determining the potential for trace-element bioaccumulation in the tissues of various wildlife species.

Of particular concern when assessing the potential impacts of trace-element ingestion are those species which inhabit the aquatic-terrestrial interface. Many waterfowl and shorebirds are likely to obtain food items from both terrestrial and aquatic communities. Mallards and blue-winged teal, for example, filter bottom sediments of marshes and lakes for invertebrates, algae, etc., but also consume grain such as millet, wheat, and corn, and consequently can obtain trace elements in both terrestrial and aquatic habitats. Particular attention should be given to identifying accurately the feeding areas of waterfowl and other wetland birds during the breeding season and winter months. The relatively short time intervals spent in wetlands along the migratory route will not likely result in the ingestion of large amounts of food contaminated with trace elements. See p. 110 for a discussion of waterfowl use of active ashdisposal ponds.

Specific trace-element uptake by animals in the natural environment. There have been a few investigations of trace-element uptake by wildlife in the natural environment. Earthworms were reported to accumulate high body burdens of cadmium, nickel, lead, and zinc along roadsides in Maryland (Gish and Christensen 1973). Metal residues were highest in earthworms inhabiting areas of highest traffic volume. Correlations between soil concentrations and earthworm tissue concentrations decreased with decreasing atomic weight of the metal. Earthworms accumulated up to 331.4 ppm lead and 670.0 ppm zinc. Ratios of amounts of metals (ppm, dry weight) in earthworms to those in soil averaged 11.2, 1.9, 0.95 and 5.7 times that in soil for cadmium, nickel, lead, and zinc, respectively. Since earthworms are consumed by many species of birds and certain species of amphibians, reptiles, and mammals, a strong potential exists for biomagnification of these four elements through the food chain.

Various terrestrial arthropods are known to incorporate lead (Giles et al. 1973; Price et al. 1974; Rolfe and Haney 1975). In one study of insects inhabiting areas along highways, body tissue concentrations of 10.3, 15.5 and 25.0 ppm (oven dry weight) were observed for species that suck plant juices, chew plant parts, and prey on other insects (Price et al. 1974). In low lead areas, tissue concentrations were 4.7, 3.4, and 3.3 ppm, respectively.

Rolfe and Haney (1975) observed a negative correlation between distance from a highway and lead concentrations of various tissues for five small mammal species in central Illinois. Insectivores (short-tailed shrew) had the highest total body concentrations followed by herbivores (prairie vole) and granivores (deer mouse). The total body lead concentrations of shrews (mean = 18.4 ppm) in high traffic areas may be the result of food chain biomagnification since insects taken from these same areas had relatively high concentrations of lead. No visible signs of adverse effects from trace elements were detected for any of the species examined. In general, bone, spleen, and kidney tissues contained higher lead concentrations than did lung and liver tissues for the five species examined.

## Studies of Trace-Element Impacts on Terrestrial Ecosystems

It is virtually impossible to quantify the effects of emitted trace elements generically. In addition to extremely variable site-specific factors affecting the environmental movement and pathways of trace elements (e.g., meteorological conditions, topography, soil type, endogenous trace-element concentrations, land use, soil microorganisms, and plant and animal species), emissions from the stack are also site-specific depending on coal type (e.g., bituminous, lignite), coal seam, variability of trace-element concentrations within a seam, power plant design, and emission-abatement equipment design and efficiency. Even if New Source Performance Standards for particulates (see Appendix A) are assumed to be met, there will still be a great deal of variability in the actual trace-element concentrations of the emitted particulates.

There are relatively few studies of mass balance and partitioning of trace elements through coal-fired power plants. Due to the large variability of measured trace-element flow in these studies, calculations and predictions of generalized trace-element emissions such as that given for a 100-MWe plant using Eastern Interior coal (Table 11) are inevitably imprecise and at best only a rough estimate. Furthermore, the modeling of aerial transport and deposition of particulates may be off by a factor of at least two or three when a specific site and corresponding meteorological data are known. However, if specific sites are not used (as in this document), aerial concentration and deposition estimates could be in error by a factor of 10-20. Additionally, it is difficult to estimate the proportion of the stack emission that will be deposited within a given radius (e.g., 100 km) from the stack. Some studies (Berry and Wallace 1974; Dvorak et al. 1977) have made the conservative assumption that all of the particulates emitted are deposited within the designated study area. In the literature surveyed, the study of Vaughan et al. (1975) was the only one that used what they considered to be a more realistic estimate; they assumed that only 6% of the stack emission was deposited within 50 km of the 300-m stack and that the other 94% entered the upper atmosphere where it would become indistinguishable from particulate trace elements from other sources.

Given the present lack of data on this subject, the most pragmatic way to approach the inherent difficulties and variabilities of determining and assessing trace-element emissions, deposition, resultant soil concentrations and availabilities, endogenous soil trace-element levels, plant uptake, and trace-element movement through food chains is to make conservative assumptions and assess the impacts of a "worst case." By taking this approach, trace elements that appear to have little chance of seriously affecting terrestrial systems may be separated from those that have potential for causing adverse impacts. Two analyses (Dvorak et al. 1977; Dvorak and Pentecost et al. 1977) have taken this approach to the assessment of the impacts of trace-element emissions from a single, conventional model power plant may have relatively little impact to terrestrial ecosystems <u>provided that</u> New Source Performance Standards for particulates (0.1 1b/10<sup>6</sup> Btu heat input) are met and that tall stacks are used.

The deposition of 11 trace elements (As, Ba, Cd, Cr, Co, Pb, Mn, Hg, Se, V, and Zn) emitted from a 1000-MWe model plant (with a 300-m stack) hypothetically sited in five regions of the United States, was modeled, and a worst-case approach was utilized to assess the impacts of the 11 elements on terrestrial ecosystems over the expected 30-year operating life of the plant (Dvorak et al. 1977). Assuming average endogenous trace-element concentrations and based on conservative assumptions of (1) trace-element retention in the soil, (2) availability, and (3) plant uptake, trace-element emissions from the five different model plants in this analysis were not expected to adversely affect vegetation. (Because of the conservative assumptions, particularly that of total trace-element availability for uptake, calculated trace-element concentrations in plants were high enough to be toxic for some elements and some plant species. However, conservative calculations of the percent increase in the soil trace-element concentrations over average total endogenous concentrations were considered insignificant. Thus, the high, conservative, calculated plant tissue concentrations were more the result of endogenous soil concentrations than deposited trace elements.)

Within the scope of the study (Dvorak et al. 1977), it was impossible to quantify the effects of trace-element emissions on livestock and other animals. However, cadmium was considered potentially dangerous because of the inability of mammals to excrete it (Berry and Wallace 1974). Cadmium has a relatively long biological half-life (Lagerwerff 1972; Hiatt and Huff 1975; Friberg et al. 1971) and, therefore, can be an accumulative poison in mammals (Berry and Wallace 1974; Hiatt and Huff 1975). The calculated tissue concentrations of cadmium in plants (up to 32.9 ppm for the Eastern Interior regional siting, burning Illinois coal) did exceed the dietary levels of cadmium (15 ppm) considered injurious to animals and man (Underwood 1962). The calculated tissue concentrations of selenium in vegetation, especially around the Northern and Southern Appalachian regional sitings of the 1000-MWe model plant (up to 9.6 ppm at the Northern Appalachian site), also exceeded the lowest dietary concentration considered to cause chronic poisoning in cattle (1-4 ppm in fodder) (Russell 1944). Also, because selenium concentrations in many western soils are quite high (Rosenfeld and Beath 1964), grazing areas of marginal toxicity could become unusable due to selenium deposition from coal combustion. However, due to the extremely conservative assumptions made in this study, cadmium and selenium should only be considered potentially hazardous and should be flagged for future research.

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In a similar worst-case analysis of predicted emissions of As, Be, Cd, Pb, and Se from a single 3000-MWe model plant (with a 244-m stack) sited in southern Illinois (Dvorak and Pentecost et al. 1977), no serious adverse impacts to vegetation, herbivores, or carnivores were expected.

This study also assumed average endogenous trace-element concentrations in soil, total retention of deposited trace elements in soil, a conservative soil dilution factor, and total availability of the deposited and endogenous trace elements. However, the plant uptake concentration ratios used (see Table 27) were less conservative (lower) than those used in Dvorak et al. (1977). The concentration ratios used in Dvorak and Pentecost et al. (1977) appeared to give more realistic plant tissue concentrations for uptake estimates assuming total availability, because they are based on the ratio of average plant concentration to average total soil concentration.

Worst-case analysis of predicted As, Be, Cd, Pb, and Se emissions from a clustered siting pattern (twelve 3000-MWe model plants) in southern Illinois (Dvorak and Pentecost et al. 1977) indicated that arsenic deposition around the clustered siting pattern resulted in calculated plant uptakes of 1.11 to 1.60  $\mu$ g/g (ppm). Soybean and other legumés are not considered to have much tolerance for arsenic (Liebig 1966; Vallee et al. 1960) and tissue concentrations of 1  $\mu$ g/g have been reported to be toxic to soybean (Deuel and Swoboda 1972). Arsenic was the only element of the five analyzed in which the calculated plant uptake exceeded the lowest concentration toxic to plants that was found in the reviewed literature. Thus, given the limitations of the worst-case approach, the possibility of arsenic emissions in this case study causing adverse effects in vegetation of low tolerance cannot be ruled out by this analysis.

No adverse impacts to grazing animals due to trace-element emissions from the clustered siting pattern were expected. However, the possibility of bioaccumulation, particularly of cadmium, to toxic levels in the food chain was noc assessed. Additionally, neither of the above analyses attempted to assess the effects of deposited trace elements on scavengers, decomposers, soil organisms, and other invertebrates.

The effects of fluoride emissions on vegetation and herbivores were also assessed by Dvorak and Pentecost et al. (1977). Fluoride emissions from the single 3000-MWe plant were not expected to have adverse effects on vegetation. However, the clustered siting pattern may have some adverse effects on sensitive species such as sorghum, fruit trees (peaches, cherries, and apricots), and conifers. Because fluoride is an accumulative toxicant, injury usually occurs as a result of fluoride build-up in leaves of the affected vegetation over a period of weeks or months (Hill 1969). At least a portion of a 202 km<sup>2</sup> area north of the cluster of power plants was expected to be subjected to annual average ground-level fluoride concentrations high enough to accumulate over a growing season to tissue concentrations that can cause foliar marking in sorghum (McCune 1969). The predicted 24-hour maximum short-term ground-level fluoride damage in fruit trees and conifers (McCune 1969). Fluoride accumulation in vegetation was not expected to reach levels which could adversely affect grazing animals or other livestock (cattle are quite sensitive to fluoride).

Another study (Vaughan et al. 1975) modeled the transport and deposition of trace-element emissions from a 1400-MWe model plant sited near St. Louis, Missouri. The assumptions were that (1) the plant burned a representative average composition, low-sulfur western coal, (2) the plant had 95% efficient electrostatic precipitators and a stack height of 300 m, and (3) 6% of the particulate emissions would be deposited within a 50 km radius of the plant, whereas the remaining 94% of the emission would be lost to the upper atmosphere. The assumptions made in this study, although conservative, were not worst-case. Of the 22 elements (Ag, As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Te, Tl, Th, Ra, V, W, and Zn) studied in terms of effects on vegetation, seven elements (Cd, Co, Cu, Hg, Mo, Ni, and W) were considered to merit some concern and perhaps a more intensive evaluation of potential for adverse effects in terrestrial systems. However, the predicted increases of these elements (over a 40-year operating life of the power plant) in the soil and vegetation were not expected to have toxic effects on vegetation. Additionally, the authors concluded that the use of other coal types in this model would generally not produce an increase in emission rates large enough to raise biologically available element concentrations to greater than 10% above biogeochemical background levels. The authors also noted that available literature on Ga, Ge, Ra, Te, Th, Tl, and V was insufficient to evaluate the potential for adverse effects caused by these elements.

Three studies (Klein and Russell 1973; Horton et al. 1977; Lyon 1977) have measured actual trace-element concentrations in the soils and vegetation surrounding operating coal-fired power plants. Klein and Russell (1973) sampled soils, native grasses, maple leaves, and pine needles at sites near a 650-MWe power plant on the eastern shore of Lake Michigan near Holland, Michigan. The plant came on-line in 1962 and burns Ohio coal. The 122-m (400-ft) stack, which is equipped with a 90% efficient electrostatic precipitator, is somewhat shorter than the stacks used in the modeling studies. The terrain is flat and the soils are sand with a thin cover of decomposed organic matter. Based on samples taken from the top 2 cm, soils near the plant exhibited increased concentrations of Ag, Cd, Co, Cr, Cu, Fe, Hg, Ni, Ti, and Zn when compared to the background concentrations measured for similar soils away from the power plant. Additionally, concentrations of Cd, Fe, Ni, and Zn in vegetation were increased over background concentrations for vegetation. However, increased plant-tissue concentrations were not high enough to be

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toxic; they were less than or approximately equal to the average concentrations for plant tissue according to Bowen (1966). It was not clear whether or not the plant samples were washed prior to sample digestion and analysis to remove trace elements adsorbed to the leaf surfaces.

Horton et al. (1977) sampled soils and vegetation (broom sedge, dog fennel, and panic grass) at sites near (within 17 km) the Savannah River Plant at Aiken, South Carolina. The plant, in operation since 1952, has four units and each has a relatively short, 38-m stack. From 1952 until late 1975, particulate emission control depended on mechanical collectors which were 75% efficient at best. During late 1975 and early 1976, electrostatic precipitators with > 99% efficiency were installed. Sampling took place before the installation of the precipitators. This plant is located in an area typical of the coastal plains in the southeastern United States. Soils are sandy and have low pH's. Of the 29 trace elements analyzed, seven (Ba, Be, Cu, Hg, Mn, Se, and Sr) showed a significant negative correlation between the logarithm of soil concentration and the logarithm of distance from the power plant, thus suggesting increases in soil trace-element concentrations of up to 2-4 times (for sampling sites 1.8 km from the stack versus sites 16.5 km from the stack) due to the power plant emissions. In vegetation, Be, Co, Mo, and V in dog fennel and Sr in panic grass exhibited significant negative correlations between the logarithms of plant tissue concentration and distance from the plant. Comparison of tissue concentrations at 1.8 km from the stack to those at 16.5 km from the stack indicated increased concentrations of these elements in vegetation by a factor of approximately 1.5 to 3. Significant differences in tissue concentrations were found among the three plant species for Ba, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sc, Sr, V, and Zn. Concentrations of Ba, Be, Cu, Ni, and Sr were highest in dog fennel, but Hg, Mn, Pb, and Zn were highest in panic grass, thus illustrating species-to-species variability in uptake. Circumstantial evidence was presented in this study which indicates that trace elements in particulate deposition may be less available to plants than trace elements "naturally" occurring in the soil.

Finally, in the Oak Ridge National Laboratory study (Lyon 1977), soils were sampled from the area surrounding the 870-MWe Thomas A. Allen Power Plant near Memphis, Tennessee, on the floodplain of the Mississippi River. The Allen plant, completed in 1959, has three units and each has a 122-m (400-ft) stack with an electrostatic precipitator. The area surrounding the plant is primarily used for cotton and soybean production. There are a few stands of woodland (primarily floodplain species such as sycamore and cottonwood) and some swampland. About 13 km (8 mi) to the south, the terrain changes to river bluffs and rolling hills, mostly in pasture. Soil samples [15-cm cores--top and bottom 2.5 cm analyzed] were taken at 1.6-km (1-mi) intervals from 32 km (20 mi) south of the plant to 32 km north of the plant, because of predominantly north-south winds. The investigators found it difficult to determine changes in the traceelement concentration of the soil as a result of the power-plant emissions because of the variable nature of endogenous concentrations in the soils of this area. This variability was probably caused primarily by periodic floodings of the Mississippi River, the mixing of soil by agricultural tillage, and the use of agricultural chemicals including fertilizers, herbicides, and insecticides in the study area. The authors concluded that no appreciable portion of the trace-element concentrations in the soils surrounding the Allen plant can be attributed to emissions from the power plant because (1) the concentrations varied, (2) there were no trends of higher to lower concentrations with distance, and (3) there was no significant sharp decrease in concentration with depth in the soil as might be expected from atmospheric deposition.

One study (Casey et al. 1976) measured actual trace-element concentrations in wildlife found near an operating coal-fired power plant. Casey et al. (1976) compared tissue concentrations of calcium, sodium, potassium, strontium, zinc, and copper in white-tailed deer, deer mice, redback vole, and meadow vole in areas adjacent to a 215-MWe coal-fired (lignite-fired) plant operating since 1966 near Stanton, North Dakota. A second lignite-fired power plant (530-MWe, on line since 1967) located < 1 km northwest of the plant under study also contributed to traceelement deposition in the study area. For all species examined, no significant differences were observed between experimental and control areas for each of these elements in bone, kidney, liver, or fresh antler tissues. In additional studies, no significant differences between control and experimental areas were observed in mercury, cadmium, lead, selenium, and molybdenum for both liver and skin tissue of deer mice. The authors attributed this to the relatively short lifetime (6-12 months) of the mice, a time too short for the bioaccumulation of quantities of trace elements sufficient to demonstrate detectable differences.

The Walker Branch Wastershed study conducted by Oak Ridge National Laboratory (Van Hook et al-1977) has examined the distributions and cycles of cadmium, lead, and zinc in the major vegetation components and soils of a mixed deciduous forest ecosystem in eastern Tennessee. Three coalfired electric generating stations with a combined coal consumption  $7 \times 10^6$  MT/year are the major anthropogenic sources of atmospheric trace-element emissions in the vicinity (14-km radius) of the Walker Branch Watershed. Discharges of cadmium, lead, and zinc from the three plants have been conservatively estimated as 0.09, 0.95, and 9.46 MT/year, respectively. The transport and turnover of cadmium, lead, and zinc through vegetation was found to be relatively rapid (3-4 years) however, these elements were apparently retained by the soil. Although the 01 and 02 litter horizons (02 > 01) and the smallest lateral roots (< 0.5 cm diameter) were the major sites of cadmium, lead, and zinc accumulation, the watershed soils were the long-term sink. The A1 soil horizon generally contained the highest concentrations of the three elements; this was associated with the higher organic matter content of the surface soil horizons. Concentrations of cadmium, lead, and zinc in living vegetation were generally in the order: roots > foliage > branch > bole. Examination of the biogeochemical cycles of these three trace elements generally indicated that element inputs to the watershed ecosystem are much greater than losses and that losses are much less than the trace-element standing pools (g/ha of Cd, Pb, or Zn); thus, the elements are being retained by the system. Although no measurable adverse effects have been attributed to present trace-element concentrations in the Walker Branch Watershed, the authors warn that terrestrial organisms may be affected by long-term accumulation if trace elements are introduced to the ecosystem at higher than natural concentrations. Also, the accumulated trace elements could eventually be released to surface waters and groundwaters, thus affecting aquifers and aquatic ecosystems.

The effects on terrestrial ecosystems of long-term accumulation of trace elements may be illustrated by studies of ecosystems affected by trace-element emissions from smelters, which emit considerably higher concentrations of trace elements. Jackson and Watson (1977) have studied the effects of lead, cadmium, zinc, and copper emissions on a forested ecosystem located near a lead smelter in operation since 1968 in southeastern Missouri. Deposition rates of lead, cadmium, zinc, and copper measured within 0.4 km of the smelter were 103, 0.72, 6.4, and 2.1 g/m<sup>2</sup>/year, respectively. During 1974-1975, two stages of ecosystem disruption were associated with trace-element accumulations: (1) an initial stage (1.2-2.0 km from the stack) characterized by an accumulation of 02 litter with no measurable effects on soil-litter biota, and (2) an advanced stage (0.4-0.8 km from the stack) characterized by depletion of soil and litter nutrient pools with evidence of depressed communities and nutrient translocation.

Other studies are presently under way to observe trace-element effects on biota at the Colstrip Power Plant in southeastern Montana (Preston and Lewis 1977) and the Columbia Electric Generating Station near Portage, Wisconsin (Inst. Environ. Stud. (1976a).

In order to determine the potential impacts to terrestrial ecosystems of trace-element emissions from a given coal-fired power plant, as many factors as possible that may affect trace-element behavior should be considered concurrently. By examining the background information on soils, endogenous levels, and vegetation and animals, the characteristics of the site which may increase the possibility of trace-element impacts, and characteristics which may reduce trace-element impacts, can be identified. Unfortunately the system is not quite so simplistic; factors which cause the release of deposited trace elements from one system (e.g., leaching of certain elements to lower soil horizons) will also cause those elements to be inputs into another system (e.g., continued leaching of certain elements from lower soil horizons to groundwater). It is easy, based on the modeling and monitoring studies discussed in this section, to begin to feel that trace-element Transformations in Soils, this might be true in the "short" term (30-40 years), but in the long term, soils which have served as "sinks" and have fixed trace elements in unavailable forms may become saturated and no longer have the capacity to sorb additional trace elements, or for some other reason (e.g., acid rain) may release large quantities of previously fixed elements.

It appears that one of the most important factors affecting the quantity of particulate deposition per unit area is stack height. Much larger quantities of particulates are deposited closer to plants with short stacks (such as those of many older oil- and gas-fired power plants which may be converted to coal) than plants with tall stacks. The tall stacks allow greater dispersal and dilution of particulates in the air, and thus may contribute to regional trace-element loadings. A comparison of particulate deposition from power plants with different stack heights is presented in Table 31. Of course, meteorological factors and topography can also affect deposition. For example, the siting of a power plant in a valley may greatly affect deposition patterns (see Fig. 11).

Due to the site-specific nature of trace-element impact assessment, no quantitative estimates of "typical" trace-element depositon based on combustion of standard coals for various power plant sizes will be given. However, if one has access to predicted trace-element emissions and deposition rates for the power plant in question, conservative estimates of resultant trace-element concentrations in soils and plants may easily be calculated. Calculations for conservative soil concentrations are as follows:

Deposition  $(g/m^2) \times \frac{1}{10^4} \frac{m^2}{cm^2} \times \frac{1}{d} \times \frac{10^6}{1} \frac{\mu g}{g} \times \frac{1}{D_b}$  = Total added soil concentration  $(\mu g/g)$  (18)

	350-MWe power plant <sup>b</sup>			1000-MWe power plant <sup>C</sup> Anticipated average Area affected		
Distance from stack (km)	Anticipated range of deposition (mg/m²/yr) <sup>d</sup>	Area affected (km <sup>2</sup> )d	Distance from stack (km)	Anticipated average deposition (mg/m²/yr)	Area affected (km <sup>2</sup> )	
0.5	22,000 -76,000	0.11	Not given <sup>e</sup>	123.38	38.75	
1.0	22,000 -42,000	0.49		88.13	312.6	
2.5	130 -6,700	2.2		52.88	6,196	
5.0	220 -890	4.9		17.63	13,750	
7.5	96 -400	7.4				
10.0	20 –79	29				
20.0	3.7 -16	79				
30.0	1.7 -7.1	120				
40.0	1.1 -4.5	160				
50.0	0.37-1.4	370				
75.0	0.13-0.55	740				
100.0	0.09-0.33	460				

Table 31. Comparison of Particulate Deposition Rates for a 350-MWe Power Plant with a Short Stack and a 1000-MWe Power Plant with a Tall Stack<sup>a</sup>

<sup>a</sup>Data for the 350-MWe plant (short stack = 75 m) were calculated for this report. Data for the 1000-MWe plant (tall stack = 300 m) are from Dvorak et al. (1977). Although the two plants vary in MWe produced, the particulate emission rates are approximately equal: 0.84 MT/day (0.93 tons/day) for the 350-MWe plant; 0.85 MT/day (0.94 tons/day) for the 1000-MWe plant. <sup>b</sup>Calculations made for Eastern Interior coal (ash content = 10%). <sup>c</sup>Data are for Western coal (ash content = 6%). Comparisons were made with Western coal because the 6% ash content was the

<sup>C</sup>Data are for Western coal (ash content = 6%). Comparisons were made with Western coal because the 6% ash content was the highest used by Dvorak et al. (1977). <sup>d</sup>Deposition with the lack of specific wind-direction information was conservatively assumed to be in one of sixteen 22.5°

"Deposition with the lack of specific wind-direction information was conservatively assumed to be in one of sixteen 22.5" sectors 33% of the time. The deposition ranges and corresponding areas affected represent the deposition in this one sector.

esector. In Dvorak et al. (1977) deposition rates were not calculated for concentric rings and sectors around the power plant as in this report. Based on representative meteorological data for the model plant site, isopleths of deposition rates were generated for an area surrounding the plant with an 80.5 km radius. The areas with the highest deposition rates were generally 20-35 km from the plant. In this equation, deposition  $(g/m^2)$  means the deposition (not aerial concentration) over a designated length of time of the trace element under study, d represents the depth in cm of the soil that the trace element is assumed to be retained in, and Db represents the bulk density of the soil in  $g/cm^3$ . Use of this calculation without modification assumes that (1) all of the deposition in a given area is retained by an assumed surface layer of soil (of depth d), (2) none of the element is lost from this volume of soil either by leaching, or surface runoff or erosion, and (3) the deposited element is distributed equally throughout the assumed soil volume.

The studies of Dvorak et al. (1977) and Dvorak and Pentecost et al. (1977) assumed an effective soil depth of 3 cm (worst-case) based on reports of trace-element retention in soil surface layers around smelters and power plants (see footnote on page 72). Then it was assumed that the calculated trace-element concentration was totally available to plant roots and that the whole plant root system was exposed to this concentration (even though it was really only in the top 3 cm of soil). Vaughan et al. (1975) assumed an effective soil depth of 20 cm which may be more realistic in terms of the plant root zone, but does not reflect the reports of retention in soil surface layers.

Bulk density  $(D_b)$  of the soil can be either measured or estimated by consulting with Soil Survey Reports for the area, local Soil Conservation Service offices, or University Agricultural Experiment Stations or Cooperative Extension Services. Bulk densities generally range from 1.0 to 2.0 g soil/cm<sup>3</sup> (Brady 1974). Bulk density is a weight measurement which considers the entire soil volume, both solid particles and pore spaces. Thus, bulk density is dependent upon soil texture and structure as well as the degree of soil compaction. Sandy soils generally have a higher bulk density than well-granulated, finer-textured surface soils such as silt loams, clay loams, and clays. Figure 19 illustrates the relationship between soil texture, compactness, and bulk density. Very compact subsoils may have bulk densities  $\geq 2.0$  g/cm<sup>3</sup> regardless of texture. If good bulk density estimates are not available, the assumption of about 1.5 g/cm<sup>3</sup> for a loamy soil could be made (as in Dvorak et al. 1977; Dvorak and Pentecost et al. 1977; and Vaughan et al. 1975).



COMPACTNESS OF SOIL ZONE

Figure 19. Generalized Relationship between Compactness and the Range of Bulk Densities Common in Sandy Soils and in Those of Finer Texture. Sandy soils generally are less variable in their degree of compactness than are the finer-textured soils. For all soils, the surface layers are more likely to be medium to loss in compactness than are the subsoils. From Brady (1974) (with permission, see credits). The calculation described in Equation 18 was contrived as and should be used only as a guide, particularly if the very conservative assumption of total availability is made.

An idea of potential plant-tissue concentrations of the elements in question can be obtained by adding soil endogenous and deposited trace-element concentrations together and multiplying by the concentration ratios given in Table 27. Again, this calculation is only a conservative estimation of a highly site- and plant-species-specific phenomenon and should be used only as a guide.

It is expected that, at best, with the information presented here and data available elsewhere, it will only be possible to determine potential adverse effects of trace-element combustion emissions in a qualitative manner for the near future (30-40 years). Finally, to date, the studies and models of the fate and effects of trace elements emitted by coal combustion have examined many trace elements, but the effects of each of these elements on terrestrial ecosystems have only been considered individually. Yet almost all of the emitted trace elements are introduced to the system via the deposition of particulates (to which many elements are adsorbed). Thus, although the introduced concentrations of single elements may be relatively low as a result of coal combustion, the concentrations and interactions of all the elements being introduced together may have effects that at this time, cannot be quantified. Synergistic and antagonistic interactions between various trace elements have been reported; however, there is virtually no information available to indicate the possible interactions and effects of the introduction to a system of all the elements adsorbed to particulates.

#### Aquatic Impacts

Trace elements can reach aquatic systems from natural sources including (1) precipitation, (2) runoff, (3) groundwater, (4) the atmosphere, and (5) the aquatic system's own substrate. The amounts of trace elements entering aquatic systems from each of the above sources can be and has been augmented by man. The amounts of naturally produced trace elements which enter the system generally are small. Background or ambient concentrations of trace elements usually reflect the geologic composition of the drainage basin, although the relationship is not exact since erosion and solubility of the various elements differ and aquatic biota can act selectively on many elements.

The quantity of trace elements released to the environment is increasing because of cultural, industrial, and agricultural activities. Although many water quality regulations have been established to regulate specific sources, many unregulated sources exist. The discharges of trace elements to the oceans from biogeochemical processes are less than discharges from mining operation (Table 32). If other sources such as wastewater treatment, electric power production, and industrial sources are added, the amounts of trace elements liberated to the environment become even greater. The data on release rates of trace elements to the atmosphere from the combustion of fossil fuels are given in Table 33.

	Rate (10 <sup>3</sup>	MT per year)
Element	Geological rate (in rivers)	Man-induced rate (mining)
Iron	25,000	319,000
Manganese	440	1,600
Copper	375	4,460
Zinc	370	3,930
Nickel	300	358
Lead	180	2,330
Molybdenum	13	57
Silver	5	7
Mercury	3	7
Tin	1.5	166
Antimony	1.3	40

Table 32. Man-Induced Mobilization of Metals Exceeding Natural Rates by Geological Processes, As Estimated from Annual River Discharges to the Oceans<sup>a</sup>

<sup>a</sup>Originally from Massachusetts Institute of Technology (1970). Adapted from Waldichuk (1974) (with permission, see credits).

	Release to	atmosphere (10 <sup>3</sup> MT	per year)
Element-	Coa 1	0i1	Total
Aluminum	1400	0.08	1400
Arsenic	0.7	0,0002	0.7
Barium	70	0.02	70
Beryllium	0.41	0.00006	0.41
Bismuth	0.75	N.D.b	-
Cadmium	N.D.	0.002	-
Calcium	1400	0.82	1400
Cerium	1.6	0.002	1.6
Chromium	1.4	0.05	1.5
Cobalt	0.7	0.03	0.7
Copper	2.1	0.023	2.1
Erbium	0.085	0.0002	0.085
Gallium	1	0.002	1
Germanium	0.7	0.0002	0.7
Holmium	0.042	N.D.	-
Iron	1400	0.41	1400
Lanthanium	1.4	0.0008	1.4
Lead	3.5	0.05	3.6
Lithium	9	N.D.	-
Magnesium	280	0.02	280
Manganese	7	0.02	7
Mercury	0.0017	1.6	1.6
Molybdenum	0.7	1.6	2.3
Neodymium	0.65	N.D.	-
Nickel	2.1	1.6	3.7
Potassium	140	N.D.	•
Praeseodymium	0.31	N.D.	-
Rhenium	0.007	N.D.	-
Rubidium	14	N.D.	-
Samarium	0.22	N.D.	-
Scandium	0.7	0.0002	0.7
Silver	0.07	0.00002	0.07
Sodium	280	0.33	280
Strontium	70	0.02	70
Terbium	0.042	N.D.	
Thulium	0.014	N.D.	-
Tin	0.28	0.002	0.28
Titanium	70	0.02	70
Tungsten	N.D.	N.D.	
Uranium	0.14	0.001	0,14
Vanadium	3.5	8.2	12
Ytterbium	0.07	N.D.	-
Yttrium	1.4	0.0002	1.4
Zinc	7	0.04	7
Zirconium	N.D.	N.D.	-
		-	

# Table 33. Mobilization of Metallic Elements into the Atmosphere by Burning of Fossil Fuels<sup>a</sup>

<sup>a</sup>Adapted from Waldichuk (1974) (with permission, see credits). Fossil-fuel data from Bertine and Goldberg (1971).  ${}^{b}N.D. =$  no data provided by Waldichuk (1974). <u>Trace-element behavior in aquatic systems</u>. The rules of coordination chemistry (complex formation) (Stumm and Morgan 1970) apply to the behavior of trace elements or minerals once they reach aquatic systems in a dissolved state. The trace metals form associations with water molecules (hydration) or with organic molecules (chelation). The activity or mobilization of trace elements in aquatic systems is influenced by the oxidation-reduction (redox) potential and pH, but primarily activity is determined by the stability of the element-complex (Brooks 1977; De Groot 1973). Many attempts have been made to model the behavior and mobilization of trace elements in freshwater and seawater systems, but the results have been unsuccessful due to the many confounding factors involved. Many of these models contain assumptions that an equilibrium exists between available and chemically-physically bound fractions of trace elements. These equilibria occur; however, they are not permanent, nor predictable, due to the dynamic physical, chemical, and biological processes constantly modifying the concentration and chemical activity of trace elements in aquatic systems. Within aquatic systems the trace-element concentration is divided among the free ionic forms, inorganic ion pairs, inorganic complexes, organic complexes, inorganic colloids, organic colloids, and living organisms and their remains (Fig. 20). The concentration of each of these ionic forms changes continually and is affected by temperature, salinity, solubility, water hardness, chemical speciation, biological activity, and other environmental and chemical factors (Kinkade and Erdman 1975; Mullins 1977).



In true solution

Free metal ions	Inorganic ion pairs; inorganic complexes	Organic complexes, chelates	Metal species complex bound to high molecular organic material	Metal species in the form of highly dispersed colloids	Metal species sorted on colloids	Precipitates organic particles, remains of living organisms
Cu <sup>2+</sup> (aq.)	Cu2(OH)2+	Metal-SR	Metal-lipids	Fe00H	Metal <sub>x</sub> (OH) <sub>y</sub> , MeCO <sub>3</sub> ,	
Fe <sup>3+</sup> (aq.)	Pb(C03)2-	Metal-OOCR	Metal-humic-acid	Fe(OH)3	MeS, etc.,	
Pb <sup>3+</sup> (aq.)	CuCO3	CH2C-0	polymers	Mn(IV) oxides	on	
	Agsh NH <sub>2</sub>	NH <sub>2</sub> 0	Metal polysaccharides	Mn <sub>7</sub> 0 <sub>13</sub> •5H <sub>2</sub> 0	Clays, FeOOH, or	
	C4C1 <sup>+</sup>	, Cu		Na4Mn14027	Mn(N) oxides	
	CaOH+	0 NH2		Ag <sub>2</sub> S		
	Zn(OH)3 <sup>-</sup>	0-C-CH2				
[	Ag <sub>2</sub> S <sub>3</sub> H <sub>2</sub> <sup></sup>					
Diameter ra	nge:	1 — 10 A° — — — — — — — — — — — — — — — — — —	100 A°			ĺ

Figure 20. Forms of Metal (Me) Species in Natural Waters. Adapted from Stumm and Bilinski (1973) (with permission, see credits).

Within the substrates or sediments of aquatic systems, trace elements--primarily heavy metals--are associated with organic compounds or clay particles. In the Tennessee River which flows through the industrial city of Knoxville, heavy metals were dissolved from carbonates in the river, transported downstream in solution, and then incorporated in clay sediments deposited behind a dam at a downstream reservoir (Perhac 1974). In a study of heavy metal transport in the lower Mississippi River, Hartung (1974) found that Cd, Cr, Pb, Mn, Hg, and As were transported primarily in suspended particles. In sediments of a river in Arkansas, Fe, Cu, Cr, Ni, Mn, Pb, Zn, and Na concentrations decreased downstream as the amount of carbonate rock increased and shale decreased. Steele and Wagner (1975) postulated that hydrous iron oxides were the major transport mechanism for Co, Cr, Ni, Cu, Mn, and K, whereas other elements such as Mg, Ca, Zn, Cd, and Pb were transported in fragmented substrate particles.

Many studies have shown that the major portion of metal transport in rivers is through organometallic particulates, with a much smaller fraction carried in solution (Goldschmidt 1958; Gibbs 1973; Trefry and Presley 1976). These complexes form from the large class of water-staining organic acids, especially the humic acids, which constitute the major portion of organic matter in soils and water. In estuarine waters of the Mississippi River Delta and Florida Everglades, Andren and Harriss (1975) found mercury to be associated with dissolved organic matter having properties similar to soil fulvic acid. In Back River, a tributary of Chesapeake Bay, the annual discharges of Cd, Cr, Cu, Pb, and Zn to the bay from wastewater treatment plants were estimated to be within an order of magnitude of the fluvial inputs (Helz et al. 1975). Transport and deposition of mercury in estuarine sediments of the Gulf of Mexico was largely affected by interactions with organic matter, and 54 to 82% of the total dissolved mercury was associated with a fulvic acid type substance (Lindberg et al. 1975). One component of fluvial matter is humic acids. Humic acids are known to have strong binding (chelating) capabilities for trace elements. In a study on the binding capacity of humic acids and trace elements, Benes et al. (1976) found that cobalt, zinc, and mercury can be strongly bound. Ramamoorthy and Kushner (1975) compared the binding capacity of Ottawa River water with fulvic acid for cadmium, copper, mercury, and lead. They determined that bivalent metals could be bound by humic substances in the river water, but fulvic acid was not the active binding component. Surface area and organic content of sediments were the primary factors determining the amount of mercury bound from freshwater solutions (Ramamoorthy and Rust 1976). However, in waters with high inorganic mineral content, carbonate and bicarbonate components are major binding agents (Ramamoorthy and Kushner 1975). Zitko and Carson (1976) postulate that competition for active sites is created by bicarbonate and carbonate ions which are associated with water hardness. However, the competition may not be a significant factor for cations, such as copper or mercury, which are strongly bound to organics.

Perel'man (1967) presented a scheme for determining the rate of mobilization of trace elements which takes into account redox potential, pH, and concentration of the element in water and in the geologic components of the drainage basin. This procedure was used to determine relative mobilization of selected trace elements under different environmental conditions (Table 34). It is important to note the changes in relative mobilization caused by redox potential and pH. Strongly acid systems promote the solution of many heavy metals thus making them available for uptake by biota. Conversely, alkaline systems promote the precipitation of insoluble hydroxides and sulfides (Sorum 1960).

	Environmental conditions					
Relative mobility	Oxidizing aerobic	Acid	Neutral to alkaline	Reducing anaerobic		
Very high	<u> </u>			· · ·		
High	Zn	Zn, Cu, Ni, Hg				
Medium	Cu, Ni, Hg, Cd	Cd	Cd			
Low	Pb	Pb, Mn	Pb, Mn	Mn		
Very low to immobile	Mn, Cr	Cr	Cr, Zn, Cu, Ni, Hg	Cr, Zn, Cu, Ni, Hg, Cd, Pb		

Table 34. Relative Mobilities of Selected Metals in Aquatic Systems<sup>a</sup>

<sup>a</sup>Adapted from Brooks (1977); based upon data of Andrews-Jones (1968).

Ionic forms of trace elements in water are regulated partly by precipitation reactions and adsorption-desorption reactions. The concentrations of ionic forms depend on the amount that enters the system and the amount of dilution water available, as well as factors discussed above.

<u>Trace elements and biota</u>. When trace elements are liberated by natural processes (e.g., erosion and weathering in a drainage basin), the concentrations in waters are low. Cultural sources have increased the concentration of trace elements in many aquatic habitats. Biota which have adapted to environments with small loadings of trace elements are now exposed to greatly increased levels of these materials. (For listings of trace-element toxicities in aquatic biota, see Appendix F. For additional information, see Becker and Thatcher 1973).

This section will deal primarily with two topics: (1) how biota affect the concentrations and ionic forms of trace elements (including uptake, accumulation, transformation, and elimination), and (2) the effect of trace elements on biota (including sublethal and lethal or toxic effects at the organism level and at the population or community level).

<u>Microorganisms</u>. Microorganisms can affect the ionic concentrations and chemical forms of trace elements in several ways. Many trace elements are necessary micronutrients (required in small quantities for biochemical processes). Certain heavy metals are required by nitrogen-fixing bacteria and blue-green algae, i.e., iron and molybdenum are incorporated in metallo-enzymes of nitrogen fixation (Lehninger 1973). Trace elements are also required in minute quantities as catalysts for biochemical reactions, e.g., zinc, magnesium, and manganese (Giese 1968).

Microorganisms are active in the processing and conversion of trace elements in the ecosystem. They play a significant role in various stages of the biogeochemical cycles of carbon, oxygen, sulfur, nitrogen, phosphorus, iron, and manganese (Kuznetsov 1970). Some microbial populations are capable of processing mercury to methylmercury (McEntire and Neufeld 1975), whereas others are able to convert elemental selenium to dimethyl selenide in sediments (Chau et al. 1976). Methylation of mercury was found to be greater under reducing conditions than oxidation conditions (Jacobs 1973). Methylation of mercury under aerobic and anaerobic conditions depends on the metabolic activity of the microbial population and total concentration and availability of mercuric ions (Bisogni and Lawrence 1973).

Conversions of inorganic complexes to organometallic compounds occur with elements other than mercury and selenium. Microorganisms in lake sediments can convert some inorganic and organic compounds of lead to tetraethyl lead (Wong et al. 1975). Microbial conversions also involve arsenic (Wood 1973, 1974), tin, platinum, gold, and thallium (Agnes et al. 1971; Huey et al. 1974).

Conversions by bacteria are also important in the cycling of various trace elements within aquatic systems. Patrick and Loutit (1976) found that bacteria concentrate metals from the water, and the metals are then passed on to other organisms in the food chain. In a laboratory study, marine bacteria from Corpus Christi Bay were found to remove 85% of the zinc and 70% of the cadmium from solution and transport them to the substrate (McLerran and Holmes 1974). Bacterial removal of these elements from solution was accomplished through two possible mechanisms: (1) the metal was associated with bacterial cells (either adsorbed to or incorporated in the cell) and the cell settled out of solution, or, (2) the metal was precipitated from the solution by metabolic activity, probably as a sulfide or coprecipitated with iron sulfide. Microorganisms can have an alternate effect and compete with sediments for uptake of certain heavy metals such as mercury (Ramamoorthy et al. 1977). Although microorganisms are utilized in wastewater treatment to remove heavy metal ions (Adams et al. 1973), concentrations that are too high can inhibit microbial action (Jackson and Brown 1969) by poisoning the enzyme systems.

<u>Aquatic plants</u>. Aquatic plants are known to concentrate trace elements. Phytoplankton are capable of accumulation and concentration of trace elements in excess of their physiological requirements (Leland et al. 1977). Aquatic bryophytes concentrate heavy metals (Dietz 1973), and rooted aquatic macrophytes accumulate some trace elements such as Cd, Ni, Pb, Cu, Zn, and Hg (Eriksson and Mortimer 1975; Heisey 1975). The mechanism of trace-element uptake is a two step process whether the element is absorbed from the water by algae or from the sediments by rooted aquatic macrophytes. Initially, the trace-element ion is adsorbed to the cell wall. Then, through an ion exchange process, it is transported through the cell wall to internal tissues (Cossa 1976; Schultz-Baldes and Lewin 1976; Spooner 1949).

A number of environmental factors may affect the uptake of trace elements by plants. Styron et al. (1976) found that certain marine algae have uptake optima which depend on temperature and salinity. Interactions among trace elements and/or the organism can affect uptake in some algae. For example, high copper concentrations (1.0 ppm) enhanced nickel uptake in *Scenedesmus* (Stokes 1975).

Physiological factors can affect accumulation and uptake rates. Uptake rates of iron, manganese, and titanium for some marine algae were greater in light than dark (Gryzhankova et al. 1975), but light conditions did not affect copper uptake by two freshwater algae (Mierle and Stokes 1976). Uptake rates also depend on population growth rates. Cadmium uptake was higher during the exponential growth phase of a diatom than during other growth phases (Cossa 1976), and copper and nickel uptake declined in older cultures of *Scenedesmus* (Stokes 1975).

Based on the uptake and accumulation capacity of some algae, certain genera have been proposed as indicators of trace-element pollution. Although high concentrations of trace elements may not be present in the water body at all times, i.e., in the case of intermittent doses of effluents discharged to rivers or occasional contamination in precipitation runoff, the ability of aquatic plants to accumulate and maintain trace elements can be used to determine if such events have occurred. For example, elevated concentrations of copper, iron, nickel, and zinc were found in *Oscillatoria*, indicating a trace-element contamination episode even though water samples did not reflect the high concentrations of these metals (Trollope and Evans 1976).

Concentration factors for the various trace elements will vary according to the element and the specific plant. After exposure, concentrations of trace elements in several genera of freshwater algae varied among genera, and specific genera were found to concentrate copper, iron, nickel, lead, and zinc at different rates (Trollope and Evans 1976). Examples of concentration factors of certain trace elements in duckweed and aquatic bryophytes, a major food material of waterfowl, are given in Tables 35 and 36. These high concentration factors have led some researchers to suggest that aquatic plants other than algae be used as indicators of trace-element pollution (Mayes and McIntosh 1975).

	Concentrati	Concentration		
Element	Lemna	Water	factor	
Cadmium	2.4	0.0038	632	
Zinc	32.6	0.0290	1,124	
Lead	13.3	0.0157	847	
Copper	33.4	0.0350	954	
Nickel	10.3	0.0270	382	
Silver	0.033	0.0004	82	
Cobalt	· 6.7	0.0150	447	
Iron	1,771.0	3.16	560	
Manganese	1,622.0	0.1485	10,923	

Table 35. Mean Concentrations and Concentration Factors of Trace Elements in Duckweed (*Lemna minor*) and its Pond Waters<sup>a</sup>

<sup>a</sup>Data from Hutchinson and Czyrska (1975).

Table 36. Concentration Factors of Heavy Metals by Bryophytes<sup>a</sup>

Metal	Concentration factor
Lead	5,300
Copper	3,900
Nickel	1,700
Zinc	10,300
Iron	4,100
Manganese	28,900
Merčury	> 930

<sup>a</sup>Data from Dietz (1973).

Trace elements can have a variety of effects on aquatic plants including changes in physiology, productivity, community composition, and species abundance. Elevated concentrations of trace elements, e.g., copper at  $25 \mu g/L$ , inhibit photosynthesis in phytoplankton populations (Nielsen and Laursen 1976). This inhibitory action is also affected by pH, humus content of the water, copper tolerance of individual species, and population density. Bartlett et al. (1974) found that the initial effect of low concentrations of either copper, zinc, or cadmium was a reduction in growth rate; increased concentrations stopped growth, and a further increase was lethal. Of the three elements tested, copper was the most toxic. This property of copper has been known for a long time, and copper sulfate has been used extensively as an algicide.

The effects of exposure to a single trace contaminant can be modified by the addition of one or more different trace contaminants. In concert, the combined effects can be (1) additive, the same as the sum of exposure to the individual components, (2) antagonistic, less than the effects of each component taken additively, or (3) synergistic, greater than the additive effects. Wissmar (1972) determined that combinations of copper, zinc, and cadmium had a synergistic effect on algae. Hutchinson and Czyrska (1975) found that low levels of cadmium (0.01 ppm) reduced growth in duckweed and floating fern (*Salvinia*); however, when cadmium was combined with zinc, the effect was synergistic as was the combined effect of copper and nickel.

On the population or community level, trace-element additions can alter species composition and abundance. Patrick (1975) found a shift in algal species composition from primarily diatoms to blue-green algae in communities exposed to trace-element additions, and Johnson et al. (1970) found decreases in the density of phytoplankton populations as well as the diversity. Not all algal species respond in the same manner. Certain species or strains of algae may be more tolerant than others, and there is evidence that a tolerance response can be developed. Stokes et al. (1973) found that natural populations of algae which had chronic exposure to nickel, copper, and silver had higher tolerances than similar laboratory strains which had no previous exposure. This indicates a mechanism of tolerance to the toxicant rather than a mechanism of toxicant exclusion as a method for algal survival. Whether this ability is inherent in all algal species, or only a select few, remains to be determined as does the actual tolerance mechanism itself.

<u>Invertebrates</u>. Invertebrates have adapted to practically all aquatic habitats and developed numerous varieties of life histories and feeding behaviors. Due to this large variability, only certain groups or species have been studied, primarily those with known biological or economic importance.

Trace-element uptake by invertebrates depends primarily upon metabolism and feeding behavior of the organism as well as the form of the trace element in the environment. In a radioactive tracer study of oysters, Harrison et al. (1976) found uptake to occur from both food items and water. Uptake of Cs-137 was mostly from water, Co-60 uptake was mostly from particles, and Zn-65 and Mn-54 uptake were from both sources. In other studies (Luoma and Jenne 1975a, 1975b), silver, cadmium, cobalt, and zinc uptake by deposit-feeding clams depended on the physicochemical characteristics of the sediment. As the metal binding capacity of the sediment decreased, uptake increased.

Uptake of trace elements is not constant but will vary seasonally and with the life history and physiology of the organism. Frazier (1975) studied seasonal uptake and elimination of manganese, iron, zinc, copper, and cadmium in oysters. Uptake of manganese and iron was correlated to shell growth, but zinc and copper uptake was not. Body burdens, the amount of the trace element in the body, showed a gradual increase during spring and summer followed by rapid losses during late summer to early fall. During this period, 30% of the zinc and 50% of the copper were lost in less than a month. Cadmium was similar in behavior to zinc and copper. These data indicate the relationship between trace-element uptake and physiology. Concentrations of manganese and iron are closely related to the shell growth process; copper, zinc, and cadmium are closely related to gonadal development and spawning. Temporal fluctuations in traceelement concentrations in animals may also reflect changing environmental conditions or changing and Masso (1975) found the mercury content of zooplankton varied over two orders of magnitude during a year and attributed the variance to environmental changes.

Smith et al. (1975) determined mercury levels in water, sediment, and filter-feeding clams from lakes with and without mercury contamination. Mercury uptake increased with elevated mercury concentrations in the water, but temperature had no apparent effect on the uptake or elimination rates. Conversely, Pringle et al. (1968) found that uptake rate was closely correlated with temperature. These two conflicting reports in molluscs may indicate that there are at least two mechanisms involved in uptake. The work of Smith et al. (1975) suggests that there is a diffusion of the trace element into the organism followed by the formation of stable complexes which are eliminated at a steady rate. This is supported by other work (Craig 1967). Pringle et al. (1968) hypothesized an active-transport uptake mechanism which is dependent on the metabolic activity of the cells and therefore has greater temperature dependence. In both cases, the rate of accumulation would also depend on the binding strength of the complex formed and its stability.

The biological retention time of a trace element in the organism depends on such factors as where the element is stored, what form it is in, the metabolic rate of the organism, and the toxicity of the concentration. Tracer studies have been used to determine the retention time or biological half-life of certain trace contaminants in invertebrates. Harney (1974) found the half-life retention time (amount of time required for the concentration of the trace element in the organism to be reduced by 50% through any mechanism) for Zn-65 in a freshwater mollusc to be 103 days after the organism was transferred to a noncontaminated environment.

Elimination of trace elements from organisms can be accomplished by a variety of mechanisms including diffusion, active transport, spawning, secretion, molting, and defecation. A radiotracer study of the flux of cadmium through a small marine crustacean (Benayoun et al. 1974) determined that the major uptake of cadmium was through ingestion. The most significant elimination of the trace element was through defecation. Approximately 10% of the cadmium ingested was incorporated into internal tissues, primarily in the viscera. Defecation accounted for 84% of the total cadmium flux through the animal. Cadmium was concentrated by a factor of nearly five in the fecal pellets.

Concentrations of trace elements within invertebrates will vary in the tissues. Whole body concentrations can be much greater than the concentrations found in the environment. Concentration factors for freshwater and marine invertebrates are given in Table 37.

Toxicity of trace elements to invertebrates varies according to the specific element and its form, and among the different species. Baudouin and Scoppa (1974) found that three species of zooplankton have different sensitivities to Cd, Co, Cr, Cu, Mn, Hg, Pb, and Zn. The order of sensitivity among the three species was similar. Winner and Farrell (1976) compared acute and the second se

Trace element	Freshwater invertebrates	Marine invertebrates
Antimony	10	5
Arsenic	333	333
Beryllium	10	200
Cadmium	2,000	250,000
Chromium	20	2,000
Cobalt	200	1,000
Copper	1.000	1,670
Germanium	33	15,700
Lead	100	1,000
Manganese	40,000	10,000
Mercury	100,000	33,300
Molvbdenum	10	10
Nickel	100	250
Radium	250	100
Selenium	167	1,000
Silver	769	3,330
Tellurium	75	100,000
Thallium	15,000	15,000
Thorium	500	2,000
Tin	1,000	1,000
Tungsten	10	30
Vanadium	3,000	50
Zinc	10,000	100,000

Table 37. Concentration Factors of Trace Elements in Freshwater and Marine Invertebrates Based on Edible Portions<sup>a</sup>

<sup>a</sup>Data from Vaughan et al. (1975).

and chronic toxicities of copper to four different-sized species of *Daphnia*. The two larger species were significantly more tolerant than the two smallest. However, concentrations which reduced life spans were not significantly different.

Sublethal effects of trace elements on invertebrates are perhaps more significant to the ecosystem than the acute toxic effects. Sublethal effects can be classified as either (1) affecting the fitness of the organism, or (2) affecting the structure or function of the community; the second is a function of the first. Trace-element effects which reduce the fitness of the organism include: changes in physiology, such as modification of osmoregulation (Schmidt-Nielsen 1974); shell deposition (Frazier 1975); and growth, development, and reproduction (Reinhart and Myers 1975). Sublethal effects on the population or community level include reductions in abundance, diversity, and production. All of these effects reduce the available biomass, nutrients, and/or energy for transfer to higher trophic levels.

Although little work has been reported on aquatic insects and trace elements, Nehring (1976) has proposed that certain insects can be used as monitors of heavy metals. He determined that a mayfly and a stonefly were more tolerant to heavy metals (copper, lead, and zinc) than fish and that these insects accumulated the elements in a proportion relative to the concentration in the water.

<u>Fish</u>. Uptake of trace elements by fish occurs primarily through two routes: (1) active or passive absorption through the gills and (2) ingestion. Eisler (1967) found that killifish accumulate zinc through the gills. However, Hoss (1974) found that zinc was normally obtained through ingestion of food that contained zinc. Sandholm et al. (1973) compared uptake of selenium from water and food and concluded that only small amounts of selenium were obtained from water, the majority obtained via food. Similar conclusions were reached by Pentreath (1973) working with plaice. Although there is some controversy as to the major source of trace elements accumulated by fish, the general consensus from the literature is that ingestion of contaminated food items is the major mechanism.

The chemical form of the trace element is an important factor in uptake. In experiments with rainbow trout, Buhler et al. (1977) found that uptake and elimination of chromium involved two forms of the element. The metal exists in two different valence states, 3+ and 6+, and they contend that these two forms react differently. The hexavalent form is easily diffused through the gills, and both uptake and elimination is rapid until an equilibrium with the

medium is reached. The trivalent form is much slower to be taken up and eliminated due to binding with proteins. Olson et al. (1973) demonstrated that both inorganic mercury and methylmercury can be absorbed through the gills, but uptake of the methylmercury form is more rapid.

Some aspects of water quality such as pH, alkalinity, and temperature affect the chemical form of trace elements and therefore their uptake rates. Uthe et al. (1973) suggested that uptake of mercury by rainbow trout is related to seasonal changes in temperature. They found that the accumulation rate was greatest during the first warm period of summer and that uptake was greatly reduced during the remainder of the year. These data also suggest that uptake is a function of feeding. During the early summer, trout maximize feeding and growth. Under such conditions, uptake from contaminated food items would also be greatest.

The pH of the environment has a pronounced effect on the form and therefore the uptake of certain trace elements, primarily heavy metals. When the solution is acidic, most heavy metal ions are liberated into solution and available for uptake through the gills. When the pH is basic, hydroxides are formed and the complexes are taken up through food sources. For example, Merlini and Pozzi (1977) found that the uptake of lead was three times greater at pH 6 than at 7.5. Tsai et al. (1975) determined that inorganic mercury was less available for uptake by fish in alkaline water than in acidic water. Mercury complexes formed under alkaline conditions were postulated as the reason for reduced uptake. Other environmental factors that affect uptake include dissolved oxygen and carbon dioxide concentration, hardness, organic ligands present, temperature, and the presence of other trace elements.

Retention and elimination of trace elements from fish has been studied in some detail, primarily with respect to mercury. Most studies have found mercury to be quite unreactive or static once it is incorporated into fish tissue. Mercury content in largemouth bass and northern pike correlated better with length than with either weight or age (Abernathy et al. 1975; Olsson 1976). A negative correlation between mercury content and condition factor  $[W/L^3]$  where W = weight and L = length (in fish)] was also found. Mercury concentration in fish appears to be more a function of growth rate than age. These correlations indicate that mercury is taken up as a function of feeding, that retention time is long, and that elimination is slow. Evidently, the trace element is bound within the tissues in an insoluble form and cannot be lost even during periods of starvation and weight loss. A slow decline in the methylmercury content of weight gain rather than loss of the contaminant (Laarman et al. 1976). Northern pike heavily contaminated with methylmercury eliminated only 30% of the body burden after one year in uncontaminated waters, and the distribution of the compound in various tissues remained basically unchanged (Lockhart et al. 1972). Methylmercury appears to be tightly bound in fish tissues. Giblin and Massaro (1973) estimated that the half-life retention time of methylmercury in rainbow trout was greater than 200 days.

Elimination of trace elements from fish appears to depend to some extent on the original source of uptake. Losses of zinc and manganese from plaice (Pentreath 1976) and methylmercury from trout (Routhla and Miettinen 1975) were slower when the original source of the contaminant was food rather than water.

Concentration factors for trace elements in freshwater and marine fishes are given in Table 38.

Trace elements have two general effects on fishes: (1) direct lethal effects when concentrations are high, and (2) indirect sublethal effects when concentrations or exposures are chronic.

The direct lethal effect can be caused by physiological action of trace elements in different tissues or organs of the fish. In many cases, the cause of death is the interference of the trace element with some enzyme system. Initial exposure to trace elements usually occurs through the gills, and Lloyd (1960) has shown that acute lethal concentrations of zinc destroy fish gills. Zinc-poisoned fish experience impaired oxygen uptake (Skidmore 1970) as well as impaired osmoregulation (Lewis and Lewis 1971). The mechanism which causes death in this situation appears to involve the production of lactic acid, a product of anaerobic glycolysis (Hodson 1976) in oxygen-starved gill tissues. Both cadmium and copper also inhibit the oxidation of lactate in rainbow trout gills (Bilinski and Jonas 1973). Another major site of heavy metal accumulation is the liver. Metals are known to poison liver enzymes in killifish (Jackim et al. 1970). The second class of toxic effects of trace elements on fishes is the sublethal or chronic effects. These include inhibition or interference with neurophysiological activity, enzyme activity, and hormonal balance; increased susceptibility to disease or parasites; and teratogenic, carcinogenic, and mutagenic effects. Other sublethal effects at the organism level are reduced growth, behavioral modifications, reduced survival, reduced reproductive capacity, and reduced fitness.
Trace element	Freshwater fish	Marine fish
Antimony	1	40
Arsenic	333	333
Beryllium	2	200
Bismuth	15	15
Cadmium	200	3,000
Chromium	40	400
Cobalt	20	100
Copper	200	677
Germanium	3,300	3,300
Lead	300	300
Manganese	100	600
Mercury	1,000	1,670
Molybdenum	10	10
Nickel	100	100
Radium	50	50
Selenium	167	4,000
Silver	2	3,330
Tellurium	400	-
Thallium	10,000	10,000
Thorium	30	10,000
Tin	3,000	3,000
Tungsten	1,200	30
Uranium	10	10
Zinc	1,000	2,000

Table 38. Concentration Factors of Trace Elements in Edible Portions of Freshwater and Marine Fish<sup>a</sup>

<sup>a</sup>Data from Vaughan et al. (1975).

In a three-year study of brook trout exposed to low levels of lead  $(0.9-474 \mu g/L)$ , Holcombe et al. (1976) found that the early life stages were more sensitive to lead than later stages. Low-level exposure produced a blackened caudal region which preceded development of scoliosis in young fish. The spinal curvature appeared to be caused by affected musculature, since the scoliosis disappeared when the fish were anesthetized and their muscles relaxed. However, if the scoliosis remained for several weeks, it became permanent due to calcification of the spine. A biochemical inhibition of metabolism was postulated as the cause since lead is known to have an affinity for reactive sites on enzymes (Pakkala et al. 1972). Other effects of chronic exposure--hyperactivity, erratic swimming, muscular spasms, and loss of equilibrium-indicate that lead also affects the nervous system of the fish.

Another effect of exposure of fish to sublethal concentrations of a toxicant is a reduction in feeding. This response has been observed in various salmonids during exposure to copper (Lett et al. 1976; Drummond et al. 1973).

Perhaps more significant in the ecological context is the overall effect of sublethal exposures to a toxicant. Although specific responses are important for understanding how a toxicant affects an organism, these responses must be viewed in the context of how the responses affect species fitness, energy transfers through trophic structures, and other species interactions. One aspect of sublethal effects is a reduction in viability of the organism. Reduced viability can result from the impairment of metabolism by a toxicant, which may be considered a direct effect, or from the increased probability of mortality from an external source, which may be considered an indirect effect.

One such indirect effect is increased susceptibility to predation. Kania and O'Hara (1974) tested this effect by exposing mosquito fish to varying sublethal concentrations of mercury (0.01, 0.05, and 0.1 ppm). The contaminated fish were then exposed to predation by largemouth bass. Contaminated fish were preyed upon at a significantly higher rate than control fish. The ramifications of this study suggest that bioaccumulation of trace elements in predators may be increased above a normal rate by selective ingestion of more contaminated than uncontaminated prey. Concentration or bioaccumulation factors determined in field studies may contain this bias.

Another important aspect of fish behavior in response to trace elements is that of mobility. Fish are mobile, and their movements are normally in response either to internal, physiological

stimuli or to external, environmental stimuli. Sprague (1964, 1965) and Saunders and Sprague (1967) reported that Atlantic salmon exhibit an avoidance reaction to copper and zinc. Both young salmon and spawning migrants were able to detect and actively avoid relatively low concentrations of these elements (4.3  $\mu$ g/L Cu and 56  $\mu$ g/L Zn). A similar ability was determined for rainbow trout (Sprague 1968) and goldfish (Kleerekoper et al. 1973). This aspect of fish behavior, the ability to select suitable habitat, is often ignored in standard bioassay procedures. All laboratory bioassay results should be suspect when applied to field situations. The physiological response of an organism to a toxicant can be greatly modified by environmental conditions and will vary dependent upon such conditions.

The standard bioassay procedure involves exposing test organisms to various concentrations of a toxicant or combination of toxicants for specified time periods under controlled laboratory conditions. The median tolerance limit (TLm) or lethal concentration which kills 50% of the test organisms  $(LC_{50})$  is determined graphically from the various combinations of exposure times, concentrations, and mortalities. In the majority of the determinations, the time exposure is 96 hours, and the result is referred to as the 96 hour TLm or  $LC_{50}$ . However, the testing is conducted under control conditions. This means that all environmental variables are held constant except those being tested. Comparison of laboratory determined lethal concentrations to field situations have not always indicated similar results. For example, Burdick (1967) cited a case where a trout stream contained 0.15 mg/L of copper which had been determined to be a lethal concentration, and yet no trout deaths were attributable to copper toxicity.

There are a number of environmental variables that affect the relative toxicity of trace elements. The major factors are pH, alkalinity, hardness, dissolved oxygen and carbon dioxide concentrations, salinity, and temperature (Becker and Thatcher 1973). Usually, when hardness,  $CO_2$  concentration, and pH increase, the toxicity of trace elements--particularly the heavy metals--decreases.

Within a species, resistance to a toxicant can vary with the age, sex, life history stage, physiological condition, exposure history, or even from individual to individual. In several instances, it has been demonstrated that eggs are more tolerant to trace elements than larvae or even some juvenile or adult stages. For example, fish embryos at four stages of development and fry were exposed to increasing concentrations of selenium (Niimi and LaHam 1975). Embryo mortality was negligible, but newly hatched fry exhibited increasing mortality with increased concentration. Similar results were found with exposure of early life stages of chinook salmon to copper (Hazel and Meith 1970), and with bluegills, larvae were more susceptible to copper than older fish (Benoit 1975).

Rarely will there be a single toxicant in a natural situation; usually an effluent contains several toxic components. The combined effect or toxicity of all the constituents of the waste is of major concern, not just the effects of individual components, because trace elements can act either additively, antagonistically, or synergistically.

Some species are more tolerant to some toxicants than others, and within a species some individuals may be more tolerant than other individuals. In some species, tolerance to trace elements can be acquired, a concept which is similar to temperature acclimation. Lloyd (1960) found that rainbow trout were more resistant to the lethal effects of zinc when the fish had prior exposure to sublethal concentrations. Sinley et al. (1974) found that more tolerant individuals were produced from zinc-exposed eggs.

<u>Bioaccumulation, bioconcentration, and biomagnification</u>. Trace elements in aquatic systems undergo differential uptake by biota. Bioaccumulation (the ability of an organism to concentrate an element above abiotic environmental levels), bioconcentration [the influence of size (weight, length) on the pattern of elemental concentration within an organism], and biomagnification (the tendency for trace elements to be concentrated with trophic level transfer) are three topics of major concern in a discussion of trace elements in aquatic systems. Since the study of traceelement cycling is in its infancy, few studies are available for discussion. However, the studies that have been done indicate that bioaccumulation, bioconcentration, and biomagnification deserve greater consideration.

In a study of trace-metal concentrations in the Illinois River, Mathis and Cummings (1973) found that Cu, Ni, Pb, Cr, Li, Co, and Cd were highest in worms, intermediate in clams, and lowest in fish muscle tissue (Table 39). Zinc was highest in clams, intermediate in worms, and lowest in fish muscle. Some caution should be used in interpreting the results of this study, because whole body analysis, including gut contents, was done for tubificids and clams, whereas only filleted muscle tissue was analyzed for fish. Had the entire fish been used, concentrations would have been higher since other tissues--e.g., liver, kidneys, bone--are known accumulation sites.

			Mean concentra	tion (ppm)						
Trace element I	Water	Carnivorous fish <sup>D</sup>	Omnivorous fish <sup>b</sup>	Clams	Tubificid worms	Sediments				
Copper	0.001	0.13	0.21	1.5	23	19				
Nickel	0.002	0.12	0.17	1.4	. 11	27				
Lead	0.002	0.57	0.64	2.9	17	28				
Chromium	0.021	0.12	0.22	5.6	10	17				
Lithium	0.010	0.004	0.004	0.083	.1.3	3.8				
Zinc	0.031	3.49	5.02	69.6	41	81				
Cobalt	0.03	0.10	0.10	0.9	1.6	6				
Cadmium	0.0006	0.03	0.03	0.54	1.1	2				

Table 39. Concentrations of Trace Elements in the Illinois River and Biota<sup>a</sup>

<sup>a</sup>Data from Mathis and Cummings (1973). <sup>b</sup>Muscle tissue.

The study by Mathis and Cummings (1973) should not be singled out to be viewed with caution. In many studies pertaining to trophic metal transfer, the gut contents are not removed from invertebrates. Elwood et al. (1976) have adequately demonstrated that gut contents can significantly add to the elemental concentration of an organism for many elements. It is true, for instance, that a fish consuming benthic insects could potentially utilize the gut contents of the insect, as well as the insect itself, for a food source; from the standpoint of interpreting trophic magnification, a misinterpretation could result. Elwood et al. (1976) found that the calculated percentage of the body burden associated with gut contents for elemental concentration of an single species (*Tipula* spp.). The contribution of gut contents to the elemental concentration of the organism could vary from species to species, depending among other things upon feeding habits, habitat, instar differences, body size differences between species, and so forth.

In a study of an unpolluted stream, Enk and Mathis (1977) found biota to accumulate cadmium and lead above water concentrations. Concentrations were generally highest in invertebrates (mayflies, damselflies, caddis flies, and snails), intermediate in sediments, and lowest in fish. Food chain magnification was not observed. Concentrations of lead and cadmium appeared to be more a function of food habit and habitat. Organisms associated with the sediments and/or with detrital feeding habits accumulated more of the metals than predatory species.

One factor complicating studies on biomagnification is the influence of bioconcentration. Individual variability in metal concentration, partly owing to size difference of individuals, can mask trends in elemental trophic transfer. Concentrations of metals in an organism can show positive, negative, or no relationship with size, depending on a number of physical, chemical, and biological factors related both to the organism and metal(s) in question. Bioconcentration has received increased attention ever since mercury has been demonstrated to accumulate with age, weight, and size (length) of fish (e.g., Scott and Armstrong 1972; Cross et al. 1973; Scott 1974). In fish, most heavy metals, except for mercury, that are associated with coal in more than trace quantities either show no increase with size or a decrease with size (Brooks and Rumsey 1974; Giesy and Weiner 1977; Mathis and Kevern 1975; Vinikour 1977).

Guthrie and Cherry (1976) examined the biota of a stream receiving fly ash settling-basin effluent. Biota were analyzed for content of trace elements, and mean annual concentrations were determined (Table 40). In almost every case, fish had the lowest concentrations of the trace elements; notable exceptions were calcium and selenium where fish contained the highest concentrations.

Concentrations in biota of trace elements by chemical groups are shown in Figures 21, 22, and 23 (Guthrie and Cherry 1976). The major role of each biotic form in the cycling of specific trace elements varied, and no single species was found to concentrate any element to a greater degree than all other species. However, cattails (a rooted macrophyte) concentrated over 50% of total manganese, duckweed (a floating macrophyte) concentrated > 40% of total titanium, tadpoles 40% of total chlorine, midges 38% of total chromium, and crayfish 31% of total calcium. Plants were more efficient concentrators of manganese and potassium than animals; however, no distinction was made among rooted, floating, or algal plants. As a group, the primary producers did not rank higher than third as concentrators of any group of elements. Midges were the most efficient concentrators of Co, Hg, Cu, Cr, As, and Sb.

			Concentration	(ppm)	
Trace	<u>Abiotic</u>			Biotic	
element	Water	Benthos	Plants	Invertebrates	Fish
Aluminum	13.0	40,657.0	3,985.1	1,199.3	215.5
Iron	16.9	20,912.4	1,113.2	1,202.6	154.7
Potassium	6.1	8,149.2	1,803.6	2,666.2	1,946.2
Calcium	9.2	1,844.8	850.1	2,656.4	5,752.9
Magnesium	4.1	5,460.8	656.2	369.4	307.2
Titanium	0.9	2,388.5	109.4	71.5	15.1
Sodium	7.7	688.0	267.9	703.8	309.8
Chlorine	3.8	84.1	198.2	364.9	131.4
Barium	0.7	294.2	36.3	50.2	20.0
Strontium	0.3	236.0	60.3	48.4	36.3
Manganese	0.07	46.2	70.2	21.5	10.0
Cerium	0.2	129.7	9.7	4.3	1.6
Tin	0.1	85.0	18.0	20.7	3.4
Rwbidium	0.4	51.6	8.2	29.0	8.5
Vanadium	0.04	63.9	4.7	4.4	0.6
Chromium	0.2	38.4	5.7	9.7	2.8
Zinc	0.4	6.4	5.0	14.9	11.8
Arsenic	0.06	19.7	4.2	2.1	0.5
Lanthanum	< 0.01	20.3	1.4	1.4	0.1
Thorium	0.03	15.3	1.3	1.7	0.3
Bromine	0.1	1.2	3.0	10.1	2.9
Selenium	0.1	6.1	1.8	2.6	9.4
Cobalt	0.1	10.6	1.7	1.7	0.5
Iodine	0.1	4.6	1.3	3.4	0.4
Uranium	0.01	8.0	0.7	0.3	0.1
Cadmium	0.1	1.7	1.5	4.0	1.3
Cesium	< 0.01	3.9	0.6	0.7	0.5
Antimony	0.07	1.0	0.8	2.1	0.7
Mercury	0.03	0.8	0.5	0.5	0.2

# Table 40. Concentrations of Trace Elements in Abiotic and Biotic Components of an Ash Basin Receiving Stream<sup>a</sup>

<sup>a</sup>Adapted from Guthrie and Cherry (1976).

Bioaccumulation and biomagnification of trace elements depend on a number of factors. To date, no single encompassing theory has adequately described trace-element cycling through biota. This is no doubt due to the differential behavior of trace-element forms in different aquatic systems. Uptake and transfer through trophic interactions are modified by the physicochemical form (ionic or particulate) of the trace element, and by the nature of the organisms and their habitat, substrate-sediment associations, and food habits.

Trace elements are released through coal combustion and enter aquatic systems either by direct discharge or indirect input (groundwater, terrestrial litter, runoff, and atmospheric fallout). In an aquatic system, trace elements are predominately associated with the sediments, which act as both sink and reservoir; relatively small amounts are found dissolved in the water. From the sediments, trace elements are accumulated by both rooted vegetation and benthic invertebrates. Phytoplankton both adsorb trace elements to their cell walls as well as absorb them. Grazers and lower-order consumers seem to concentrate trace elements to the highest degree. The greatest bioaccumulation or concentration factors are found in sediment or detrital feeders. Higher order consumers or predators accumulate trace elements both from water and food, but food appears to be the major source. Some discrimination appears to occur at this trophic transfer since trace-element concentrations are usually lower in predators than in their prey. Although this is contradictory to biomagnification theory, several studies have indicated this occurrence. The ultimate fate of trace elements is return to the sediments or translocation downstream, unless components of the aquatic system are removed from the system by human harvest or predation by birds or mammals.



Figure 21. Accumulation of Heavy Metals in Abiotic and Biotic Components of the Drainage System Relative to a Highest Concentration of 100%. Numbers in parentheses represent the mean total concentration in ppm. From Guthrie and Cherry (1976) (with permission, see credits).



Figure 22. Accumulation of Nitrogen Family Elements and Light Metals in Abiotic and Biotic Components of the Drainage System Relative to a Highest Concentration of 100%. Numbers in parentheses represent the mean total concentration in ppm. From Guthrie and Cherry (1976) (with permission, see credits).





## Studies of Trace-Element Impacts in Aquatic Ecosystems

In assessing trace-element loading to aquatic systems from coal combustion, it is important to consider the quantity and quality of water which may receive particulate emissions from the power plant. It is possible that sufficient water is available to meet the designed cooling requirements of the power plant, but because of low water quality, additions of trace elements from deposition of particulates may result in concentrations exceeding acceptable values. This may be particularly true in the case of long-term exposure of a lake or pond which may or may not be used for cooling-water purposes.

A review of the literature failed to reveal any studies and/or modeling of effects of particulate emissions from coal-fired power plants located on estuaries or marine systems. However, there have been at least three studies which examine potential impacts to freshwater systems from trace elements emitted from coal-fired power plants.

In Dvorak et al. (1977), it was assumed that the trace elements emitted daily from a model 1000-MWe power plant were diluted in the daily discharge volume of a single hypothetical watershed with a mean annual discharge of 28.3 m<sup>3</sup>/s (1000 cfs). Potential sites located in five regions of the continental United States were modeled. In addition, trace-element concentrations for the type of coal burned were also determined. Enrichment factors were determined by dividing the concentrations found in the coal type burned by the average background concentration of trace elements in the surface waters of the regional areas. For purposes of comparison, enrichment potential was also calculated using national-average values of trace-element concentrations in surface water and the average concentration of trace elements in the coal types used. The results of these analayses are presented in Table 41.

Based on this study, it can be seen that As, Cd, Co, Cu, Pb, Mo, Ni, and V may enrich background concentrations by less than 5%. The elements barium, chromium, manganese, and zinc may enrich background concentrations by 5-20%. Both mercury and selenium were found to potentially enrich the background by more than 100%.

Water quality criteria were compared with trace-element concentrations resulting from the summation of the average background level plus the input from the 24-hour operation of the model 1000-MWe power plant to a  $28.3-m^3/s$  (1000-cfs) stream discharge (Table 42).

The possibility of more than one watershed being in the zone of maximum deposition was also considered. It was assumed that maximum deposition will occur within an 80-km (50-mi) radius [ $20,342 \text{ km}^2$  ( $7,854 \text{ mi}^2$ )] of the power plant. Where the deposition area exceeds the drainage area, the potential for enrichment to a single watershed is reduced. Streams in various regions of the United States with sufficient drainage area for accumulation of 28.3-m<sup>3</sup>/s or 1000 cfs (mean annual discharge) were compared. The results indicated that only in the arid western areas is it likely that the deposition zone [ $20,342 \text{ km}^2$  ( $7,854 \text{ mi}^2$ )] is exceeded by sufficient drainage area to produce a discharge of  $28.3 \text{ m}^3$ /s (1000 cfs) in the river (Dvorak et al. 1977). It has been shown that a stream with a mean annual discharge of  $28.3 \text{ m}^3$ /s (1000 cfs) provides enough dilution water to reduce the concentration of most trace elements below the toxicity threshold to aquatic biota and below the current water quality criteria.

The potential for trace-element enrichment in lentic systems was also examined by Dvorak et al. (1977). Factors affecting trace-element enrichment in ponds and lakes include proximity to the plant, drainage area, water input vs. output rates, surface area, and total volume. Proximity to the power plant relative to prevailing wind direction is also important, because a pond or lake located downwind from the power plant is going to be subjected to heavier loading than a pond or lake located equidistant but in a different direction.

The following assumptions were made in the model:

- 1. Power plant life of 30 years
- 2. Lake area =  $130 \text{ km}^2$
- 3. Average depth = 15 m
- 4. Volume =  $1.12 \times 10^8$  L
- 5. The lake is a closed system with no outlet
- 6. No biological uptake or sedimentation takes place
- 7. Deposition rates were based on the values for a model plant located in Illinois and burning Illinois coal.

The results of this analysis are presented in Table 43. Although the assumptions create a worst-case situation, the resulting concentrations do not exceed the water quality criteria or the toxicity threshold of most aquatic biota.

The second model (Dvorak and Pentecost et al. 1977) examines potential trace-element enrichment in four selected drainage basins in southern Illinois. These included three large

Element	Northern Appalachian <sup>b</sup>	Southern Appalachian <sup>C</sup>	Eastern Interior <sup>d</sup>	Four Corners <sup>e</sup>	Pacific Northwest <sup>f</sup>	United States (mean)9
Silver	0.9	. 🛋	3.4	5.8	0.9	2.6
Aluminum	22	30	18	50	30	74
Arsenic	47	50	69	53	68	64
Boron	42	24	105	179	30	101
Barium	25	25	39	60	27	43
Beryllium	0.12	0.16	. –	-	0.02	0.19
Cadmium	3	· . –	6	2	5	9.5
Cobalt	9	-	18	11	8	17
Chromium	6	6	7	16	6	9.7
Copper	17	11	14	10	9	15
Iron	19	37	35	40	32	52
Manganese	2.7	3.7	9.8	12	2.8	58
Molybdenum	33	25	88	130	30	68
Nickel	8	4	15	12	. 10	19
Phosphorus	48	42	243	121	47	120
Lead	14	17	33	32	15	23
Strontium	62	47	105	697	68	217
Vanadium	12	-	20	105	13	40
Zinc	49	28	45	51	40	64
Selenium <sup>h</sup>	0.3	0.2	0.1	10	0.1	0.2
Mercury <sup>i</sup>	-	-	-	-	· _	0.07

Table 41. Mean Concentration of Various Trace Elements (	ug/L) for Major Drainage
Basins in Selected Regions, and Average Concent	ration Based on
Values from all Major Drainages in the Uni	ted States <sup>a</sup>

<sup>a</sup>From Dvorak et al. (1977). Data from Kopp and Kroner (1970).
<sup>b</sup>Rivers: Delaware, Schuylkill, Susquehanna, Potomac, Shenandoah.
<sup>c</sup>Rivers: Tennessee, Clinch.
<sup>d</sup>Rivers: Upper Mississippi, Red, Rainy, Illinois.
<sup>e</sup>Rivers: Colorado, San Juan, Animas, Green.
<sup>f</sup>Rivers: Columbia, Willamette, Pend Oreille, Yakima, Spokane, Clearwater, Snake.
<sup>g</sup>Based on 1577 samples, 1464 aluminum analyses.
<sup>h</sup>Values of Lakin (1973).
<sup>i</sup>Value of Riley and Chester (1971).

river systems (the Wabash, Ohio, and Mississippi rivers) as well as two smaller river systems (the Big Muddy River and the Kaskaskia River). Again, a worst-case approach was used. Final concentrations (FC) for the various trace elements were calculated in the following manner:

$$FC = \frac{AE}{AD} + AC$$

(19)

where

- AE = total annual emission (mg/year)
  - AD = total annual discharge (liters/year)

AC = ambient concentration of the trace element in the river water before inputs (mg/L).

The enrichment factors (EF) were calculated in a manner similar to the first model discussed. Expressed mathematically,

$$EF = \frac{FC}{AC}$$

(20)

Pegion of		Drainac	je area <sup>a</sup>	Disc	harge <sup>a</sup>	Calcula for 28 (1000 disch	ted area .3 m <sup>3</sup> /s cfs) arge <sup>D</sup>
United States	River	km <sup>2</sup>	mi <sup>2</sup>	m <sup>3</sup> /s	cfs	km <sup>2</sup>	mi²
Northern Appalachian	Allegheny Susquehanna	29,550 67,310	11,410 25,990	530 990	18,810 35,060	1,580 1,920	610 740
Southern Appalachian	Cumberland Tennessee	45,580 104,120	17,598 40,200	790 1,810	28,030 64,050	1,630 1,630	630 630
Eastern Interior	Illinois Wabash White	65,530 74,070 66,040	25,300 28,600 25,497	580 750 830	20,670 26,600 29,360	3,160 2,780 2,250	1,220 1,075 870
Four Corners	Colorado	434,600	167,800	410	14,530	29,910	11,550
Pacific Northwest	Willamette	18,850	7,280	700	24,780	750 <sup>°</sup>	290

Table 42. Drainage Statistics and Calculated Area Required for a Discharge of 28.3 m<sup>3</sup>/s (1000 cfs) for Selected Rivers within Various Regions of the United States

<sup>a</sup>Data (English units) from Iseri and Langbein (1974).

<sup>b</sup>Data from Stallard and Yang (1970).

Table 43. Concentration of Selected Trace Elements in a Hypothetical Lake Following 30 Years of Direct Deposition<sup>a</sup>

Element	Trace-element concentration (µg/L)
Arsenic	0.05
Barium	0.14
Cadmium	0.04
Chromium	0.16
Cobalt	0.05
Lead	0.57
Manganese	0.20
Mercury	0.07
Selenium	0.14
Vanadium	0.18
Zinc	1.25

<sup>a</sup>From Dvorak et al. (1977).

Enrichment factors that amounted to less than a 10% increase over the ambient concentration were assumed to indicate no measurable increase (NMI).

Final results of these analyses indicated that there was a low potential for aquatic impacts from additional trace-element loading due to power-plant emissions to the large river systems (i.e., the Wabash, Ohio, and Mississippi rivers). However, results of the analyses also indicated that increased trace-element loading to the smaller river systems (i.e., Big Muddy River and Kaskaskia River) may increase concentrations beyond federal and state water quality criteria and toxicity thresholds.

In the study of Vaughan et al. (1975), it was determined that available metal concentrations in runoff water will amount to 1/1000 of their concentrations in soil (Vaughan's study is described on page 83). The authors did not discuss atmospheric deposition of the trace elements. Only copper, mercury, and molybdenum were observed to significantly increase in concentration in runoff water. In addition, the authors noted that Cd, Cr, Mn, Tl, V, and Zn may warrant closer inspections if stack emissions were increased 100 times. Concentrations of trace elements in runoff water did not exceed water quality criteria or the toxicity threshold of most aquatic biota.

#### Impacts of Radioactive Emissions on Fish and Wildlife

The radioactive elements released to the atmosphere from a coal-fired plant are the naturally occurring radionuclides in the coal. These radionuclides are primarily those that have existed since primordial times, and their daughter products, and have not completely decayed because of their long half-lives. The primordial radionuclides that are associated with the emissions from coal combusion are K-40, U-235 and decay products, U-238 and decay products, and Th-232 and decay products. Potassium-40 is present as a fixed proportion (0.0118%) of naturally occurring potassium. Since the level of potassium in most biological systems is under homeostatic control, the level of K-40 in most living organisms will not be affected by the K-40 releases from a coal-fired plant. The U-235 decay series contributes only a small fraction of the radioactivity of the U-238 and Th-232 decay series.

The concentration of U-238 and Th-232 in coal is extremely variable and can range from less than 0.2 ppm to 47 ppm (Swanson and Medlin et al. 1976). Most of the radioisotopes in the coal will be left in the slag and ash so that their concentration in slag and ash will be higher than in coal. The concentrations of uranium and thorium in fly ash are approximately 16 and 12 times higher, respectively, than in coal (Klein et al. 1975b). The concentration of uranium and thorium in coal and fly ash is given in Table 44. Additional values for radioactivity in fly ash are given in Table 18.

Table 44. Approximate	Average Concentration of Uranium
and Thorium in the	Three Standard Coal Types
and Ass	ociated Fly Ash <sup>a</sup>

	Coal	(ppm)	Fly ash	(ppm)b
Coal type	Uranium	Thorium	Uranium	Thorium
Western	0.8	2.0	12.8	24.0
Northern Appalachian	1.0	2.8	16.0	33.6
Eastern Interior	1.4	1.6	22.4	19.2

<sup>a</sup>Data from Swanson and Medlin et al. (1976).

<sup>2</sup>Assuming the concentration in fly ash is 16 times that in coal for uranium and 12 times that in coal for thorium.

The uranium and thorium decay series are expected to be in equilibrium. Thus, rates of release of the decay products will be the same as that of the parent nuclide. The uranium decay series includes U-238, Th-235, Pa-234, U-234, Th-230, Ra-226, Po-218, Pb-214, Bi-214, Po-214, Pb-210, Bi-210, Po-210; and the thorium decay series includes Th-232, Ra-228, Ac-228, Th-228, Ra-224, Pb-212, and Bi-212. It is assumed that the radon present in the coal is in equilibrium with the parent and that it is all released during combustion. The quantities of these radio-nuclides released per year are given in Table 45 for the four model power plants using the three standard coal types.

To fully assess the impact of the release of radioactive particulates on fish and wildlife, it is necessary to characterize the ecosystem and to identify the more sensitive or more important species in that ecosystem. An analysis can then be made for the species of concern regarding the effect of radiation from ingestion, inhalation, and external exposure. An approximation of the animal dose would be the dose that humans receive from coal plants. The animal dose will vary depending on the animal's breathing rate, body weight, position in the trophic chain, and extent to which it is either a carnivore or herbivore. To translate the dose into a health effect, it is necessary to consider factors such as the metabolic rate and life span of the animal; in general, the higher the metabolic rate and greater the life span, the greater the expected health effect.

Dlant size		E	mission ra	ites (Ci/yr)	
(MWe)	Coal type	U	Rn-222	Th	Rn-220
100	Western	3.1 × 10-4	0.08	1.9 × 10 <sup>-4</sup>	0.07
	Northern Appalachian	$2.6 \times 10^{-4}$	0.1	$1.8 \times 10^{-4}$	0.09
	Eastern Interior	6.4 × 10 <sup>-4</sup>	0.14	$1.8 \times 10^{-4}$	0.05
350	Western	1.1 × 10 <sup>-3</sup>	0.28	6.5 × 10 <sup>-4</sup>	0.25
	Northern Appalachian	9.7 × 10 <sup>-4</sup>	0.35	6.7 × $10^{-4}$	0.32
	Eastern Interior	$2.2 \times 10^{-3}$	0.49	$6.2 \times 10^{-4}$	0.18
700	Western	$2.2 \times 10^{-3}$	0.56	1.3 × 10 <sup>-3</sup>	0.49
	Northern Appalachian	1.9 × 10 <sup>-3</sup>	0.7	1.3 × 10- <sup>3</sup>	0.63
	Eastern Interior	$4.6 \times 10^{-3}$	0.98	$1.3 \times 10^{-3}$	0.35
2100	Western	$6.6 \times 10^{-3}$	1.68	4.0 × 10 <sup>-3</sup>	1.47
	Northern Appalachian	5.6 × 10-3	2.1	3.9 × 10 <sup>-3</sup>	1.89
,	Eastern Interior	$1.4 \times 10^{-2}$	2.94	$3.8 \times 10^{-3}$	1.05

#### Table 45. Average Emission Rates of Uranium and Thorium Series Isotopes and Radon for the Four Model Plants and Three Standard Coal Types

A study by McBride et al. (1977) used a 1000-MWe coal-fired plant which had emissions of radioactive elements within an order of magnitude of those in this study. Dose contributions from the ingestion, inhalation, and external exposure pathways were considered. The whole-body and lung doses to humans were calculated to be 1.9 mrem/year, whereas the bone dose was 18.2 mrem/year. This can be compared to natural background doses of 80 mrem/yr to whole body, 180 mrem/year to lung, and 120 mrem/year to bone (Natl. Comm. Radiat. Protect. Meas. 1975). The natural background dose to animals is actually 5 to 10% higher since animals live in the open, without the benefit of shielding afforded by housing structures. Table 46 gives the annual doses from the 1000-MWe coal-fired plant and natural background.

	Dose rate	(mrem/year)
	Coal-fired plant <sup>a</sup>	Natural background
Whole body	1.9	80
Lung	1.9	180
Bone	18.2	120
2		

Table 46. Comparison of Dose Rate to Man between Emissions from a 1000-MWe Coal-Fired Plant and Natural Background Radiation

<sup>a</sup>Data from McBride et al. (1977).

The radiation dose to animals due to emissions from a 1000-MWe coal-fired plant is expected to be much lower than from natural background. This estimate is based on calculations done for man and may not be accurate for fish and some species of animals, especially those higher up the trophic chain. However, considering the low doses involved, the only health effect that might be observed would be an increase in the cancer rate, and then only after a long latent period that extends into decades. Assuming that the latent period in animals is as long as in man, any carcinogenic effect would have minimal impact because the latent periods exceed the life spans of the animals.

#### Terrestrial Impacts of Fly Ash and Scrubber Sludge Disposal

Impacts to soils, vegetation, and animal life arise from (1) preemption of land, (2) waterfowl use of active disposal ponds, and (3) runoff and seepage from disposal sites.

<u>Preemption of land</u>. Land is an increasingly valuable resource, not only for agriculture and range but also for human habitation and recreation, and wildlife habitat. Estimates of the land requirements for ash and scrubber-sludge disposal at each of the four model power plants are given in Tables 47 and 48.

Table 47. Forty-Year Land Area Requirements for Ash Disposal from Combustion of Western, Appalachian, and Eastern Interior Coal Types<sup>a</sup>

			Lai	nd area required	1	
	Wester	Northern Western coal Appalachian coal		Eastern Interior coal		
Plant size (MWe)	(ha)	(acres)	(ha)	(acres)	(ha)	(acres)
100	11	28	8	20	16	40
350	40	98	28	70	57	140
700	79	195	57	140	113	280
2100	238	588	170	420	340	840

<sup>a</sup>Calculated using data from Cooper (1975) on land area requirements for sludge and ash disposal. "Ash" refers to precipitator fly ash and bottom ash combined; density = 80 lb/ft<sup>3</sup>, dry. Depth of waste ponds assumed to be 3 m (10 ft).

Table 48. Forty-Year Land Area Requirements for SO<sub>2</sub>-Scrubber Sludge Disposal from Combustion of Western, Northern Appalachian, and Eastern Interior Coal Types, Using Either Limestone or Lime Scrubbers<sup>a</sup>

	Land area required									
	No	rthern Appa	lachian (	coal		Eastern Interior coal				
	Limestone		Lime		Limestone		Lime			
Plant size (MWe)	(ha)	(acres)	(ha)	(acres)	(ha)	(acres)	(ha)	(acres)		
100	32	80	29	72	58	144	45	112		
350	113	280	102	252	204	504	159	392		
700	226	558	204	503	406	1003	316	781		
2100	680	1680	612	1512	1225	3024	953	2352		

<sup>a</sup>Calculated using data from Cooper (1975) on land area requirements for sludge and ash disposal. Sludge assumed to be 50% solids; depth of ponds assumed to be 3 m (10 ft).

Onsite disposal of the waste either temporarily or permanently removes that area from further or multiple use for the lifetime of the plant. Disposal in mined-out pits or natural ravines, that frequently serve as catch basins for precipitation and runoff, eliminates any use of such areas for aquatic habitat or for human recreation. However, disposal in a mined-out pit, if followed by reclamation, would allow future use of the surface. Efforts to reclaim a given disposal site--e.g., covering with earth and revegetating--may or may not be successful, depending on the properties of the disposed material, availability of good earth cover materials, and climate of the region. Scrubber sludge, in particular, must be chemically treated or otherwise hardened if any further use is to be made of the site. There is a tendency to use low, swampy areas for settling ponds or disposal sites (MacFarlane et al. 1975). This practice will remove wetlands that serve as waterfowl nesting and feeding habitat and that may be critical to migrating or resident endangered species.

Quantitative measures of land-use impacts, aside from areal measurements, have not been developed due to the difficulty of determining social values that would characterize a given locality. The assessment of land-use impacts, therefore, can presently be made only on a qualitative basis. At best, the area of a given waste-disposal site and the extent to which that area is used for cropland, range, wildlife habitat, and recreation can be determined, and the loss of land productivity evaluated.

<u>Waterfowl use of active disposal ponds</u>. The presence of a large body of standing water can sometimes be attractive to migrant waterfowl as a resting and feeding area, particularly if there are sources of food nearby. Ash-settling ponds are examples of such bodies of water. Waterfowl using these ponds are thus exposed to particulates and chemicals dissolved in the water. An additional hazard is present if transmission towers and lines are located close to, or cross, the ponds. The Illinois Natural History Survey has reported on studies carried out at a power plant in Illinois (Anderson et al. 1975; Anderson 1976). At this plant, a slag pit is situated close to a lake used for power plant cooling. Land surrounding the lake is intensively farmed for corn and soybeans. The slag pit supports lush aquatic vegetation (mainly brittle naiad) during late summer and early fall. The naiad appears to attract waterfowl which add nitrogen and phosphorus to the water, which promotes a dense growth of naiad the following year. Every fall from 1973-1975, between 200 to 400 waterfowl (0.2-0.4% of the maximum number present) were killed by collision with the high-voltage transmission lines that cross the slag pit. (Anderson 1976).

Conclusive evidence was also obtained that waterfowl were ingesting slag, presumably from this particular slag pit (Anderson et al. 1975). Over three sampling periods, 16 species of waterfowl were examined; 11 species were found to contain slag in their gizzards. A total of 453 gizzards were examined, 66% of which contained slag. The material was found more consistently and 90% of mallard and widgeon gizzards, respectively, compared to 19-60% of diving duck gizzards. Analysis of the slag indicated high concentrations of calcium, iron, potassium, lead, chromium, and other metals. It was suggested by the investigators that ingestion of slag by waterfowl could have both beneficial and adverse effects--i.e., the birds were obtaining essential minerals as well as potentially toxic metals from the slag (Anderson et al. 1975).

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Runoff and seepage from waste-disposal sites. During the operation of a power station, runoff from the onsite waste impoundment area is unlikely if dikes are properly constructed to hold the waste ash or sludge within the impoundment. Accidential releases can occur, however, due to excessive rains and/or poor dike construction. In such instances, additions of waste constituents to the soils immediately adjacent to the break will occur, but are unlikely to affect offsite areas.

Active disposal locations offsite, particularly those situated in natural ravines or natural depressions, are subject to runoff and/or washout unless the impoundment was designed to cope with the maximum rainfall expected at the site. Clay-cored earth dams are more resistant to washout than dams constructed of the fly-ash material itself. Assessment of the structural integrity of the impoundment site requires the expertise of a qualified engineer. The shortterm effects of dam-washout to the terrestrial environment would be destruction of herbaceous vegetation and possibly of small animals; the long-term effects of washout would result from additions of large quantities of potentially toxic trace elements to the soils in the path of the washout, with eventual adverse effects on vegetation and herbivores.

Vertical and lateral seepage from ash and scrubber sludge disposal sites can occur, particularly where the waste material is deposited as a slurry. Briefly, the major impact of seepage is the addition of potentially toxic elements and ions to groundwater and/or soil. Contamination of groundwater results in eventual contamination of animal and human drinkingwater sources. The recommended maximum concentration limits for livestock drinking-water sources are given in Table 30. Potentially toxic elements in seepage can also eventually be deposited in natural waterways.

At a generating station in Wisconsin, field studies on the environmental impact of an ashdisposal pond are in progress. Information published to date indicates that seepage from the pond was as high as 1,323 L/day (350 gal/day) when the ash pond was first filled. Seepage was mainly into a marsh area where a thin layer of peat overlies fine sand. As the pond filled with ash, the seepage rate was "greatly reduced." It was concluded that seepage will be "substantial" from areas where there is standing water abutting the dikes (Inst. Environ. Stud. 1976b). A change in normal water levels of bogs and marshes, as a result of seepage from ash and sludge settling ponds, can change the nature of these wetlands, not only in areal extent but in terms of vegetation species changes brought on by raised water levels and/or influx of chemical constituents.

Seepage from waste-disposal sites into soil introduces constituent elements, including radionuclides, into the plant growth medium. In this section, the factors that influence the transport of seepage and solute through the soil and into the root zone are discussed, with the aim of providing some background information that will allow an estimate of the magnitude of a potential seepage problem at the specific site under evaluation.

Seepage and transport of potentially toxic elements and ions from sludge- and ash-disposal sites are influenced by a number of factors, the most important being (1) permeability of the impoundment materials, (2) concentration and chemical form of the element in question and pH of the pond leachate, and (3) physical and chemical properties of the soil.

<u>Permeability of impoundment materials</u>. For purposes of this report, permeability is defined as the rate of transport of liquid (e.g., seepage) through a given thickness of a material, and has the units of distance/time. Hughes and Cartwright (1972) have indicated that a well-compacted earth impoundment bottom has a permeability of about  $10^{-6}$  cm/s, which would allow about 1700 L (450 gal) of leachate per day to move into the underlying strata "from an area the size of a football field." Addition of soil cements during compaction can reduce permeabilities several orders of magnitude below  $10^{-6}$  cm/s (Williams 1975). Such a liner would be quite effective if the ash were deposited in a dry state. An impoundment lined with clay, particularly bentonitic clay treated with sodium, would have permeabilities on the order of  $10^{-8}$  cm/s (U.S. Nucl. Reg. Comm., <u>unpublished</u>). Synthetic liners such as plastic or rubber are reputed to have essentially zero permeabilities, but the durability of these liners over a 30-year period has not been proven (see p. 140).

At disposal sites where there is no pretreatment of the impoundment area (no soil compaction or liner applied), the permeability of the impoundment bottom, and eventual addition of seepage to groundwater or surface water, will depend on the physical characteristics of the underlying strata. If the impoundment area is excavated to bedrock, permeability of the rock and penetration of seepage to the aquifer is dependent on the type of rock, i.e., granite and shale are relatively impermeable whereas sandstone and sand are quite permeable. If there is no excavation to bedrock, again the eventual contamination of groundwater and rate of seepage will depend on the physical characteristics of the soil: a sandy soil will allow more rapid transport than a clay soil. Permeabilities of soil range from less than  $3.5 \times 10^{-5}$  cm/s (0.05 inches/ hour) to more than  $7.0 \times 10^{-3}$  cm/s (10 inches/hour).<sup>2</sup>

Holland et al. (1975) conducted laboratory tests with ash and scrubber sludge leachates through soil samples in cylindrical tubes. The characteristics of the soils used are given in Table 49. Leachates and soils from five electric generating stations, as well as soils of varying clay content from other sites, were tested. Soil columns of 15 cm length and 3.3 cm inside diameter were used; the soils were disturbed and homogenized. The results indicated that a clay soil, with an average permeability of  $7.4 \times 10^{-6}$  cm/s, removed selenium and chromium from the leachate at a rate equivalent to the removal of over 95% of these elements after 10 years of continuous flow through a 12-m (40-ft) soil depth. A sandy soil did not remove selenium and chromium to the same level as the clay soil, but it was concluded that 15 m (50 ft) of the sandy soil would remove over 95% of copper, arsenic, or zinc after 10 years of flow. The vertical depth required of a given soil to reduce the concentration of certain trace elements to less than 5% of the pond concentration is given in Figure 24 and Table 50. Table 50 was prepared with values derived from a model, using results of the laboratory tests. Extrapolation from these data to the assessment of field behavior should be done with caution, and may not be applicable in many cases. However, the study does provide data indicating that the following trace elements should be of concern regarding contamination of groundwater: selenium, boron, chromium, barium, and mercury. With regard to contamination of soils and the food chain, these and other elements adsorbed by the soil should also be of concern.

The leachate from ponds that move through a particular soil will displace ions that are already present in the soil, and move them downward with the seepage flow. Most soils are relatively low in trace elements (except for iron and aluminum), but there are areas, e.g., the arid west and southwest, that have abnormally high concentrations of selenium, molybdenum, or boron (see Appendix E). In such areas, which can be identified most often by consultation with the district Soil Conservation Service, attention should be given to this aspect of pond leachate movement.

<sup>2</sup>These values are rough approximations, based on rates through saturated undisturbed soil cores under a 1.3-cm (0.5-inch) head of water (U.S. Dep. Agric. 1951) and should not be used in a specific case without field tests.

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There is a tendency to use low, swampy areas for settling ponds or disposal sites (MacFarlane et al. 1975). This practice will remove wetlands that serve as waterfowl nesting and feeding habitat and that may be critical to migrating or resident endangered species.

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Active disposal locations offsite, particularly those situated in natural ravines or natural depressions, are subject to runoff and/or washout unless the impoundment was designed to cope with the maximum rainfall expected at the site. Clay-cored earth dams are more resistant to washout than dams constructed of the fly-ash material itself. Assessment of the structural integrity of the impoundment site requires the expertise of a qualified engineer. The shortterm effects of dam-washout to the terrestrial environment would be destruction of herbaceous vegetation and possibly of small animals; the long-term effects of washout would result from additions of large quantities of potentially toxic trace elements to the soils in the path of the washout, with eventual adverse effects on vegetation and herbivores.

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Seepage and transport of potentially toxic elements and ions from sludge- and ash-disposal sites are influenced by a number of factors, the most important being (1) permeability of the impoundment materials, (2) concentration and chemical form of the element in question and pH of the pond leachate, and (3) physical and chemical properties of the soil.

<u>Permeability of impoundment materials</u>. For purposes of this report, permeability is defined as the rate of transport of liquid (e.g., seepage) through a given thickness of a material, and has the units of distance/time. Hughes and Cartwright (1972) have indicated that a well-compacted earth impoundment bottom has a permeability of about  $10^{-6}$  cm/s, which would allow about 1700 L (450 gal) of leachate per day to move into the underlying strata "from an area the size of a football field." Addition of soil cements during compaction can reduce permeabilities several orders of magnitude below  $10^{-6}$  cm/s (Williams 1975). Such a liner would be quite effective if the ash were deposited in a dry state. An impoundment lined with clay, particularly bentonitic clay treated with sodium, would have permeabilities on the order of  $10^{-8}$  cm/s (U.S. Nucl. Reg. Comm., <u>unpublished</u>). Synthetic liners such as plastic or rubber are 30-year period has not been proven (see p. 140).

At disposal sites where there is no pretreatment of the impoundment area (no soil compaction or liner applied), the permeability of the impoundment bottom, and eventual addition of seepage to groundwater or surface water, will depend on the physical characteristics of the underlying strata. If the impoundment area is excavated to bedrock, permeability of the rock and penetration of seepage to the aquifer is dependent on the type of rock, i.e., granite and shale are relatively impermeable whereas sandstone and sand are quite permeable. If there is no excavation to bedrock, again the eventual contamination of groundwater and rate of seepage will depend on the physical characteristics of the soil: a sandy soil will allow more rapid transport than a clay soil. Permeabilities of soil range from less than  $3.5 \times 10^{-5}$  cm/s (0.05 inches/ hour) to more than  $7.0 \times 10^{-3}$  cm/s (10 inches/hour).<sup>2</sup>

Holland et al. (1975) conducted laboratory tests with ash and scrubber sludge leachates through soil samples in cylindrical tubes. The characteristics of the soils used are given in Table 49. Leachates and soils from five electric generating stations, as well as soils of varying clay content from other sites, were tested. Soil columns of 15 cm length and 3.3 cm inside diameter were used; the soils were disturbed and homogenized. The results indicated that a clay soil, with an average permeability of  $7.4 \times 10^{-6}$  cm/s, removed selenium and chromium from the leachate at a rate equivalent to the removal of over 95% of these elements after 10 years of continuous flow through a 12-m (40-ft) soil depth. A sandy soil did not remove selenium and chromium to the same level as the clay soil, but it was concluded that 15 m (50 ft) of the sandy soil would remove over 95% of copper, arsenic, or zinc after 10 years of flow. The vertical depth required of a given soil to reduce the concentration of certain trace elements to less than 5% of the pond concentration is given in Figure 24 and Table 50. Table 50 was prepared with values derived from a model, using results of the laboratory tests. Extrapolation from these data to the assessment of field behavior should be done with caution, and may not be applicable in many cases. However, the study does provide data indicating that the following trace elements should be of concern regarding contamination of groundwater: selenium, boron, chromium, barium, and mercury. With regard to contamination of soils and the food chain, these and other elements adsorbed by the soil should also be of concern.

The leachate from ponds that move through a particular soil will displace ions that are already present in the soil, and move them downward with the seepage flow. Most soils are relatively low in trace elements (except for iron and aluminum), but there are areas, e.g., the arid west and southwest, that have abnormally high concentrations of selenium, molybdenum, or boron (see Appendix E). In such areas, which can be identified most often by consultation with the district Soil Conservation Service, attention should be given to this aspect of pond leachate movement.

<sup>2</sup>These values are rough approximations, based on rates through saturated undisturbed soil cores under a 1.3-cm (0.5-inch) head of water (U.S. Dep. Agric. 1951) and should not be used in a specific case without field tests.

Soil designation	Textural classification <sup>a</sup> (grain-size analysis)	Mineralogy of < 2-mµ (clay) fraction <sup>b</sup>	Specific gravity <sup>c</sup>	Average <sup>d</sup> TOC (ppm)	Average <sup>e</sup> CEC (meq/100 g)	Average permeability <sup>f</sup> (cm/s)
Station 1	Sand	70% illite, 20% montmo- rillonite, 10% kaolinite	2.58	2,540	3.8	5.1 $\times$ 10 <sup>-4</sup>
Station 2	Clay	90% illite, 5% montmo- rillonite, 5% kaolinite	2.43	14,390	N.D. <sup>g</sup>	5 × 10 <sup>-8</sup>
Station 3	Clay	90% kaolinite, 10% mont- morillonite	2.76	1,270	31	7.4 × 10 <sup>-6</sup>
Station 4	Silt loam-silty clay loam	60% illite, 20% montmoril- lonite, 20% kaolinite	2.30	72,700	30	$1.2 \times 10^{-5}$
Station 5	Loam-clay loam	60% illite, 30% montmoril- lonite, 10% kaolinite	2.45	7,710	21	2.1 × 10 <sup>-5</sup>

Table 49. Characteristics of Soils Used in the Leachate Experiments of Holland et al. (1975)

<sup>a</sup>Dry-sieving, pipetting, and centrifugation. <sup>b</sup>X-ray diffraction analysis, 1 mµ =  $10^{-6}$  m. <sup>c</sup>Pycnometer determination with tetrachloromethane. <sup>c</sup>Oxidation to CO<sub>2</sub> by persulfate and wet combustion analyzer. (TOC = Total organic carbon.) <sup>c</sup>I N NH<sub>4</sub>OAc displacing Na<sup>+</sup> at pH = 8.2. (CEC = Cation exchange capacity in units of milliequivalents of cation per 100 g of  $f_{g}^{soil}$  soil,  $f_{g}^{soil}$  solution of the second standard structure standard structure structur



Removal of Trace Elements from Pond Leachate as a Function of Time. Figure 24. Characteristics of the soils at these stations are given in Table 49. The tables for determining approximate depth required for reduction of trace-element levels to less than 5% of the pond concentration are given in Table 50. From Holland et al. (1975).

Table	50.	7	Tables	for	Dete	ermining	i Ar	oprox	imate	Ver	rtic	all	Depth	Required	for	Reduction
		of	Trace-	-Elem	nent	Leve1s	to	Less	than	5%	of	the	Pond	Concentra	itior	1 <sup>a</sup>

In soils		Depth (m) r	equired -	ash leacha	te	Depth (m) required - sludge_leachat				te
station no. <sup>b</sup>	Arsenic	Chromium	Copper	Fluorine	Selenium	Chromium	Copper	Fluorine	Mercury	Zinc
				After	two years		·····			
1 3 4 5	<4.9 <2.7 <1.2 <2.1	60 ~2.7 2.1 >30	<4.9 <2.7 <1.2 N.D.	610 >15 >21 ∿29	37 3 5.2 4.6	60 18 17 29	<0.9 <1.2 <0.9 <0.9	60 10 24 29	27 <1.2 <1.5 <1.2	0.9 <1.2 <0.9 <1.2
				After	ten years					
1 3 4 5	<15 <10 <3.4 <7	215 10 7 >130	<15 <10 <3.4 N.D.	3,050 >85 >110 120	150 11 19 16	305 88 67 170	3 <5.8 <3 ∿3	305 49 94 170	130 <5.8 <5.5 3.7	4.9 <5.8 <3 3.7
				After	100 years					
1 3 4 5	<150 <79 <23 <58	2,285 79 55 1,280	<150 <79 <23 N.D.	30,480 >855 >61 1,130	1,555 85 170 70	305 855 670 1,280	27 <49 <19 24	3,050 425 945 1,280	1,220 <49 <43 26	37 <49 <19 2.6

<sup>a</sup>Data derived from Holland et al. (1975). This table is to be used with Figure 24. Table values assume depth to blower boundary of removal zone << depth to impermeable layer. N.D. = Not determinable. Effective porosities of 10% were assumed for all soils except soil from Station No. 1 which was assumed to be 50% due to its high sand content. Soil from Station No. 2 was very clayey, permitting very little flow and offering virtually complete protection.

Seepage from an ash pond at the Four Corners generating plant in Arizona, after 10 years of operation, was found to have high concentrations of total dissolved solids, although traceelement content was low. The pH of the seepage water was 7.7 (Roffman et al. 1977). Another study with soil columns in the laboratory indicated that soil ionic constituents are displaced by effluent from municipal landfills, particularly under acid conditions with iron and aluminum in the incoming liquid (Fuller et al. 1975).

Effects of the pond leachate pH on the concentration and chemical form of trace elements. The solubilities of most trace elements in water tend to decrease as pH is increased (Frascino and Vail 1976). The pH of ash-pond liquors are usually high, i.e., between 6 and 11, which tends to precipitate the trace elements on hydroxides of iron and aluminum. Scrubber-sludge liquors can be acidic [pH 5 to 5.5 (Cooper 1975)] and are often neutralized by combining the sludge with the coal ash. The pH of most ash- and scrubber-pond leachates will be neutral or alkaline, which prevents solubilization of large quantities of the trace elements. However, if the underlying or surrounding soils are acidic, some of these elements may become soluble. This situation can occur in areas of high rainfall and highly leached soils. Soils in the arid west or southwest tend to be neutral to slightly alkaline, and trace elements would tend to remain insoluble and largely unavailable for plant uptake. A number of other factors besides pH affect the availability of a given element, but in general, trace-element-toxicity effects should be of more concern when the absorbing medium (i.e., the soil) and transporting medium (pond leachates) are acidic than if they are neutral to alkaline. Adsorption of potentially toxic elements in the soil reduces the hazard to groundwater, but increases the hazard from uptake by vegetation and subsequent toxic effects on herbivores. This impact is highly dependent on the chemical form of the element and its availability to plants (see pp. 71-77).

Briefly, as ash- or sludge-pond leachate moves through a given soil, cations in the leachate adsorb onto the clay minerals and organic matter, displacing cations--usually calcium or magnesium and hydrogen--originally on the adsorption sites. Eventually, the cation exchange capacity (see below) of that soil is exceeded and the soil can no longer adsorb additional concentrations; thus, the higher the concentration of a given element in the leachate, the greater the concentration that eventually reaches groundwater, and the greater will be the concentration present in the soil for eventual uptake by vegetation.

<u>Physical and chemical properties of soil</u>. The physical properties of a soil that influence movement of leachate laterally and vertically from a waste-disposal site include textural grade (proportion of sand, silt, and clay) and bulk density (the weight of a given volume of soil)-properties which affect hydraulic conductivity. The problem of calculating the flow path and flow rate of leachate from a pond is complex and extremely site-specific. Models can be formulated which, with the use of a digital computer, can be used to simulate the flow of leachate from a given pond under given conditions. A rough estimate of pond leakage can be made more simply, however, as was done in the case of a landfill site in Illinois. In that case, Darcy's equation

$$Q = kA \frac{dH}{dL}$$

was used to estimate the thickness of liner required for "total attentuation" of leachate for each meter thickness of overlying refuse during a 20-year fill life, using soil columns in the laboratory (Cartwright et al. 1977).

The variables in Equation 21 are: Q = flow rate in cm<sup>3</sup>/s, k = hydraulic conductivity, A = area of the landfill in cm<sup>2</sup>, dL = thickness of the liner in cm, dH = head of water across the liner in cm. The hydraulic conductivity, k, can be estimated by laboratory determinations on undisturbed core samples of the soils.

The transport of trace metals and other dissolved material in the leachate is even more complex, and depends on additional factors such as distribution coefficients and diffusivity.

The chemical properties of a soil that influence the transport of solutes include ion adsorption capacity, which in turn is influenced by the type of clay mineral present. A given soil has a finite capacity to adsorb cations and very little or no capacity to adsorb anions. In general, the higher the clay content and organic matter of a soil, the greater is its cation adsorption capacity (or, more correctly, its cation exchange capacity). The particular clay mineral in a given soil also influences its cation exchange capacity, i.e., soils with a higher proportion of montmorillonitic clays have higher adsorption capacities than those with the same amount of kaolinitic clays. Hydrous micas (e.g., illite) are clay minerals similar to montmorillonite in structure but do not have as high cation exchange capacities, and are intermediate between montmorillonitic and kaolinitic clays. Hydrous oxides of iron and manganese also provide sites for cation adsorption. The clay fraction present in a given soil usually consists of a mixture of clay minerals; the types of minerals present are primarily dependent on climatic conditions and the nature of the parent material from which the soil was formed. Very generally, the greater the weathering process the higher will be the proportion of hydrous

(21)

Bable on selection of

oxides and kaolinitic clay in the soil. Parent materials high in bases, e.g., magnesium, tend to produce montmorillonitic clays. Again very generally, montmorillonites and illites tend to predominate in the soils of the semiarid and arid United States, whereas kaolinitic clays and hydrous oxides tend to predominate in the humid East or South (see Table 51).

Table 51. Clay Minerals Found to Predominate in Different Soil Ordersa

. <u></u>				Don	ninant	clay r	ninera	ls	
Soil order	General weathering intensity	Typical location in U.S.	Hydrous oxides	Kaolinite	Montmorillonite	Illite	Vermiculite	Chlorite	Intergrades
Entisol	Low	Variable			x	х			
Inceptisol		Variable				х			х
Aridisols		Desert				х	х	х	х
Vertisols		Ala., Tex.			х				
Mollisols		Central U.S.			х	х	х	х	
Alfisols		Ohio, Pa., N.Y.		х	х	х		х	х
Spodosols		New England	x			х	•		х
Ultisols	V V	Southeast U.S.	x	х			x		х
Oxisols	High	Tropical zones	х	х					х

<sup>a</sup>From Brady (1974) (with permission, see credits). Soil orders are major classifications of soils and are briefly described in Appendix G. A soil map of the United States, delineating soil orders, can be found in Brady (1974).

In summary, the seepage and transport of potentially toxic ions from ash- and sludgedisposal ponds is a complex process, the magnitude of which is site-specific. It will be difficult to obtain quantitative estimates of seepage concentrations and patterns of flow without input from hydrologists and hydraulic engineers who, in turn, will find it difficult to predict correct trace-element concentrations in the leachate as it moves through the soil. A qualitative assessment will be useful in siting and pond-construction decisions. The following section includes a table from which the potential severity of a seepage problem at a given disposal site can be determined.

## Assessment of the Potential for Adverse Effects to the Terrestrial Environment from Waste-Disposal Site Seepage

Currently, all soils in the United States are being evaluated for their limitations for waste disposal. These ratings can be found in published Soil Survey Reports for various counties; included in the reports are reasons for the limitations. Unfortunately, most counties in a large number of states do not have completed Soil Survey Reports published; other reports are of older vintage when such ratings were not routinely made. Inquiries to the district Soil Conservation Service regarding published and unpublished data on the soils of a specific site should be an initial step in any assessment of land disposal impacts. Soil Survey Reports also contain a wealth of information on the vegetation, wildlife, and land use of a given county, as well as data on the geology, soils, climate, topography, and depths to the seasonally high water table.

In the absence of soil survey information, Table 52 can provide some measure of the potential for impact from seepage, given some general information about a particular site and assuming that the impoundment area is unlined. (Lining of an impoundment area implies, here, the correct placement of clay or a synthetic material on the bottom and sides of the impoundment.) It must be emphasized that the table does not include all factors involved in the evaluation of seepage effects; rather, it lists the major factors related to specific site characteristics that could be readily evaluated. It is essential to realize that the factors must be considered concurrently, rather than as separate entities. An explanation of these factors follows, and a hypothetical example is presented to illustrate the use of the table.

	Relative probability of						
Factor	Groundwater contamination	Food chain contamination via soil					
Nature of waste							
Dry	Low to moderate	Low to moderate					
Slurry	High	High					
Acid	High	High					
Alkaline	Low to moderate	Low to moderate					
Nature of substrata <sup>a</sup>							
Granite	Extremely low	Not applicable					
Shale	Low	Not applicable					
Sandstone	Moderate	Not applicable					
Sand	High	Not applicable					
Soil	High	High					
Nature of soils							
Clays	Low	High					
Loams	High	High					
Sands, sandy loams	Very high	High to low					
Rainfall zone <sup>b</sup>							
< 25 cm (< 10 inches)	Low	Low to high					
25-76 cm (10-30 inches)	Low to high	Hiah					
> 76 cm (> 30 inches)	High	High, except for sandy areas					

#### Table 52. Potential for Adverse Effects to Groundwater and the Terrestrial Food Chain from Seepage from Unlined Ash and Sludge Waste-Disposal Sites

<sup>a</sup>Defined as the layer or layers of natural material beneath the waste, or between the waste impoundment and the groundwater aquifer. <sup>b</sup>Annual average precipitation.

Nature of waste. When the ash and sludge are deposited dry, or with no standing water, there will be very little or no seepage of waste liquors, but leaching by rainfall may occur. The chances for the leachate reaching the groundwater are high in a region where rainfall is high. If the groundwater aquifer is below a relatively impervious layer such as granite or shale, contamination of the aquifer is unlikely. Such an impervious layer will not, however, protect the food chain, except where the soils are sandy; in this latter case, the contaminants will tend to be washed downward, away from the root zone of most plants.

If the waste is deposited as a slurry, chances of contamination of both groundwater and the food chain are high, unless the impoundment area is lined or impervious layers are present.

Because trace metals are relatively insoluble in alkaline media, chances of movement of the trace elements to groundwater are low when the waste is alkaline, particularly in regions of low rainfall. However, these relatively insoluble forms may become slowly soluble (and more readily available to vegetation) over the long term--due to physical, chemical and biological processes in the soil. Very little, if anything, is known about this aspect of waste material in soils.

<u>Nature of substrata</u>. Where the disposal area is not excavated to bedrock, the underlying strata is the natural soil. In cases where the impoundment is excavated to bedrock, the material forming the sides of the impoundment is usually surface soil and subsoil. In either case, unless the impoundment basin is completely lined (e.g., with clay or with a synthetic liner) lateral seepage through the soil can occur, particularly if the waste is deposited as a slurry.

Contamination of groundwater is related to the permeability of the impoundment material; in general, the permeability of such material increases in the order granite < shale < sandstone < soil < sand. In regions where the rainfall is low (i.e., less than 25 cm/year), seepage to groundwater will be unlikely in areas underlain by all but the most permeable material unless the water table is high (e.g., less than 5 meters below the surface). In areas of high water table, installation of a liner, particularly if the impoundment is underlain by sandstone, soil, or sand would be essential to preclude contamination of the groundwater even if the waste were deposited in a dry state.

An impermeable substrata, on the other hand, would essentially have no effect on the chances for food chain contamination by waste impoundment leaching; such contamination will be dependent on the nature of the surrounding soils and the amount of rainfall.

<u>Nature of soils</u>. At most waste-disposal sites, it can be assumed that the waste will be in physical contact with the surrounding soils, unless the impoundment is lined. One property of soils that is a major factor in transport of seepage is soil texture, i.e., the proportions of sand, silt, and clay. "Sand" refers to particle sizes between 2 mm and 0.05 mm diameter, "silt" between 0.05 mm and 0.002 mm diameter, and "clay" less than 0.002 mm diameter [USDA Classification (Brady 1974)]. The size range of "sand" is further classified as follows: very coarse sand, 2.0-1.0 mm; coarse sand, 1.0-0.5 mm; medium sand, 0.5-0.25 mm; fine sand, 0.25-0.10 mm; very fine sand, 0.10-0.05 mm. The textural names used in soil science to designate the proportions of the sand, silt, and clay size classes are given in Table 53.

	Range in percent	
Sand	Silt	Clay
85-100	0-15	0-10
70-90	0-30	0-15
43-80	0-50	0-20
23-52	28-50	7-27
0-50	50-88	0-27
0-20	8-10	0-12
45-80	0-28	20-35
20-45	15-53	27-40
0-20	40-73	27-40
45-65	0-20	35-55
0-20	40-60	40-60
0-45	0-40	40-100
	Sand 85-100 70-90 43-80 23-52 0-50 0-20 45-80 20-45 0-20 45-65 0-20 0-45	Range in percentSandSilt85-1000-1570-900-3043-800-5023-5228-500-5050-880-208-1045-800-2820-4515-530-2040-7345-650-200-2040-600-450-40

Table 53. Percentages of Sand, Silt, and Clay in the Textural Classes<sup>a</sup>

<sup>a</sup>From U.S. Dep. Agric. (1961).

These textural names can be modified by the following designations: coarse = greater than 25% coarse sand; fine = 50% or more fine sand, less than 25% coarse sand; very fine = 50% or more very fine sand.

Although a high clay content in a soil tends to decrease concentrations of cations in seepage to groundwater, such retention in the soil allows a greater concentration source for eventual uptake by vegetation. Even where the waste is deposited dry, leaching by rainwater can introduce potentially toxic elements to the soils from the waste if the impoundment area is not lined. If the soils are sandy, there is a tendency for rainfall to leach away the cations from the root zone, but this increases the chances for groundwater contamination.

There are regions of the country where high concentrations of certain elements such as selenium and molybdenum occur locally (see Appendix E). In these regions, addition to the soil of these elements from waste seepage over the long term may aggravate the potential for adverse effects to wildlife.

<u>Rainfall zone</u>. The amount of rainfall entering a waste-disposal site and environs markedly affects the potential for adverse effects from the waste at sites where the waste-disposal impoundments are not lined. If the average annual rainfall is low, seepage from the wastedisposal site will tend to remain in the upper layers of the soil, thus increasing the chances for uptake by vegetation; however, seepage to groundwater will be unlikely, depending on the depth at which the water table occurs. In zones of high rainfall, ionic constituents of waste will tend to be leached rapidly to groundwater, particularly where the substrata is sandy. High rainfall will also tend to move dissolved material laterally into the soil; in sandy soils, these dissolved materials would tend to be leached from plant root zones, whereas in soils with higher proportions of clay, a larger fraction of the dissolved constituents would be retained in the soil and may eventually be available for plant uptake. Other factors. The four factors discussed above are important in the transport of wastepond constituents into soils and groundwater. The ultimate appearance of adverse effects to vegetation and wildlife will be dependent also on the nature of the vegetation. For example, introduction of selenium and/or molybdenum into certain species of vegetation may cause no adverse effects to the vegetation; herbivores, however, may become toxified. Calcium is not normally considered a toxic element, but if present in the soil at high levels, particularly at alkaline pH, it can cause a phosphate deficiency in vegetation by tying up the phosphate as insoluble calcium phosphate. Sulfates and chlorides are plant nutrients, but if present in high concentrations in areas of low rainfall, they can cause salinization of the soil. Salinized soil is a poor medium for the growth of most vegetation.

The presence of a unique community (e.g., a bog or marsh) on or in the close environs of ash/sludge ponds dictates that careful evaluation of seepage flow be made. Such site-specific factors should be included in the assessment of seepage effects.

<u>Illustrative example</u>. To illustrate the use of Table 52, consider a hypothetical site with the following characteristics:

1. The site is located in a region where the annual average rainfall is less than 25 cm (10 inches).

2. Directly beneath the waste ponds is a sandy loam soil overlying a sandstone formation that includes a groundwater aquifer.

3. Ash and sludge are slurried to the ponds, which are not lined. The waste slurries are alkaline.

Reference to Table 52 indicates that the chances of groundwater contamination will be high, due primarily to the slurry nature of the waste, the sandy loam soil, and the sandstone substrata. Rainfall plays little part in this instance. The chances for food chain contamination will also be high, due primarily to the slurry nature of the waste which would tend to seep laterally into the sandy soil, as well as vertically downward. The low rainfall of the area would be insufficient to wash the contaminants below the root zone of most plants, particularly because areas of low rainfall generally also have high evaporation rates, which would tend to move solutes upward with soil water. It is very likely that contamination of the vegetation will not occur immediately; the alkaline nature of the waste indicates that most of the potentially toxic elements will be insoluble. Over the long term, however, these elements may slowly become available and accumulate in perennial vegetation.

If the waste is deposited dry, however, the potential for groundwater contamination is low despite the sandy nature of the substrata, because the rainfall is very likely insufficient to leach contaminants down to the aquifer. Contamination of the food chain will also tend to be low due to insufficient water (low rainfall) to move contaminants into the surrounding soil, and the relative insolubility of the contaminants (alkaline waste).

At this site, therefore, seepage contamination of groundwater or vegetation (unless some other site-specific factor indicates otherwise) is of minor concern if the waste is to be deposited in the dry state. Indeed, a recommendation can be made to the effect that the waste should be deposited dry. However, in that case, attention must be focused on protecting air quality by suitable dust-control measures until reclamation can be accomplished.

This example indicates the importance of proper reclamation of the disposal site after operation, i.e., an adequate depth of earth cover prior to revegetation to ensure that plant roots do not penetrate to the waste material if toxic effects are expected. An additional aspect of the earth cover is the attenuation effect on radon emanation and gamma radiation from the radioactive elements in the waste.

<u>Summary</u>. In summary, the adverse effects of seepage from waste-disposal sites will depend upon interrelated site-specific factors. At best, an evaluation can be made of the <u>potential</u> for adverse effects to occur, based on a number of site characteristics. Placement of durable liners, and/or siting disposal areas over relatively impervious substrata, will reduce the chances for adverse effects of seepage (see page 140); correct placement of monitor wells during operation will provide information necessary for long-term evaluation.

### Aquatic Impacts of Fly Ash and Scrubber Sludge Disposal

Procedures for solid waste disposal (i.e., fly ash and scrubber sludge) can cause impacts to aquatic systems from three sources: (1) consumptive water use, (2) direct discharges, and (3) seepage and overflow from waste-disposal basins. The major impacts from all of these sources except consumptive water use result primarily from the contamination of water resources by trace elements, either by direct discharge to or indirectly through groundwater. The effects of trace elements in aquatic systems have been extensively discussed (see p. 88) and will not be repeated here.

<u>Consumptive water use</u>. The volume of water required for solid waste disposal will depend on the specific waste-disposal procedure employed. If each waste product is handled separately and slurried or sluiced to onsite settling basins or disposal ponds and no water recycling is practiced, large volumes of water will be transported to these basins. Combined waste transport to onsite basins will also require large volumes of water. After settling of the solids, the supernatant water may be discharged to surface waters, evaporated, or recycled. Consumptive use is greatest if dewatering is by evaporation, least if the supernatant is discharged to surface waters, and intermediate if the water is recycled. Estimates of water used for solid waste disposal are presented in Table 54. For the four sizes of power plants considered in this report, the amounts of water used will be: 1,635-1,797 L/hour (100 MWe), 5,722-6,279 L/hour (350 MWe), 11,445-12,558 L/hour (700 MWe), and 34,335-37,674 L/hour (2100 MWe) without recycling. Recycling will reduce the amount of water consumed by an order of magnitude (Fig. 25).

Table 54. Water Requirements for Waste Disposal at a Coal-Fired Power Plant<sup>d</sup>

	Waste	Water (L/MW∙h)				
Туре	Weight (kg/MW∙h as dry waste)	No recycling	Recycling			
Bottom ash	5.1	20.4 <sup>b</sup>	2.2 <sup>d</sup>			
Fly ash	20.0	79.5 <sup>b</sup>	8.5 <sup>d</sup>			
Lime sludge	27.3	63.6 <sup>C</sup>	11.6 <sup>d</sup>			
Limestone sludge	33.9	79.5 <sup>C</sup>	14.6 <sup>d</sup>			

<sup>a</sup>Assumes 70% plant capacity.

Assumes slurry with 30% solids by weight.

CSludge with 30% solids by weight.

Assumes 70% solids by weight.

Impacts to aquatic systems from consumptive use of water result from the ramifications of water loss. Although the estimates of consumptive water loss for solid waste disposal are not large compared to the volumes of major lakes or the discharges of major rivers (i.e., Lake Michigan or Ohio River), these amounts may be significant on a site-specific basis in smaller watersheds. Water removed from an aquatic system reduces the size of that system. The consequences of reducing the size of an aquatic system are reduction in available habitat, a change in the location or extent of the productive littoral zone, and, conversely, an increase in the density of the organisms present. In an extreme case, where the initial volume of the water body is such that withdrawal for consumptive use will be a significant portion of the total water available, a situation similar to reservoir drawdown will occur. The biota of the water body will become concentrated in a smaller volume, and species interaction--i.e., territorial competition and predator-prey systems--will be greatly accentuated. However, this is an extreme. In most cases, there will be no demonstrable effect of the loss of water taken for waste disposal. This is not to imply that there will be no effect, but rather that the present state of knowledge on instream-flow needs is not sufficiently developed to evaluate the effects of minor reductions of water volume upon an entire physical, chemical, and biological complex that is an aquatic ecosystem.

<u>Direct discharges</u>. Effluent guidelines established by the USEPA regulate the amount of total suspended solids and oil and grease contained in bottom ash or fly ash transport water discharges and restrict pH to an acceptable range (see Appendix A). The composition of such effluents is usually controlled by individual state requirements. The composition of untreated waters which have been used for solid waste disposal can contain significant amounts of trace elements in solution.

During extreme storm precipitation events, it may be possible for the waste-disposal basins to overflow (most basins are designed to contain a 10-year precipitation runoff event), with subsequent discharge to the surface waters. The composition of this overflow would be similar to the normal dissolved and suspended contents of the disposal basin but would be more dilute due to the increased volume of water. Overflow events are rare, and proper construction practices-which include a retaining berm, dike, or dam around the basin--would probably preclude the possibility of severe surface-water contamination by basin overflow.





- Abernathy, A. R., et al. 1975. Mercury concentrations in fish in Lakes Keowee and Jocassee, South Carolina. Proj. No. B-07-191-00-573. Environmental Systems Engineering Department, Clemson University, Clemson, S. C. [As cited in Leland et al. (1977).]
- Adams, C. E., Jr., W. W. Eckenfelder, and B. L. Goodman. 1973. Proceedings of the 9th National Conference on Heavy Metals in the Aquatic Environment. Vanderbilt University, Nashville, Tenn.
- Adams, F., and R. W. Pearson. 1967. Crop response to lime in the Southern United States and Puerto Rico, pp. 161-206. <u>In</u> R. W. Pearson and F. Adams (eds.), Soil Acidity and Liming, No. 12 in the series, Agronomy. American Society of Agronomy, Madison, Wisconsin. [As cited in National Research Council (1973).]
- Agnes, G., H. A. O. Hill, J. M. Pratt, S. C. Ridsdale, F. S. Kennedy, and R. J. P. Williams. 1971. Methyl transfer from methyl vitamin Bl2. Biochem. Biophys. Acta. 252:207-212.
- Aitken, W. W. 1936. The relation of soil erosion to stream improvement and fish life. J. For. 34:1059-1061.
- Alarie, Y. C. 1975. Long term exposure to sulfur dioxide, sulfuric acid mist, fly ash, and their mixtures--results of studies in monkeys and guinea pigs. Arch. Environ. Health 30:254-262.
- Allaway, W. H. 1968. Agronomic controls over the environmental cycling of trace elements. Adv. Agron. 20:235-274.
- Anderson, W. L. 1976. Waterfowl Collisions with Power Lines at a Coal-fired Power Plant. Illinois Natural History Survey, Urbana. 18 pp. (mimeo).
- Anderson, W. L., S. S. Hurley, and J. W. Seets. 1975. Waterfowl Studies at Lake Sangchris. Final Report, September 1974-April 1975. Illinois Natural History Survey, Urbana. 37 pp. (mimeo).
- Andren, A. W., and R. C. Harriss. 1975. Observations on the association between mercury and organic matter dissolved in natural waters. Geochim. Cosmochim. Acta. 39:1253-1258.
- Andrews-Jones, D. A. 1968. The application of geochemical techniques to mineral exploration. Mineral Ind. Bul. 11:1-31.
- Anonymous, 1974. Air pollution effects on soybeans. TVA Today 5(3):2-3.
- Archibald, P. A., and E. Gentile. 1971. Distribution of phytoplankton in selected streams of the Slippery Rock Creek Watershed. Pa. Acad. Sci. 45:66-70.
- Arvik, J. H., and R. L. Zimdahl. 1974. Barriers to foliar uptake of lead. J. Environ. Qual. 3:369-373.
- Baker, D. E. 1974. Copper: soil, water, plant relationships. Fed. Proc. 33:1188-1193.
- Barrett, E., and G. Brodin. 1955. The acidity of Scandinavian precipitation. Tellus 7:251-257.
- Bartlett, L., F. W. Rabe, and W. H. Funk. 1974. Effects of copper, zinc, and cadmium on Selanastrum capricornutum. Water Res. 8:179-185.
- Baudouin, M. F., and P. Scoppa. 1974. Acute toxicity of various metals to freshwater zooplankton. Bull. Environ. Contam. Toxicol. 12:745-751.
- Beamish, R. J. 1972. Lethal pH for the white sucker *Catostomus commersoni* (Lacepede). Trans. Am. Fish. Soc. 101:355-358.
- Beamish, R. J. 1974a. Loss of fish populations from unexploited remote lakes in Ontario, Canada, as a consequence of atmospheric fallout of acid. Water Res. 8:85-95.
- Beamish, R. J. 1974b. Growth and survival of white suckers (*Catostomus commersoni*) in an acidified lake. J. Fish. Res. Board Can. 31:49-54.
- Beamish, R. J. 1976. Acidification of lakes in Canada by acid precipitation and the resulting effects on fishes. Water Air Soil Pollut. 6:501-514.

- Beamish, R. J., and H. H. Harvey. 1972. Acidification of the La Cloche Mountain Lakes, Ontario, and resulting fish mortalities. J. Fish. Res. Board Can. 29:1131-1143.
- Beamish, R. J., W. L. Lockhart, J. C. Van Loon, and H. H. Harvey. 1975. Long-term acidification of a lake and resulting effects on fishes. Ambio 4:98-102.
- Becker, C. D., and T. O. Thatcher (eds.). 1973. Toxicity of Power Plant Chemicals to Aquatic Life. WASH-1249. Prepared by Battelle Pacific Northwest Laboratories, Richland, Washington, for the U.S. Atomic Energy Commission. 1 v. (various pagings).
- Bell, H. L. 1971. Effect of low pH on the survival and emergence of aquatic insects. Water Res. 5:313-319.
- Benayoun, G., S. W. Fowler, and B. Oregioni. 1974. Flux of cadmium through euphausiids. Mar. Biol. 27:205-212.
- Benes, P., E. T. Gjessing, and E. Steinnes. 1976. Interactions between humus and trace elements in freshwater. Water Res. 10:711-716.
- Benoit, D. A. 1975. Chronic effects of copper on survival, growth, and reproduction of the bluegill (*Lepomis machrochirus*). Trans. Am. Fish. Soc. 104:353-358.
- Berry, W. L., and A. Wallace. 1974. Trace Elements in the Environment--Their Role and Potential Toxicity as Related to Fossil Fuels--A Preliminary Study. University of California, Laboratory of Nuclear Medicine and Radiation Biology. 66 pp.
- Bertine, K. K., and E. D. Goldberg. 1971. Fossil fuel combustion and the major sedimentary cycle. Science 173:233-235.
- Bick, H., and S. Kunze. 1971. A review of autecological and saprobiological data on freshwater ciliates. Int. Rev. Gesamten Hydrobiol. 56:337-384.
- Biddings, J., and J. N. Galloway. 1976. Literature Reviews on Acid Precipitation. I, The Effects of Acid Precipitation on Aquatic and Terrestrial Ecosystems. Center for Environmental Quality Management, Cornell University, Ithaca, N.Y.
- Biesinger, K. E., and G. M. Christensen. 1972. Effects of various metals on survival, growth, reproduction, and metabolism of *Daphnia magna*. J. Fish. Res. Board Can. 29:1691-1700.
- Bilinski, E., and R. E. E. Jonas. 1973. Effects of cadmium and copper on the oxidation of lactate by rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 30:1553-1558.
- Bingham, F. T., A. W. Marsh, R. Branson, R. Mahler, and G. Ferry. 1972. Reclamation of saltaffected high boron soils in western Kern County. Hilgardia 41(8):195-211. [As cited in Bingham (1973).]
- Bingham, F. T. 1973. Boron in cultivated soils and irrigation waters, pp. 130-138. <u>In</u> E. L. Kothny (ed.), Trace Elements in the Environment. Adv. Chem. Ser. 123. American Chemical Society, Washington, D.C.
- Bisogni, J., and A. Lawrence. 1973. Kinetics of microbially mediated methylation of mercury in aerobic and anaerobic aquatic environments. Tech. Rep. 63. Cornell University, Water Resources and Marine Science Center, Ithaca, N. Y. 180 pp.
- Bond, J. 1971. Noise--its effects on the physiology and behavior of animals. Agric. Sci. Rev. 9:1-10.

Bowen, H. J. M. 1966. Trace Elements in Biochemistry. Academic Press, Inc., London. 241 pp.

- Boyd, H. W. 1971. Manganese toxicity to peanuts in autoclaved soil. Plant Soil 34:133-144.
- Bradfield, R., L. P. Batjer, and J. Oskamp. 1934. Soils in relation to fruit growing in New York. Part IV, The significance of the oxidation-reduction potential for evaluating soils for orchard purposes. N. Y. (Cornell) Agric. Exp. Stn. Bull. 592. [As cited in Labanauskas (1966).]
- Bradshaw, A. D. 1976. Pollution and evolution, pp. 135-159. In T. A. Mansfield (ed.), Effects of Air Pollutants on Plants. Cambridge University Press, Cambridge.
- Brady, N. C. 1974. The Nature and Properties of Soil, 8th ed. Macmillan Publishing Co., Inc., New York. 639 pp.

- Brandt, C. J., and R. W. Rhoades. 1972. Effects of limestone dust accumulation on composition of a forest community. Environ. Pollut. 3:217-225.
- Brandt, C. J., and R. W. Rhoades. 1973. Effects of limestone dust accumulation on the lateral growth of forest trees. Environ. Pollut. 4:207-213.
- Brooks, J. L., and S. I. Dodson. 1965. Predation, body size and composition of plankton. Science 150:28-35.
- Brooks, R. R. 1977. Pollution through trace elements, pp. 429-476. <u>In</u> J. O'M. Bockris (ed.), Environmental Chemistry. Plenum Press, New York.
- Brooks, R. R., and D. Rumsey. 1974. Heavy metals in some New Zealand commercial sea fishes. N. Z. J. Mar. Freshwater Res. 8(1):155-166.
- Buhler, D. R., R. M. Stokes, and R. S. Caldwell. 1977. Tissue accumulation and enzymatic effects of hexavalent chromium in rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 4:9-18.
- Burdick, G. E. 1967. Use of bioassays in determining levels of toxic wastes harmful to aquatic organisms, pp. 7-12. In E. L. Cooper (ed.), A Symposium on Water Quality Criteria to Protect Aquatic Life. Am. Fish. Soc. Spec. Publ. No. 4.
- Burt, W. H., and R. P. Grossenheider. 1976. A Field Guide to the Mammals, 3rd ed. Houghton Mifflin Co., Boston. 289 pp.
- Cairns, J., Jr., J. S. Crossman, K. L. Dickson, and E. E. Herricks. 1971. The recovery of damaged streams. ASB (Assoc. Southeast. Biol.) Bull. 18(3):79-106.
- Cairns, J., Jr., and A. Scheier. 1957. The effects of temperature and hardness of water upon the toxicity of zinc to the common bluegill (*Lepomis macrochirus* Raf.). Not. Nat. Acad. Nat. Sci. Philadelphia 299:1-12.
- Carrier, R. F. 1977. Plant interactions, pp. 8-1 to 8-118. <u>In</u> H. M. Braunstein, E. D. Copenhaver, and H. A. Pfuderer (eds.), Environmental, Health, and Control Aspects of Coal Conversion: An Information Overview, Vol. 2. ORNL/EIS-95. Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Carter, J. C. H. 1971. Distribution and abundance of planktonic Crustacea in ponds near Georgian Bay (Ontario, Canada) in relation to hydrography and water chemistry. Arch. Hydrobiol. 68:204-231.
- Cartwright, K., R. A. Griffin, and R. H. Gilkeson. 1977. Migration of landfill leachate through glacial tills. Ground Water 15(4):294-305.
- Casey, T. J., J. R. Reilly, and R. J. Baltisberger. 1976. Chemical and Biological Investigations of Mice and Deer in the Vicinity of Two Coal-Fired Power Plants near Stanton, North Dakota. Res. Rep. No. 20. Institute for Ecological Studies, University of North Dakota, Grand Forks. 58 pp.
- Chapman, H. D. (ed.). 1966a. Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley. 793 pp.
- Chapman, H. D. 1966b. Zinc, pp. 484-499. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Chau, Y. K., P. T. S. Wong, B. A. Silverberg, P. L. Luxon, and G. A. Bengert. 1976. Methylation of selenium in the aquatic environment. Science 192:1130-1131.
- Clarke, R. McV. 1974. The effects of effluents from metal mines on aquatic ecosystems in Canada. Tech. Rep. No. 488. Canadian Fisheries and Marine Service, Freshwater Institute, Winnipeg. 150 pp.
- Coffin, C. C., F. R. Hayes, L. H. Jodrey, and S. G. Whiteway. 1949. Exchange of materials in a lake as studied by the addition of radioactive phosphorus. Can. J. Res. Sec. D 27:207-222.
- Cogbill, C. V. 1976. The history and character of acid precipitation in eastern North America. Water Air Soil Pollut. 6:407-413.
- Cogbill, C. V., and G. E. Likens. 1974. Acid precipitation in the northeastern United States. Water Resour. Res. 10(6):1133-1137.

- Colucci, A. V. 1976. Sulfur Oxides: Current Status of Knowledge. EPRI EA-316. Prepared by Greenfield, Attaway and Tyler, Inc., San Rafael, Calif., for the Electric Power Research Institute, Palo Alto, Calif. 1 v. (various pagings).
- Conroy, N., D. S. Jeffries, and J. R. Kramer. 1974. Acid shield lakes in the Sudbury, Ontario, region, pp. 45-61. In Proceedings of the 9th Symposium on Water Pollution Research.
- Cooper, H. B. 1975. The ultimate disposal of ash and other solids from electric power generation, pp. 183-195. <u>In</u> F. Gloyna, H. Woodson, and R. Drew (eds.), Water Management by the Electric Power Industry. Water Resources Symposium No. 8, Center for Research in Water Resources. University of Texas at Austin.
- Cooper, H. B., J. A. Lopez, and J. M. Demo. 1976. Chemical composition of acid precipitation in central Texas. Water Air Soil Pollut. 6(2-4):351-359.
- Corral, J., and C. Masso. 1975. Mercury concentrations in zooplankton from AROSA Estuary in spring and autumn. Bol. Inst. Esp. Oceanogr. 184. [As cited in Leland et al. (1977).]
- Cossa, D. 1976. Sorption of cadmium by a population of the diatom *Phyaeodactylum tricornatum* in culture. Mar. Biol. 34:163-167.
- Craig, S. 1967. Toxic ions in bivalves. J. Am. Osteopath. Assoc. 66:1000-1002.
- Cross, F. A., L. H. Hardy, N. Y. Jones, and R. T. Barber. 1973. Relation between total body weight and concentrations of manganese, iron, copper, zinc, and mercury in white muscle of bluefish (*Pomatomus saltatrix*) and a bathyldemersal fish *Antimore rostrata*. J. Fish Res. Board Can. 30:1287-1291.
- Cutler, J. M., and D. W. Rains. 1974. Characterization of cadmium uptake by plant tissue. Plant Physiol. 54:67-71.
- Darley, E. F. 1966. Studies on the effects of cement-kiln dust on vegetation. J. Air Pollut. Control Assoc. 16:145-150.
- Davidson, R. L., D. F. S. Natusch, J. R. Wallace, and C. A. Evans, Jr. 1974. Trace elements in fly ash: dependence of concentration on particle size. Environ. Sci. Technol. 8:1107-1113.
- Davis, C. R. 1972. Sulfur dioxide fumigation of soybeans: effect on yield. J. Air Pollut. Control Assoc. 22(12):964-966.
- Davis, P., and S. W. Ozburn. 1969. The pH tolerance of Daphnia pulex (Leydig, emed., Richard). Can. J. Zool. 47:1173-1175.
- De Groot, A. J. 1973. Occurrence and behavior of heavy metals in river deltas, with special reference to the Rhine and Ems river, pp. 308-325. <u>In</u> E. D. Goldberg (ed.), North Sea Science; Proceedings of the NATO North Sea Science Conference, Aviemore, Scotland. MIT Press, Cambridge, Mass.
- Deuel, L. E., and A. R. Swoboda. 1972. Arsenic toxicity to cotton and soybeans. J. Environ. Qual. 1:317-320.
- Dietz, F. 1973. The enrichment of heavy metals in submerged plants. Adv. Water Pollut. Res. 6:53-62.
- Dills, G., and D. T. Rogers, Jr. 1974. Macroinvertebrate community structure as an indicator of acid mine pollution. Environ. Pollut. 6:239-261.
- Dochinger, L. S., and T. A. Seliga. 1976. Workshop report on acid precipitation and the forest ecosystem. U.S. For. Serv. Gen. Tech. Rep. NE-26. Northeastern Forest Experiment Station, Upper Darby, Pa. 18 pp.
- Doudoroff, P., and M. Katz. 1953. Critical review of literature on the toxicity of industrial wastes and their components to fish. II, The metals on salts. Sewage Ind. Wastes 25:802-839.

Dovland, H., E. Joranger, and A. Semb. 1976. Deposition of air pollutants in Norway, pp. 14-35. <u>In</u> F. W. Braekke (ed.), Impact of Acid Precipitation on Forest and Freshwater Ecosystems in Norway. SNSF-project FR 6/76.

Dowden, B. F., and H. J. Bennett. 1965. Toxicity of selected chemicals to certain animals. J. Water Pollut. Control Fed. 37:1308-1316.

- Drummond, R. A., W. A. Spoor, and G. F. Olson. 1973. Some short-term indicators of sublethal effects of copper on brook trout, *Salvelinus fontinalis*. J. Fish. Res. Board Can. 30:698-701.
- Dvorak, A. J., et al. 1977. The Environmental Effects of Using Coal for Generating Electricity. NUREG-0252. Prepared by Argonne National Laboratory, Argonne, Ill., for the U.S. Nuclear Regulatory Commission. 221 pp.
- Dvorak, A. J., and E. D. Pentecost, et al. 1977. Assessment of the Health and Environmental Effects of Power Generation in the Midwest. Vol. II, Ecological Effects. Argonne National Laboratory, Argonne, Ill. (Draft report.)
- Eisler, R. 1967. Acute toxicity of zinc to the killifish, Fundulus heteroclitus. Chesapeake Sci. 8:262-264.
- Ellis, M. M. 1936. Erosion silt as a factor in aquatic environments. Ecology 17:29-42.
- Elwood, J. W., S. G. Hildebrand, and J. J. Beauchamp. 1976. Contribution of gut contents to the concentration and body burden of elements in *Tipula* spp. from a spring-fed stream. J. Fish Res. Board Can. 33(9):1930-1938.
- Emmelin, L. 1976. Effects of acid rain. Ambio 5(2):83-84.
- Enk, M. D., and B. J. Mathis. 1977. Distribution of cadmium and lead in a stream ecosystem. Hydrobiologia 52:153-158.
- Eriksson, C., and D. C. Mortimer. 1975. Mercury uptake in rooted higher aquatic plants. Verh. int. Ver. Limnol. 19:2087-2093.
- Ermolenko, N. F. 1966. Trace Elements and Colloids in Soils, 2nd ed. Nauka i Tekhnika Minsk. Translated from the Russian, 1972. Published for the U.S. Department of Agriculture and the National Science Foundation, Washington, D.C., by Israel Program for Scientific Translations, Jerusalem. 259 pp.
- European Inland Fisheries Advisory Commission. 1965. Water quality criteria for European freshwater fish, report on finely divided solids and inland fisheries. Int. J. Air Water Pollut. 9:151-168.
- European Inland Fisheries Advisory Committee. 1969. Water quality criteria for European freshwater fish, report on extreme pH values and inland fisheries. Water Res. 3:593-611.
- Fairfay, J. W. A., and N. W. Lepp. 1975. Effect of simulated "acid rain" on action loss from leaves. Nature 255:324-325.
- Farenbaugh, R. W. 1976. Effects of acid rain on Phaseolus vulgaris L. Am. J. Bot. 63:283-288.
- Fennelly, P. F. 1975. Primary and secondary particulates as pollutants: a literature review. J. Air Pollut. Control Assoc. 25:697-704.
- Fisher, D. W., A. W. Gambell, G. E. Likens, and F. H. Bormann. 1968. Atmospheric contributions to water quality of streams in the Hubbard Brook Experimental Forest, New Hampshire. Water Resour. Res. 4:1115-1126.
- Frascino, P. J., and D. L. Vail. 1976. Utility ash disposal: state of the art, pp. 345-368. <u>In</u> Ash Utilization. Proceedings of the Fourth International Ash Utilization Symposium, St. Louis, Mo., March 24-25. MERC/SP-76/4. U.S. Energy Research and Development Administration, Morgantown Energy Research Center, Morgantown, W. Va.
- Frazier, J. M. 1975. The dynamics of metals in the American oyster, *Crassostrea virginica*. 1, Seasonal effects. Chesapeake Sci. 16:162-171.
- Friberg, L., M. Piscator, and G. Nordberg. 1971. Cadmium in the Environment. CRC Press, Cleveland, Ohio. 166 pp.
- Fuller, W. H., N. E. Korte, E. E. Neible, and B. A. Alesh. 1975. Contribution of the soil to the migration of certain common and trace elements. Soil Sci. 122(1):223-235.
- Galloway, J. N., and E. B. Cowling. 1977. The effects of precipitation on aquatic and terrestrial ecosystems--a proposed precipitation chemistry network. Presented at 70th Annual Meeting of the Air Pollution Control Association, Toronto, June 20-24, 1977. 23 pp.

Gibbs, R. J. 1973. Mechanisms of trace metal transport in rivers. Science 189:71-73.

- Giblin, F. J., and E. J. Massaro. 1973. Pharmaco-dynamics of methylmercury in the rainbow trout (Salmo gairdneri); tissue uptake, distribution, and excretion. Toxicol. Appl. Pharmacol. 24:81-91.
- Giddings, J., and J. N. Galloway. 1976. The effects of acid precipitation on aquatic and terrestrial ecosystems, pp. 1-40. <u>In</u> Literature Reviews on Acid Precipitation. Sponsored by the Center for Environmental Quality Management and the Water Resources and Marine Sciences Center, Cornell University, Ithaca, N. Y.

Giese, A. C. 1968. Cell Physiology. W. B. Saunders Company, Philadelphia. 671 pp.

- Giesy, J. P., Jr., and J. G. Wiener. 1977. Frequency distribution of trace metal concentrations in five freshwater fishes. Trans. Am. Fish. Soc. 106(4):393-403.
- Giles, F. E., S. G. Middleton, and J. G. Grau. 1973. Evidence for the accumulation of atmospheric lead by insects in areas of high traffic density. Environ. Entomol. 2(2):299-300.
- Gish, C. D., and R. E. Christensen. 1973. Cadmium, nickel, lead and zinc in earthworms from roadside soil. Environ. Sci. Technol. 7(11):1060-1062.
- Goldschmidt, J. M. 1958. Geochemistry. Oxford University Press, Oxford, England. 730 pp.
- Gorham, E. 1976. Acid precipitation and its influence upon aquatic ecosystems--an overview. Water Air Soil Pollut. 6:457-481.
- Gorham, E., and A. G. Gordon. 1963. Some effects of smelter pollution upon aquatic vegetation near Sudbury, Ontario. Can. J. Bot. 41:371-378.
- Gosner, K. L., and I. H. Black. 1957. The effects of acidity on the development and hatching of New Jersey frogs. Ecology 38:256-262.
- Grahn, O. H. 1976. Macrophyte succession in Swedish lakes caused by deposition of airborne acid substances pp. 519-530. In Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, Ohio State University, May 12-15, 1975. U.S. For. Serv. Gen. Tech. Rep. NE-23.
- Grahn, O., H. Hultberg, and L. Landner. 1974. Oligotrophication--a self-accelerating process in lakes subjected to excessive supply of acid substances. Ambio 3:93-94.
- Granat, L., and H. Rodhe. 1973. A study of fall-out by precipitation around an oil-fired power plant. Atmos. Environ. 7:781-792.
- Greeley, R. S., R. P. Ouellette, J. T. Stone, and S. Wilcox. 1975. Sulfates and the environment, a review. MTR-6895; PB-248 122. The Mitre Corp., McLean, Va. 131 pp.
- Grennard, A., and F. Ross. 1974. Progress report on sulfur dioxide. Combustion 45:4-9.
- Gryzhankova, L. N., T. M. Udel'nova, and E. A. Boichenko. 1975. Iron, manganese and titanium compounds in marine plants. Izv. Akad. Nauk SSSR Ser. Biol. 1:76-82.
- Guthrie, R. K., and D. S. Cherry. 1976. Pollutant removal from coal-ash basin effluent. Water Res. Bull. 12:889-902.
- Haghiri, F. 1974. Plant uptake of cadmium as influenced by cation exchange capacity, organic matter, zinc, and soil temperature. J. Environ. Qual. 3:180-183.
- Harman, W. N. 1974. Snails (Mollusca: Gastropoda), pp. 275-312. In C. W. Hart, Jr., and S. L. H. Fuller (eds.), Pollution Ecology of Freshwater Invertebrates. Academic Press, New York.
- Harney, P. J. 1974. Loss of Zinc-65 and Manganese-54 from the Freshwater Mollusc Anodonta. Ph.D. Dissertation. Oregon State University, Corvallis. 107 pp.
- Harrison, F. L., et al. 1976. Role of Solubles and Particulates in Radionuclide Accumulation in Oyster *Crassostreas gigas* in the Discharge Canal of a Nuclear Power Plant. Spec. Publ. No. 1. Radioecology and Energy Resources, Ecological Society of America. 9 pp.
- Hartung, R. 1974. Heavy metals in the lower Mississippi. <u>In</u> Proc. Int. Conf. Transport Persistent Chemicals Aquatic Ecosystems, Ottawa, Canada, I-93. [As cited in Leland et al. (1976).]

Hazel, C. R., and S. J. Meith. 1970. Bioassay of king salmon eggs and sac fry in copper solutions. Calif. Fish and Game 56:121-124.

Heicklen, J. 1976. Atmospheric Chemistry. Academic Press, New York. 406 pp.

- Heisey, R. 1975. Production and heavy metal concentration of vascular aquatic macrophytes in three eastern Connecticut Rivers. M.S. Thesis. University of Connecticut, Storrs. 97 pp.
- Heitschmidt, R. K., J. L. Dodd, and W. K. Lauenroth. 1976. First-year effects of controlled sulfur dioxide fumigation on a mixed grass prairie ecosystem. II, Plant phenology and visual damage. J. Range Manage. (Abstract.)
- Helz, G. R., R. J. Huggett, and J. M. Hill. 1975. Behavior of Mn, Fe, Cu, Zn, Cd, and Pb discharged from a wastewater treatment plant into an estuarine environment. Water Res. 9:631-636.
- Herricks, E. E., and J. Cairns, Jr. 1975. Rehabilitation of streams receiving acid mine drainage. Bull. 66. Virginia Water Resources Center, Blacksburg. 284 pp.
- Hiatt, V., and J. E. Huff. 1975. The environmental impact of cadmium: an overview. Int. J. Environ. Stud. 7:277-285.
- Hill, A. C. 1969. Air quality standards for fluoride vegetation effects. J. Air Pollut. Control Assoc. 21:410-413.
- Hill, A. C., S. Hill, C. Lamb, and T. W. Barret. 1974. Sensitivity of native desert vegetation to  $SO_2$  and to  $SO_2$  and  $NO_2$  combined. J. Air Pollut. Control Assoc. 24:153-157.
- Hitchcock, A. E., and P. W. Zimmerman. 1957. Toxic effects of vapors of mercury and of compounds of mercury on plants. Ann. N. Y. Acad. Sci. 65:474. [As cited in Stahl (1969).]
- Hodgson, J. F. 1970. Chemistry of trace elements in soils with reference to trace element concentration in plants, pp. 45-58. <u>In</u> D. D. Hemphill (ed.), Proceedings of the University of Missouri's 3rd Annual (1969) Conference on Trace Substances in Environmental Health, Vol. III. University of Missouri Press, Columbia.
- Hodson, P. V. 1976. Temperature effects on lactate-glycogen metabolism in zinc-intoxicated rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 33:1393-1397.
- Holcombe, G. W., D. A. Benoit, E. N. Leonard, and J. M. McKim. 1976. Long-term effects of lead exposure on three generations of brook trout (*Salvelinus fontinalis*). J. Fish. Res. Board Can. 33:1731-1741.
- Holland, W. F., K. A. Wilde, J. L. Parr, P. S. Lowell, and R. F. Pohler. 1975. The Environmental Effects of Trace Elements in the Pond Disposal of Ash and Flue Gas Desulfurization Sludge. Research Project 202, Final Report. Prepared by Radian Corporation, Austin, Texas, for Electric Power Research Institute, Palo Alto, California. 49 pp.
- Hornbeck, J. W., G. E. Likens, and J. S. Eaton. 1977. Seasonal patterns in acidity of precipitation and their implications for forest stream ecosystems. Water Air Soil Pollut. 7:355-365.
- Horton, J. H.. R. S. Dorsett, and R. E. Cooper. 1977. Trace Elements in the Terrestrial Environment of a Coal-Fired Powerhouse. DP-1475. Savannah River Laboratory, Aiken, S. C.
- Hoss, D. E. 1974. Accumulation of zinc-65 by flounder of the genus *Paralichthys*. Trans. Am. Fish. Soc. 93:364-368.
- Hrbacek, J., M. Dvorakova, V. Korinek, and L. Prochazkova. 1961. Demonstration of the effect of the fish stock on the species composition of zooplankton and the intensity of metabolism of the whole plankton association. Int. Ver. Theor. Angew. Limnol. Verh. 14:192-195.
- Huckabee, J. W. 1973. Mosses: sensitive indicators of airborne mercury pollution. Atmos. Environ. 7:749-754.
- Huey, C., et al. 1974. The role of tin in the bacterial methylation of mercury. Proc. Int. Conf. Transport Persistent Chemicals Aquatic Ecosystems, Ottawa, Canada, II-73. [As cited in Leland et al. (1976).]
- Hughes, G. M., and K. Cartwright. 1972. Scientific and administrative criteria for shallow waste disposal. Civ. Eng. 42(3):70-73. [As cited in Williams (1975).]

- Hunter, W. R. 1964. Physiological aspects of ecology in non-marine molluscs, pp. 83-116. In K. M. Wilbur and C. M. Yonge (eds.), Physiology of Mollusca. Academic Press, New York.
- Hutchinson, G. E. 1957. A Treatise on Limnology. Vol. 1, Geography, Physics, and Chemistry. John Wiley and Sons, New York. 1015 pp.
- Hutchinson, T. C., and H. Czyrska. 1975. Heavy metal toxicity and synergism to floating aquatic weeds. Verh. int. Ver. Limnol. 19:2102-2111.
- Hutchinson, T. C., and L. M. Whitby. 1974. Heavy-metal pollution in the Sudbury mining and smelting region of Canada. I, Soil and vegetation contamination by nickel, copper, and other metals. Environ. Conserv. 1:123-132.
- Institute for Environmental Studies, Environmental Monitoring and Data Acquisition Group. 1976a. Documentation of Environmental Change Related to the Columbia Electric Generating Station, Seventh Semi-Annual Report, Spring-Summer 1975. IES Rep. 62. University of Wisconsin--Madison. 135 pp.
- Institute for Environmental Studies, Environmental Monitoring and Data Acquisition Group. 1976b. Documentation of Environmental Change Related to the Columbia Electric Generating Station, Eighth Semi-Annual Report. IES Rep. 66. University of Wisconsin--Madison. 230 pp.
- Iseri, K. T., and W. B. Langbein. 1974. Large rivers of the United States. U.S. Geol. Circ. 686. 10 pp.
- Jackim, E., M. Hamlin, and S. Sonis. 1970. Effects of metal poisoning on five liver enzymes in killifish (*Fundulus heteroclitus*). J. Fish. Res. Board Can. 27:283-390.
- Jackson, D. R., and A. P. Watson. 1977. Disruption of nutrient pools and transport of heavy metals in a forested watershed near a lead smelter. J. Environ. Qual. 6:331-338.
- Jackson, S., and U. M. Brown. 1969. Effect of Toxic Wastes on Treatment Processes and Water Courses. Conference Paper 2C. Institute of Water Pollution Control, Douglas, Isle of Man, September 1969. 14 pp.
- Jacobs, L. 1973. Methylation of Mercury in Lake and River Sediments During Field and Laboratory Investigations. Ph.D. Dissertation. University of Wisconsin, Madison. 98 pp.
- Jensen, A. L. 1971. The effect of increased mortality on the young in a population of brook trout, a theoretical analysis. Trans. Am. Fish. Soc. 100(3):456-459. [As cited by Schofield (1976).]
- John, M. K. 1973. Cadmium uptake by eight food crops as influenced by various soil levels of cadmium. Environ. Pollut. 4:7-15.
- John, M. K., and C. J. Van Laerhoven. 1976. Differential effects of cadmium on lettuce varieties. Environ. Pollut. 10:163-173.
- Johnson, C. M. 1966. Molybdenum, pp. 286-301. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Johnson, D. W. 1975. Spawning behavior and strain tolerance of brook trout (*Salvelinus fontinalis* Mitchill) in acidified water. M.S. Thesis. Cornell University, Ithaca, N. Y. 100 pp.
- Johnson, M. G., M. F. P. Michalski, and A. E. Christie. 1970. Effects of acid mine wastes on phytoplankton communities in two northern Ontario lakes. J. Fish. Res. Board Can. 27:425-444.
- Jones, H. C. 1975. Personal communication (Tennessee Valley Authority, Muscle Shoals, Alabama).
- Jones, H. C., et al. 1973. Investigation of Alleged Air Pollution Effects on Yield of Soybeans in the Vicinity of the Shawnee Steam Plant. Tenn. Val. Auth. Publ. E-EB-73-3.

Jones, J. R. E. 1938. The relative toxicity of salts of lead, zinc and copper to the stickleback (*Gasterosteus acceleatus* L.) and the effect of calcium on the toxicity of lead and zinc salts. J. Exp. Biol. 15:394-407.

- Jones, J. R. E. 1964. Fish and river pollution. Butterworths, London. 203 pp.
- Kania, H. J., and J. O'Hara. 1974. Behavioral alterations in a simple predator-prey system due to sublethal exposure to mercury. Trans Am. Fish. Soc. 103:134-136.

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- Kerr, S. R. 1971. Prediction of fish growth efficiency in nature. J. Fish. Res. Board Can. 28:809-814.
- Kinkade, M. L., and H. E. Erdman. 1975. The influence of hardness components (Ca<sup>2+</sup> and Mg<sup>2+</sup>) in water on the uptake and concentration of cadmium in a simulated freshwater ecosystem. Environ. Res. 10:308-314.

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\$

- Kleerekoper, H., J. B. Waxman, and J. Matis. 1973. Interaction of temperature and copper ions as orienting stimuli in the locomotor behavior of the goldfish (*Carassius auratus*). J. Fish. Res. Board Can. 30:725-728.
- Klein, D. H., and P. Russell. 1973. Heavy metals: fallout around a power plant. Environ. Sci. Technol. 7:357-358.
- Klein, D. H., A. W. Andren, and N. E. Bolton. 1975a. Trace element discharges from coal combustion for power production. Water Air Soil Pollut. 5:71-77.
- Klein, D. H., et al. 1975b. Pathways of thirty-seven trace elements through a coal-fired power plant. Environ. Sci. Technol. 9(10):973-979.
- Kopp, J. F., and R. C. Kroner. 1970. Trace Metals in the Waters of the United States. Federal Water Quality Administration, Cincinnati, Ohio.
- Kozlowski, T. T., and J. B. Mudd. 1975. Introduction, pp. 1-8. <u>In</u> J. B. Mudd and T. T. Kozlowski (eds.), Responses of Plants to Air Pollution. Academic Press, New York.
- Kryter, K. D. 1970. The Effects of Noise on Man. Academic Press, New York. 633 pp.
- Kubota, J., and W. H. Allaway. 1972. Geographic distribution of trace element problems, pp. 525-554. In J. J. Mortvedt, P. M. Giordano, and W. L. Lindsay (eds.), Micronutrients in Agriculture. Soil Science Society of America, Inc., Madison, Wis.
- Kuznetsov, S. I. 1970. The microflora of lakes and its geochemical activity. University of Texas Press, Austin. 503 pp.
- Kwiatkowski, R. E., and J. C. Roff. 1976. Effects of acidity on the phytoplankton and primary productivity of selected northern Ontario lakes. Can. J. Bot. 54(22):2546-2561.
- Laarman, P. W., W. A. Willeford, J. R. Olson. 1976. Retention of mercury in the muscle of yellow perch (*Perca flavescens*) and rock bass (*Ambloplites rupestris*). Trans. Am. Fish. Soc. 105:296-300.
- Labanauskas, C. K. 1966. Manganese, pp. 264-285. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Lagerwerff, J. V. 1972. Lead, mercury, and cadmium as environmental contaminants, pp. 593-637. <u>In</u> J. J. Mortvedt, P. M. Giordano, and W. L. Lindsay (eds.), Micronutrients in Agriculture. Soil Science Society of America, Inc., Madison, Wis.
- Lakin, H. W. 1973. Selenium in our environment, pp. 96-111. <u>In</u> E. L. Kothny (ed.), Trace Elements in the Environment. Adv. Chem. Ser. 123. American Chemical Society, Washington, D. C.
- Lee, R. E., Jr., H. L. Crist, A. E. Riley, and K. E. MacLeod. 1975. Concentration and size of trace metal emissions from a power plant, a steel plant, and a cotton gin. Environ. Sci. Technol. 9:643-647.
- Leeper, G. W. 1947. The forms and reactions of manganese in the soil. Soil Sci. 63:79. [As cited in Boyd (1971).]
- Leeper, G. W. 1952. Factors affecting availability of inorganic nutrients in soils, with special reference to micronutrient metals. Annu. Rev. Plant Physiol. 25:736-747. [As cited in Reuther and Labanauskas (1966).]
- Lehninger, A. L. 1973. Short Course in Biochemistry. Worth Publishers, Inc., New York. 452 pp.
- Leivestad, H., G. Hendrey, I. P. Muniz, and E. Snekvik. 1976. Effects of acid precipitation on freshwater organisms, pp. 87-111. <u>In</u> F. H. Braekke (ed.), Impact of acid precipitation on forest and freshwater ecosystems in Norway. Research Report 6. Agricultural Research Council of Norway, Norwegian Council for Scientific and Industrial Research.

- Leland, H. V., D. J. Wilkes, and E. D. Copenhaver. 1976. Heavy metals and related trace elements. J. Water Pollut. Control Fed. 48(6):1459-1486.
- Leland, H. V., S. N. Luoma, and D. J. Wilkes. 1977. Heavy metals and related trace elements. J. Water Pollut. Control Fed. 49(6):1340-1369.
- Lerman, S. L., and E. F. Darley. 1975. Particulates, pp. 141-158. <u>In</u> J. B. Mudd and T. T. Kozlowski (eds.), Responses of Plants to Air Pollution. Academic Press, New York.
- Lett, P. F., G. J. Farmer, and F. W. H. Beamish. 1976. Effect of copper on some aspects of the bioenergetics of rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 33:1335-1342.
- Lewis, R. A., N. R. Glass, and A. S. Lefohn. 1976. The Bioenvironmental Impact of a Coal-fired Power Plant, Second Interim Report, Colstrip, Montana, June 1975. EPA-600/3-76-013; PB-252 177. U.S. Environmental Protection Agency, Office of Research and Development, Corvallis Environmental Research Laboratory, Corvallis, Oregon. 314 pp.
- Lewis, S. D., and W. M. Lewis. 1971. The effect of zinc and copper on the osmolarity of blood serum of the channel catfish, *Ictalurus punctatus* Rafinesque, and the golden shiner, *Notemigonus crysoleucas* Mitchill. Trans. Am. Fish. Soc. 100:639-643.
- Li, T., and H. E. Landsberg. 1975. Rainwater pH close to a major power plant. Atmos. Environ. 9:81-88.
- Libicki, J. 1977. Impact of gob and power-plant ash disposal on ground water quality and its control, pp. 185-204. In Proceedings of Third Symposium on Coal Preparation, Louisville, Kentucky, October 18-20, 1977. National Coal Association, Washington, D.C.
- Liebig, G. F., Jr. 1966. Arsenic, pp. 13-23. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Likens, G. E., and F. H. Bormann. 1974. Acid rain: a serious regional environmental problem. Science 184:1176-1179.
- Lind, O., and R. S. Campbell. 1970. Community metabolism in acid and alkaline strip-mine lakes. Trans. Am. Fish. Soc. 99:577-582.
- Lindberg. S. E., et al. 1975. Geochemistry of mercury in the estuarine environment. Estuarine Res. 1:64. [As cited in Leland et al. (1976).]
- Linton, R. W., A. Loh, D. F. S. Natusch, C. A. Evans, Jr., and P. Williams. 1976. Surface predominance of trace elements in airborne particles. Science 191:852-854.
- Linzon, S. N. 1973. Some effects of particulate matter on vegetation in Ontario, pp. All8-Al20. In Proceedings of the Third International Clean Air Congress.
- Lisk, D. J. 1972. Trace metals in soils, plants, and animals. Adv. Agron. 24:267-325.
- Little, P., and M. H. Martin. 1972. A survey of zinc, lead and cadmium in soil and natural vegetation around a smelting complex. Environ. Pollut. 3:241-254.

Lloyd, R. 1960. The toxicity of zinc sulphate to rainbow trout. Ann. Appl. Biol. 48:84-94.

- Lloyd, R., and D. W. M. Herbert. 1962. The effect of the environment on the toxicity of poisons to fish. J. Inst. Public Health Eng. 61(3):132-145.
- Lockhart, W. L., J. F. Uthe, A. R. Kenney, and P. M. Mehrle. 1972. Methylmercury in northern pike (*Esox lucius*): distribution, elimination, and some biochemical characteristics of contaminated fish. J. Fish. Res. Board Can. 29:1519-1523.
- Loman, A. A., R. A. Blauel, and D. Hocking. 1972. Sulfur Dioxide and Forest Vegetation. Northern Forest Research Centre Inf. Rep. NOR-X-49. Canadian Forestry Service, Edmonton, Alberta, Canada.
- Lowe, R. L. 1974. Environmental requirements and pollution tolerances of freshwater diatoms. EPA-670/4-74-005. U. S. Environmental Protection Agency, Cincinnati, Ohio. 334 pp.
- Luoma, S. N., and E. A. Jenne. 1975a. Factors affecting the availability of sediment-bound Cd to the estuarine deposit-feeding clam, *Macoma balthica*. In Fourth National Symposium on Radioecology, Corvallis, Oregon. [As cited in Leland et al. (1976).]

- Luoma, S. N., and E. A. Jenne. 1975b. The availability of sediment-bound cobalt, silver, and zinc to a deposit-feeding clam. <u>In Biological Implications of Metals in the Environment.</u> 15th Hanford Life Sciences Symposium, Richland, Washington. 38 pp. [As cited in Leland et al. (1976).]
- Lyon, W. S. 1977. Trace Element Measurements at the Coal-fired Steam Plant. CRC Press, Inc., Cleveland, Ohio. 136 pp.
- MacFarlane, D. R., et al. 1975. Power Facility Siting in the State of Illinois. Part II, Environmental Impacts of Large Energy Conversion Facilities. Illinois Institute for Environmental Quality, Chicago.
- MacLean, A. J. 1976. Cadmium in different plant species and its availability in soils as influenced by organic matter and additions of lime, P, Cd and Zn. Can. J. Soil Sci. 56:129-138.
- Malone, C., D. E. Koeppe, and R. J. Miller. 1974. Localization of lead accumulated by corn plants. Plant Physiol. 53:388-394.
- Massachusetts Instute of Technology. 1970. Man's Impact on the Global Environment--Assessment and Recommendations for Action. Report, Study of Critical Environmental Problems (SCEP). MIT Press, Cambridge, Mass. [As cited in Waldichuk (1974).]
- Mathis, B. J., and T. F. Cummings. 1973. Selected metals in sediments, water, and biota in the Illinois River. J. Water Pollut. Control Fed. 45:1573-1583.
- Mathis, B. J., and N. R. Kevern. 1975. Distribution of mercury, cadmium, lead, and thallium in a eutrophic lake. Hydrobiol. 46(2-3):207-222.
- Mayes, R. M., and A. McIntosh. 1975. The use of aquatic macrophytes as indicators of trace metal contamination in freshwater lakes. <u>In</u> Proceedings of the 9th Annual Conference on Trace Substances in Environmental Health, University of Missouri, Columbia. [As cited in Leland et al. (1976).]
- McBride, J. P., R. E. Moore, J. P. Witherspoon, and R. E. Blanco. 1977. Radiological Impact of Airborne Effluents of Coal-fired and Nuclear Power Plants. ORNL-5315. Oak Ridge National Laboratory, Oak Ridge, Tenn. 43 pp.
- McCune, D. C. 1969. On the establishment of air quality criteria with reference to the effects of atmospheric fluorine on vegetation. Air Qual. Monogr. 69-3. American Petroleum Institute, New York. 33 pp.
- McEntire, F. E., and R. D. Neufeld. 1975. Microbial methylation of mercury: a survey. Water Pollut. Control 74:465-470.
- McKee, J. E., and H. W. Wolf (eds.). 1963. Water Quality Criteria, 2nd ed. Publ. 3A. The Resources Agency of California, State Water Quality Control Board, Sacramento. 548 pp. (Reprint, December 1971.)
- McLerran, C. J., and C. W. Holmes. 1974. Deposition of zinc and cadmium by marine bacteria in estuarine sediments. Limnol. Oceanogr. 19(6):998-1001.
- Merlini, M., and G. Pozzi. 1977. Lead and freshwater fishes. Part 1, Lead accumulation and water pH. Environ. Pollut. 12:167-172.
- Mierle, G., and P. Stokes. 1976. Heavy metal tolerance and metal accumulation by planktonic algae. <u>In</u> Proceedings of the 10th Annual Conference on Trace Substances in Environmental Health, University of Missouri, Columbia. [As cited in Leland et al. (1977).]
- Miller, J. E., J. J. Hassett, and D. E. Koeppe. 1975a. The effect of soil properties and extractable lead levels on lead uptake by soybeans. Commun. Soil Sci. Plant Anal. 6:339-347.
- Miller, J. E., J. J. Hassett, and D. E. Koeppe. 1975b. The effect of soil lead sorption capacity on the uptake of lead by corn. Commun. Soil Sci. Plant Anal. 6:349-358.
- Miller, R. J., and D. E. Koeppe. 1971. Accumulation and physiological effects of lead in corn, pp. 186-193. <u>In</u> D. D. Hemphill (ed.), Proceedings of the University of Missouri Fourth Annual Conference (1970) on Trace Substances in Environmental Health, Vol. IV. University of Missouri Press, Columbia.

- Moss, B. 1973a. The influence of environmental factors on the distribution of freshwater algae, an experimental study. II, The role of pH and the carbon dioxide-bicarbonate system. J. Ecol. 61:157-177.
- Moss, B. 1973b. The influence of environmental factors on the distribution of freshwater algae, an experimental study. IV, Growth of test species in natural lake waters, and conclusion. J. Ecol. 61:193-211.
- Mount, D. I. 1973. Chronic effect of low pH on fathead minnow survival, growth and reproduction. Water Res. 7:987-993.
- Mukammal, E. I. 1976. Review of present knowledge of plant injury by air pollution. W. M. O. Tech. Note No. 147. World Meteorological Organization, Geneva, Switzerland. 27 pp.
- Mullins, T. 1977. The chemistry of water pollution, pp. 331-400. <u>In</u> J. O'M. Bockris (ed.), Environmental Chemistry. Plenum Press, New York.
- Munshower, F. F., and E. J. De Puit. 1976. The Effects of Stack Emissions on the Range Resource in the Vicinity of Colstrip, Montana. Progress Report 1975. Montana Agricultural Experimental Station, Bozeman.
- National Academy of Sciences-National Academy of Engineering, Committee on Water Quality Criteria. 1974. Water Quality Criteria 1972. EPA-R3-73-033. U.S. Environmental Protection Agency. 594 pp.
- National Committee on Radiation Protection and Measurements. 1975. Natural Background Radiation in the United States. NCRP Rep. No. 45. Washington, D. C. 163 pp.
- National Research Council, Committee on Biological Effects of Atmospheric Pollutants. 1972. Lead: Airborne Lead in Perspective. National Academy of Sciences, Washington, D. C. 330 pp.
- National Research Council, Committee on Biologic Effects of Atmospheric Pollutants. 1973. Manganese. National Academy of Sciences, Washington, D. C. 191 pp.
- National Research Council, Committee on Biologic Effects of Atmospheric Pollutants. 1974. Vanadium. National Academy of Sciences, Washington, D.C. 117 pp.
- Natusch, D. F. S., J. R. Wallace, and C. A. Evans, Jr. 1974. Toxic trace elements: preferential concentration in respirable particles. Science 183:202-204.
- Nehring, R. B. 1976. Aquatic insects as biological monitors of heavy metal pollution. Bull. Environ. Contam. Toxicol. 15:147-154.
- Neiburger, M., J. G. Edinger, and W. D. Bonner. 1973. Understanding Our Atmospheric Environment. W. H. Freeman and Co., San Francisco. 293 pp.
- Nielsen, E. S., and H. B. Laursen. 1976. Effect of CuSO<sub>4</sub> on the photosynthetic rate of phytoplankton in four Danish lakes. Oikos 27:239-242.
- Niimi, A. J., and Q. N. LaHam. 1975. Selenium toxicity on the early life stages of zebra fish (*Brachydanio rerio*). J. Fish. Res. Board Can. 32:803-806.
- Olson, K. R., H. L. Bergman, and P. O. Fromm. 1973. Uptake of methyl mercuric chloride and mercuric chloride by trout: a study of uptake pathways into the whole animal and uptake by erythrocytes in vitro. J. Fish. Res. Board Can. 30:1293-1299.
- Olsson, M. 1976. Size, sex, and age of northern pike, one and five years after the mercury ban in Sweden. Ambio 5:73-77.
- Orciari, R. D., and W. D. Hummon. 1975. A comparison of benthic oligochaete populations in acid and neutral lentic environments in southeastern Ohio. Ohio J. Sci. 75(1):44-49.
- Overrein, L. N. 1976. General introduction and synthesis, pp. 9-12. <u>In</u> F. H. Braekke (ed.), Impact of Acid Precipitation on Forest and Freshwater Ecosystems in Norway. Report 6. Agricultural Research Council of Norway, Norwegian Council for Scientific and Industrial Research.

Page, A. L., F. T. Bingham, and C. Nelson. 1972. Cadmium absorption and growth of various plant species as influenced by solution cadmium concentration. J. Environ. Qual. 1:288-291.
- Pakkala, I. S., M. N. White, G. E. Brudick, E. J. Harris, and D. J. Lisk. 1972. Residues in fish, wildlife, and estuaries. Pestic. Monit. J. 5:348-355.
- Parsons, J. D. 1956. Factors influencing excessive flows of coal strip mined effluents. Trans. III. Acad. Sci. 49:25-33.
- Patrick, F. M., and M. Loutit. 1976. Passage of metals in effluents, through bacteria to higher organisms. Water Res. 10:333-335.
- Patrick, R. 1975. The role of trace elements in management of nuisance growths. EPA 660/2-75-008. U.S. Environmental Protection Agency. 250 pp.
- Pentreath, R. J. 1973. The accumulation and retention of <sup>65</sup>Zn and <sup>54</sup>Mn by the plaice, *Pleuronectes platessa* L. J. Exp. Mar. Biol. Ecol. 12:1-18.
- Pentreath, R. J. 1976. Some further studies on the accumulation and retention of <sup>65</sup>Zn and <sup>54</sup>Mn by the plaice, *Pleuronectes platessa* L. J. Exp. Mar. Biol. Ecol. 21:179-189.

Perel'man, A. I. 1967. Geochemistry of Epigenesis. Plenum Press, New York. 266 pp.

- Perhac, R. M. 1974. Heavy metal distribution in bottom sediment and water in the Tennessee River-Louden Lake Reservoir system. Water Resour. Res. Center Rep. 40. University of Tennessee, Knoxville. 7 pp.
- Pettersson, O. 1977. Differences in cadmium uptake between plant species and cultivars. Swed. J. Agric. Res. 7:21-24.
- Piper, C. S. 1931. The availability of manganese in the soil. J. Agric. Sci. 21:762-779. [As cited in Boyd (1971).]
- Piperno, E. 1975. Trace element emissions: aspects of environmental toxicology, pp. 192-209. <u>In</u> S. P. Babu (ed.), Trace Elements in Fuel. Adv. Chem. Ser. 141. American Chemical Society, Washington, D. C.
- Pough, F. H. 1976. Acid precipitation and embryonic mortality of spotted salamanders, Ambystoma maculatum. Science 192:68-70.
- Pough, F. H., and R. E. Wilson. 1976. Acid precipitation and reproductive success of Ambystoma salamanders, pp. 531-544. <u>In</u> Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, Ohio State University, May 12-15, 1975. U.S. For. Serv. Gen. Tech. Rep. NE-23.
- Pratt, P. F. 1966. Aluminum, pp. 3-12. In H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Preston, E. M., and R. A. Lewis (eds.). 1977. The Bioenvironmental Impact of a Coal-Fired Power Plant, Third Interim Report, Colstrip, Montana, December 1977. U.S. Environmental Protection Agency, Corvallis Environmental Research Laboratory, Corvallis, Oregon. 531 pp.
- Price, P. W., B. J. Rathcke, and D. Gentry. 1974. Lead in terrestrial arthropods: evidence of biological concentration. Environ. Entomol. 3(3):370-372.
- Prince, A. L. 1957. Trace element delivering capacity of 10 New Jersey soil types as measured by spectrographic analysis of soils and mature corn leaves. Soil Sci. 84:413-418.
- Pringle, B. H., D. E. Hissong, E. L. Katz, and S. T. Mulawka. 1968. Trace metal accumulation by estuarine mollusks. J. Sanit. Eng. Div. Proc. Am. Soc. Civ. Eng. 94(SA3), Paper 5970:455-475.
- Ramamoorthy, S., and D. J. Kushner. 1975. Heavy metal binding components of river water. J. Fish. Res. Board Can. 32(10):1755-1766.
- Ramamoorthy, S., and B. R. Rust. 1976. Mercury sorption and desorption characteristics of some Ottawa River sediments. Can. J. Earth Sci. 13:530-536.
- Ramamoorthy, S. S., S. Springthorpe, and D. J. Kushner. 1977. Competition for mercury between river sediment and bacteria. Bull. Environ. Contam. Toxicol. 17(5):505-511.
- Reinhart, K., and T. D. Myers. 1975. Eye and tentacle abnormalities in embryos of the Atlantic oyster drill, *Urosalpinx cinerea*. Chesapeake Sci. 16:286-288.

- Reuther, W., and C. K. Labanauskas. 1966. Copper, pp. 157-179. In H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- ReVelle, C., and P. ReVelle. 1974. Sourcebook on the Environment. Honghton Mifflin Co., Boston. 332 pp.
- Ricks, G. R., and R. H. J. Williams. 1974. Effects of atmospheric pollution on deciduous woodland. Part 2, Effects of particulate matter upon stomatal diffusion resistance in leaves of *Quercus petraea* (Mattuschka) Leibl. Environ. Pollut. 6:87-109.
- Riley, J. P., and B. Chester. 1971. Introduction to Marine Chemistry. Academic Press, London. 465 pp.
- Roback, S. S., and J. W. Richardson. 1969. The effects of acid mine drainage on aquatic insects. Proc. Acad. Nat. Sci. Philadelphia 121:81-107.
- Robinson, G. D., W. A. Dunson, J. E. Wright, and G. E. Mamolito. 1976. Differences in low pH tolerance among strains of brook trout (*Salvelinus fontinalis*). J. Fish Biol. 8:5-17.
- Roffman, H. E., R. E. Kary, and T. Hudgins. 1977. Ecological distribution of trace elements emitted by coal-burning power generating units employing scrubbers and electrostatic precipitators, pp. 192-215. <u>In</u> Fourth Symposium on Coal Utilization. National Coal Association/Bituminous Coal Research, Inc.
- Rolfe, G. L., and A. Haney. 1975. An Ecosystem Analysis of Environmental Contamination by Lead. Institute for Environmental Studies, University of Illinois, Champaign-Urbana. 133 pp.
- Romney, E. M., and J. D. Childress. 1965. Effects of beryllium in plants and soil. Soil Sci. 100:210-217.
- Rosenfeld, I., and O. A. Beath. 1964. Selenium: Geobotany, Biochemistry, Toxicity, and Nutrition. Academic Press, New York. 411 pp.
- Routhla, M., and J. K. Miettinen. 1975. Retention and excretion of <sup>203</sup>Hg-labelled methylmercury in rainbow trout. Oikos 26:385-390.
- Russell, F. C. 1944. Minerals in Pasture, Deficiencies and Excesses in Relation to Animal Health. Tech. Commun. No. 15. Imperial Bureau of Animal Nutrition, Aberdeen, Scotland. [As cited in McKee and Wolf (1963).]
- Salazkin, A. A. 1971. Zooplankton in oligotrophic lakes of the humid zone in the northwestern USSR. Gidrobiol. Zh. 7:23-28.
- Sandholm, M., H. E. Oksanen, and L. Pesonen. 1973. Uptake of selenium by aquatic organisms. Limnol. Oceanogr. 18:496-499.
- Saunders, R. L., and J. B. Sprague. 1967. Effects of copper-zinc mining pollution on a spawning migration of Atlantic salmon. Water Res. 1:419-432.
- Schmidt-Nielsen, B. 1974. Osmoregulation: effect of salinity and heavy metals. Fed. Proc. 33(5):2137-2146.
- Schofield, C. L. 1976. Effects of acid precipitation on fish. Presented at International Conference on the Effects of Acid Precipitation, Telemark, Norway, June 14-19, 1976. 20 pp.
- Schroeder, H. A. 1971. Metals in the air. Environment 13(8):18-32. [As cited in Piperno (1975).]
- Schubert, J. P., R. D. Olsen, and S. D. Zellmer. 1977. Monitoring the effects of coal refuse disposal and reclamation on surface and ground water quality. <u>In</u> Proceedings of Fourth Joint Conference on Sensing of Environmental Pollutants, New Orleans, Nov. 6-11, 1977. American Chemical Society. (In press.)
- Schultz-Baldes, M., and R. A. Lewin. 1976. Lead uptake in two marine phytoplankton organisms. Biol. Bull. 150:118-127.
- Schulz, E. J., R. B. Engdahl, and T. T. Frankenberg. 1975. Submicron particles from a pulverized coal fired boiler. Atmos. Environ. 9:111-119.

- Scott, D. P. 1974. Mercury concentration of white muscle in relation to age, growth, and condition in four species of fishes from Clay Lake, Ontario. J. Fish. Res. Board Can. 31:1723-1729.
- Scott, D. P., and F. A. J. Armstrong. 1972. Mercury concentration in relation to size in several species of freshwater fishes from Manitoba and Northwestern Ontario. J. Fish Res. Board Can. 29:1685-1690.
- Sheridan, R. P. 1976. Effects of Airborne Particulates on Nitrogen Fixation in Legumes and Algae. Presented at Symposium on Detection, Measurement, and Effects of Primary and Secondary Particulates on Plants, American Phytopathological Society, Michigan State University, East Lansing, Michigan, August 1976.
- Simmons, G. M. 1973. A preliminary report on the use of the sequential comparison index to evaluate acid mine drainage on the macrobenthos in a pre-impoundment basin. Trans. Am. Fish. Soc. 4:701-713.
- Sinley, J. R., J. P. Goettle, and P. H. Davies. 1974. The effects of zinc on rainbow trout (*Salmo gairdneri*) in hard and soft water. Bull. Environ. Contam. Toxicol. 12:193-201.
- Skidmore, J. F. 1970. Respiration and osmoregulation in rainbow trout with gills damaged by zinc sulfate. J. Exp. Biol. 52:481-494.
- Smith, A. L., R. H. Green, and A. Lutz. 1975. Uptake of mercury by freshwater clams (family Unionidae). J. Fish. Res. Board Can. 32:1297-1303.
- Smith, W. H. 1974. Air pollution effects on the structure and function of the temperate forest ecosystem. Environ. Pollut. 6:111-129.
- Sorum, C. H. 1960. Semimicro Qualitative Analysis. Prentice-Hall, Inc., Englewood Cliffs, N. J. 239 pp.
- Spooner, G. M. 1949. Observations of the absorption of radioactive strontium and yttrium by marine algae. J. Mar. Biol. Assoc. U.K. 28:587-627.
- Sprague, J. B. 1964. Avoidance of copper-zinc solutions by young salmon in the laboratory. J. Water Pollut. Control Fed. 36:990-1004.
- Sprague, J. B. 1965. Effects of sublethal concentrations of zinc and copper on migration of Atlantic salmon, pp. 332-333. <u>In</u> Biological Problems in Water Pollution, 3rd Seminar. U.S. Public Health Serv. Publ. No. 99-WP-25. R. A. Taft Sanitary Engineering Center, Cincinnati, Ohio.
- Sprague, J. B. 1968. Avoidance reactions of rainbow trout to zinc sulfate solutions. Water Res. 2:367-372.
- Sprules, W. G. 1975. Midsummer crustacean zooplankton communities in acid-stressed lakes. J. Fish. Res. Board Can. 32:389-395.
- Stahl, Q. R. 1969. Air Pollution Aspects of Mercury and Its Compounds. Litton Systems, Inc., Bethesda, Md. 99 pp.
- Stallard, J. B., and C. T. Yang. 1970. Hydraulic geometry of 12 selected stream systems of the United States. III. State Water Surv. Res. Rep. No. 32. 73 pp.
- Steele, K. F., and G. H. Wagner. 1975. Trace metal relationships in bottom sediments of a freshwater stream - the Buffalo River, Arkansas. J. Sediment. Petrol. 45:310-319.
- Stokes, P. 1975. Uptake and accumulation of copper and nickel by metal-tolerant strains of Scenedesmus. Verh. int. Ver. Limnol. 19:2128-2137.
- Stokes, P. M., T. C. Hutchinson, and K. Krauter. 1973. Heavy metal tolerance in algae isolated from polluted lakes near the Sudbury, Ontario, smelters. Water Pollut. Res. Can. 8:178-201.
- Stumm, W., and H. Bilinski. 1973. Trace metals in natural waters; difficulties of interpretation arising from our ignorance on their speciation. Adv. Water Pollut. Res. 6:39-52.
- Stumm, W., and J. J. Morgan. 1970. Aquatic Chemistry. Wiley Interscience, New York. 580 pp.
- Styron, C. E., T. M. Hagen, D. R. Campbell, J. Harvin, and N. K. Wittenburg. 1976. Effect of temperature and salinity on growth and uptake of <sup>65</sup>Zn and <sup>137</sup>Co for six marine algae. J. Mar. Biol. Assoc. U.K. 56:13-20.

- Sullivan, R. J. 1969a. Air Pollution Aspects of Arsenic and Its Compounds. Litton Systems, Inc., Bethesda, Md. 63 pp.
- Sullivan, R. J. 1969b. Air Pollution Aspects of Chromium and Its Compounds. Litton Systems, Inc., Bethesda, Md. 76 pp.
- Swaine, D. J. 1955. The Trace Element Content of Soils. Commonw. Bur. Soil Sci. Tech. Commun. No. 48. Herald Printing Works, York, England. 157 pp.
- Swanson, V. E., and J. H. Medlin, et al. 1976. Collection, Analysis, and Evaluation of Coal Samples in 1975. Open-file Rep. 76-468. U.S. Department of the Interior, Geological Survey. (Draft report.)
- Talmage, S. S. 1977. Humans: metabolism and biological effects, pp. 10-1 to 10-99. <u>In</u> H. M. Braunstein, E. D. Copenhaver, and H. A. Pfuderer (eds.), Environmental, Health, and Control Aspects of Coal Conversion: An Information Overview, Vol. 2. ORNL/EIS-95. Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Tiffin, L. O. 1977. The form and distribution of metals in plants: an overview, pp. 315-334. <u>In</u> H. Drucker and R. E. Wildung (chairmen), Biological Implications of Metals in the Environment. CONF-750929. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium, Richland, Washington, 1975. Technical Information Center, Energy Research and Development Administration.
- Trefry, J. H., and B. J. Presley. 1976. Heavy metal transport from the Mississippi River to the Gulf of Mexico, pp. 39-76. <u>In</u> H. L. Windom and R. A. Duce (eds.), Marine Pollutant Transfer. Lexington Books, Lexington, Mass.
- Trelease, S. F. 1945. Selenium in soils, plants, and animals. Soil Sci. 60:125-131.
- Treshow, M. 1970. Environment and Plant Response. McGraw-Hill Book Co., Inc., New York. 422 pp.
- Trollope, D. R., and B. Evans. 1976. Concentrations of copper, iron, lead, nickel and zinc in freshwater algal blooms. Environ. Pollut. 11:109-116.
- Tsai, S. C., G. M. Boush, and F. Matsumura. 1975. Importance of water pH in accumulation of inorganic mercury in fish. Bull. Environ. Contam. Toxicol. 13:188-194.
- Turner, R. G. 1969. Heavy metal tolerance in plants, pp. 399-410. In H. Rorison (ed.), Ecological Aspects of the Mineral Nutrition of Plants. Br. Ecol. Soc. Symp. 9. Blackwell Scientific Publications, Ltd., Oxford, England. [As cited in Tiffin (1977).]
- Underwood, E. J. 1962. Trace Elements in Human and Animal Nutrition. Academic Press, New York. [As cited in Berry and Wallace (1974).]
- Underwood, E. J. 1975. Trace elements and their physiological roles in the animal, pp. 227-241. <u>In</u> D. J. Nicholas and A. R. Egan (eds.), Trace Elements in Soil-Plant-Animal Systems. Academic Press, New York.
- U.S. Department of Agriculture, Soil Survey Staff, Bureau of Plant Industry, Soils, and Agricultural Engineering. 1951. U.S. Department of Agriculture Handbook No. 18. Agricultural Research Administration. 503 pp.
- U.S. Department of Agriculture, Forest Service. 1961. Handbook of Soils. 372 pp.
- U.S. Department of Health, Education and Welfare. 1969. Air Quality Criteria for Sulfur Oxides. Natl. Air Pollut. Control Admin. Publ. AP-50. 178 pp.
- U.S. Environmental Protection Agency. 1971a. Effects of Noise on People. EPA-NTID 300.7; PB-206 723. Prepared by the Central Institute for the Deaf, St. Louis, Mo. 165 pp.
- U.S. Environmental Protection Agency. 1971b. Effects of Noise on Wildlife and Other Animals. EPA-NTID 300.5; PB-206 720. Prepared by Memphis State University for the USEPA, Office of Noise Abatement and Control, Washington, D.C. 74 pp.
- U.S. Environmental Protection Agency. 1971c. Air Quality Criteria for Nitrogen Oxides. Air Pollut. Control Off. Publ. AP-84. Washington, D.C. 1 v. (various pagings).

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- U.S. Environmental Protection Agency. 1971d. Standards of performance for new stationary sources. Fed. Regist. 36:24876.
- U.S. Environmental Protection Agency. 1973a. Effects of Sulfur Oxides in the Atmosphere on Vegetation. Revised Chapter 5 for Air Quality Criteria for Sulfur Oxides. EPA-R3-73-030; PB-226 314. National Environmental Research Center, Research Triangle Park, N. C. 43 pp.
- U.S. Environmental Protection Agency. 1973b. Compilation of Air Pollution Emission Factors, 2nd ed. Publ. No. AP-42; PB-223 996. Office of Air and Water Programs, Research Triangle Park, N. C. 288 pp.
- U.S. Environmental Protection Agency. 1973c. Background Information on Development of National Emission Standards for Hazardous Air Pollutants: Asbestos, Beryllium, and Mercury. EPA Publ. No. APTD-1503; PB-222 802. Office of Air and Water Programs, Research Triangle Park, N. C. 104 pp.
- U.S. Environmental Protection Agency, Office of Toxic Substances. 1975a. Preliminary Investigation of Effects on the Environment of Boron, Indium, Nickel, Selenium, Tin, Vanadium, and their Compounds. Vol. III, Nickel. EPA-560/2-75-005C; PB-245 986. 89 pp.
- U.S. Environmental Protection Agency, Office of Toxic Substances. 1975b. Preliminary Investigation of Effects on the Environment of Boron, Indium, Nickel, Selenium, Tin, Vanadium, and their Compounds. Vol. VI, Vanadium. EPA-560/2-75-005F; PB-245 989. 84 pp.
- Uthe, J. F., F. M. Atton, and L. M. Royer. 1973. Uptake of mercury by caged rainbow trout (*Salmo gairdneri*) in the South Saskatchewan River. J. Fish. Res. Board Can. 30:643-650.
- Vallee, B. L., D. D. Ulmer, and W. E. C. Wacker. 1960. Arsenic toxicology and biochemistry. Arch. Ind. Health 21:132-151.
- Van Hook, R. I., W. F. Harris, and G. S. Henderson. 1977. Cadmium, lead, and zinc distributions and cycling in a mixed deciduous forest. Ambio 6:281-286.
- Vanselow, A. P. 1966. Barium, pp. 24-32. In H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Vaughan, B. E., K. H. Abel, D. A. Cataldo, J. M. Hales, C. E. Hane, L. A. Rancitelli, R. C. Routson, R. E. Wildung, and E. G. Wolf. 1975. Review of Potential Impact on Health and Environmental Quality from Metals Entering the Environment as a Result of Coal Utilization. Battelle Energy Progress Report, Pacific Northwest Laboratories--Battelle Memorial Institute, Richland, Washington. 75 pp.
- Vinikour, W. S. 1977. Concentrations of zinc, copper, cadmium, and lead in selected fish species of the Fox River from locations with varying potential metal inputs. M.S. Thesis. Northern Illinois University, DeKalb. 103 pp.
- Waldichuk, M. 1974. Some biological concerns in heavy metals pollution, pp. 1-57. <u>In</u> F. J. Vernberg and W. B. Vernberg (eds.), Pollution Physiology of Marine Organisms. Academic Press, New York.
- Wallace, A., and E. M. Romney. 1977. Roots of higher plants as a barrier to translocation of some metals to shoots of plants, pp. 370-379. <u>In</u> H. Drucker and R. E. Wildung (chairmen), Biological Implications of Metals in the Environment. CONF-750929. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium, Richland, Washington, 1975. Technical Information Center, Energy Research and Development Administration.
- Williams, R. E. 1975. Waste Production and Disposal in Mining, Milling, and Metallurgical Industries. Miller Freeman Publications, Inc., San Francisco. 489 pp.
- Wiltshire, G. H. 1972. Effect of nitrogen source on translocation of nickel in some crop plants and weeds. Kirkia 8:102-133. [As cited in USEPA (1975a).]
- Winner, R. W., and M. P. Farrell. 1976. Acute and chronic toxicity of copper to four species of *Daphnia*. J. Fish. Res. Board Can. 33:1685-1691.
- Wissmar, R. C. 1972. Some effects of mine drainage on primary production in Coeur d'Alene River and Lake, Idaho. Ph.D. Dissertation. University of Idaho, Moscow. 61 pp.
- Wong, P. T. S., Y. K. Chau, and P. L. Luxon. 1975. Methylation of lead in the environment. Nature 253:263-264.

- Wood, J. M. 1973. Metabolic cycles for toxic elements in aqueous systems. Rev. Int. Oceanogr. Med. 31-32:7-16.
- Wood, J. M. 1974. Biological cycles for toxic elements in the environment. Science 183:1049-1052.
- Zimdahl, R. L., and J. H. Arvik. 1973. Lead in soils and plants: a literature review. CRC Crit. Rev. Environ. Control 3:213-224.
- Zimmerman, P. W., and W. Crocker. 1934. Plant injury caused by vapors of mercury and compounds of mercury. Boyce Thompson Institute 6:167, from Handbook of Environmental Control, p. 181. [As cited in Berry and Wallace (1974).]
- Ziskind, R., and D. Hausknecht. 1976. Health Effects of Nitrogen Oxides. EPRI 571-1A. Prepared by Science Applications, Inc., El Segundo, Calif., for the Electric Power Research Institute, Palo Alto, Calif. 39 pp.

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Zitko, V., and W. G. Carson. 1976. A mechanism of the effects of water hardness on the lethality of heavy metals to fish. Chemosphere 5:299-303.

# MEASURES TO MITIGATE IMPACTS

#### COMBUSTION EMISSION PRODUCTS

Designers of modern coal-fired power plants can use techniques that have been developed to meet federal and state standards for emissions and ambient ground-level concentrations of harm-ful pollutants. These techniques include using low-sulfur, low-ash coal; operating pollution abatement devices; increasing stack height or plume rise; and implementing emission-limitation programs.

The burning of low-sulfur rather than high-sulfur coal will decrease the amounts of  $SO_X$  emitted by a particular plant. In addition, the cleaning of coal (Walker and Hartner 1966) lowers the amount of inorganic sulfur in the coal before it is burned. Certain coal types (Cavallaro et al. 1976) when burned produce less fly and bottom ash than other coals, thus reducing ground-level particulate concentrations. Coal cleaning will decrease both the amount of ash emitted by a plant during combustion and the total amount of coal needed to produce a given amount of heat (Walker and Hartner 1966).

Pollution abatement devices include precipitators to control particulate emissions and scrubbers to control  $SO_X$  emissions.  $NO_X$  emissions can be controlled by limiting excess oxygen and maintaining low temperatures during combustion (Heitner 1977).

If the plume from a power plant is emitted higher into the atmosphere or if the rise of the plume is enhanced by increasing its buoyancy and/or momentum, the ground-level concentrations are typically reduced. Although the USEPA no longer gives credit for tall stacks in calculating concentrations resulting from plant operations (Amendments to Clean Air Act, 7 August 1977--see Appendix A), tall stacks will reduce the actual ground-level concentrations in the vicinity of the plant (Strom 1976), although the areas affected by low concentrations are increased. Tall stacks may also extend above low-level inversions, preventing plume trapping or fumigation episodes. By reheating the flue gas after passage through the scrubbing system and by incorporating a smaller diameter stack outlet, the rise of the effluent plume above the actual stack is increased, resulting in a higher effective release height; similar benefits would occur with a physically taller stack. Hotter plumes with greater momentum also are more likely to go through inversion layers, lessening the likelihood of plume trapping or fumigation. Engineering design can match the plant and stack characteristics to the specific site, resulting in fewer incidences of high ground-level concentrations.

Because biota are most affected by the short-term, high ground-level concentrations that occur during periods of unusual meteorological conditions (which occur only a small fraction of the total operating time), methods are available to reduce these high ground-level concentrations. One method is to utilize a sulfur dioxide emission-limitation program (Leavitt et al. 1976). During periods of predicted or observed adverse meteorological conditions, electrical generation is decreased, thereby lowering  $SO_2$  emissions during a time when higher emission rates could exceed ambient  $SO_2$  standards. Power plants not in areas affected by the adverse meteorological conditions can be operated at full capacity to meet demand.

Another method to lower emissions during periods of high pollution potential is to substitute low-sulfur coal for high-sulfur coal, thereby maintaining generating capacity but reducing  $SO_2$  emissions. At other times when the pollution potential is lower, less expensive high-sulfur coal can be burned. Any technique relying upon modification of generating capacity or fuel usage is highly site-specific and requires the services of a competent meteorologist, with strategically located pollution monitors, to determine those periods during which mitigative measures should be taken and if such measures are effective.

Although any or all of these techniques may be used on occasion, it is expected that the use of flue-gas cleaning devices will be the primary method for reducing ground-level concentrations of combustion emission products.

## WASTE HANDLING AND STORAGE

#### Siting of Disposal Areas

<u>Terrestrial impacts</u>. Major impacts from waste ash and flue-gas desulfurization (FGD) sludge disposal arise from land use, runoff, and seepage, and can be prevented or reduced to some extent by attention to siting of the disposal areas.

Alteration of land use cannot usually be avoided or mitigated during operation of the station; at the end of operation, however, return of the waste-disposal sites to previous or other use can be achieved by sincere reclamation efforts.

Impacts due to runoff from the disposal ponds can largely be prevented by construction of grassed drainage ditches along the perimeter of the impoundments, and by ensuring that there is sufficient freeboard to allow for the maximum rainfall expected.

Impacts from seepage are more easily prevented than corrected. Dewatering of the sludge and ash prior to disposal will markedly reduce the potential for adverse effects of seepage. Siting of the impoundments over relatively impermeable substrata or lining of the entire impoundment with clay or a synthetic liner will essentially prevent groundwater and soil contamination. Contamination of wildlife habitats such as marshes or bogs can largely be prevented by siting the disposal area downgradient of the wetland. Such sites can be identified by hydrologists familiar with the patterns of groundwater flow and surface runoff on the site. If such sites are not available, installation of a drainage system (and probably pumping facilities) to prevent contamination of a wetland may be necessary. This procedure is expensive, relative to installation of a liner.

To reduce the potential for physical injury to waterfowl, ash settling ponds should be situated away from obstructions such as transmission towers and lines.

<u>Aquatic impacts</u>. Siting of disposal basins or landfills should capitalize on site geology and topography for control of seepage, leaching, and runoff. Preferable siting should be in areas underlain with impermeable clay or shale, if present, to prevent or reduce seepage. Although natural basins may be preferred from an engineering standpoint, such basins tend to collect runoff, and leaching of disposed material may be a problem when the natural basin-i.e., a ravine, gully, valley, etc.--is not a closed system. Siting of disposal areas with some elevation above natural depressions can allow collection of leachate and runoff for treatment.

Siting of disposal areas should maximize the distance to the nearest water body or wetland. By maximizing the distance that seepage must flow before entering the water body and by placing the disposal area in an elevated location, the distance to groundwater also may be maximized; thus, the binding capacity of the substrate for trace elements is utilized to reduce the amount of trace elements eventually reaching both surface water and groundwater locations. The binding capacity of the substrate depends on its composition and the chemical characteristics of the seepage. Binding of trace elements in the substrata may reduce the amounts entering water resources, but it is not a total solution to the trace-element problem since the trace elements would still be present in the substrata or soil. The availability of trace elements in the future will depend upon the physical and chemical aspects of their stabilization.

# Lining of Ash and Sludge Disposal Ponds

Liners are defined in this report as any natural or synthetic material purposely placed on the inside surfaces of an impoundment basin to reduce the permeability of the basin. Most existing ash and sludge disposal ponds are unlined. Compliance with increasingly more stringent local, state, and federal water quality control regulations may require that new ponds be lined. Necessity for a liner is dependent upon the properties of the ponded effluents, the quantity and chemical quality of potential leachate, the impacts of seepage, the geology and geography of the site, the availability of process water, and the regulations governing seepage.

Unfortunately, there is very little first-hand knowledge about the compatibility of various liners to ash and sludge wastes. Reports from one study (Haxo 1976) of compatibility of several types of wastes with a variety of liners provides a guide for preliminary selection (Tables 55 and 56). A liner compatibility study being conducted by Z. B. Fry at the Municipal Environmental Research Laboratory in Cincinnati, Ohio, is specific to FGD sludge and is scheduled for completion in the spring of 1978 (Jones 1976). In the interim, lining technology has been borrowed from other waste disposal technologies, primarily from tailings disposal ponds of the mining industry.

There are six major categories of liners: (1) compacted earth, (2) clay, (3) chemical sealants and soil additives, (4) stabilized wastes, (5) rigid liners, and (6) flexible synthetic

# Table 55. Effects of Immersing Liner Materials in Hazardous Wastes<sup>a</sup>

			% in	% increase in area of position of strip immersed				
			Stron	Strong acid		Strong base		
Membrane liner	Reinforcement	No.	HF1 (pH 4.8)	НNО <sub>3</sub> b (рН 1.5)	Slop water (pH 12)	Spent caustic (pH 11.3)		
Polyvinyl chloride (PVC)		10 11 17	CC NVC NVC	NVC NVC NVC	HDS HDS HDS	NVC NVC NVC		
	Nylon reinforced	40 49 59 <sup>d</sup> 67			HDS C/ HDS HDS			
	Nylon reinforced	71	NVC	<u>e/</u>	HDS	NVC		
Chlorosulfonated polyethylene (Hypalon)	Nylon reinforced Cured and reinforced	6 <sup>0</sup> 50 55	NVC <u>c/</u> NVC	NVC c/ NVC	NVC <u>c</u> ∕ NVC	NVC <u>c</u> / NVC		
Chlorinated polyethylene (CPE)	Nylon reinforced Polyester reinforced Polyester reinforced	12 <sup>d</sup> 38 39 48 73	NVC NVC NVC <u>c/</u> NVC	NVC NVC NVC NVC	NVC NVC NVC c/	NVC NVC NVC <u>c/</u> NVC		
Ethylene propylene rubber (EPDM)		8 26 <sup>d</sup>	NVC	NVC NVC	NVC NVC	NVC NVC		
Polychloroprene (neoprene)	Nylon reinforced Polyester reinforced Nylon reinforced Polyester reinforced	9 37 42 43 47 56 74	CC NVC <u>c</u> / NVC NVC NVC	SCR NVC R <u>c/</u> NVC NVC	CC NVC <u>c/</u> SHD <u>f/</u>	NVC NVC <u>c/</u> NVC NVC NVC		
Butyl rubber	Nylon reinforced	22 24 44 57 <sup>d</sup>	NVC NVC c/ NVC	NVC NVC c/ NVC	NVC NVC <u>c</u> / NVC	NVC NVC <u>c</u> / NVC		
Elasticized polyolefin (3110)		36 41	NVC NVC	NVC NVC	NVC NVC	NVC NVC		
Thermoplastic polyester	•	69 75	NVC NVC	NVC NVC	<u>g/</u>	NVC NVC		
Polyurethanes	Polyester reinforced Polyester reinforced Reinforced Nylon reinforced Polyester reinforced	45 46 51 70 72	2/ 2/ 20 00 00	C C NVC NVC	c/ c/ CC CC	<u>c/</u> <u>c/</u> NVC NVC		
Miscellaneous Liner Materials Coal tar pitch + PVC Emulsified asphalt on petromat		52 58	NVC NVC	NVC SCR/ BLS	HDS NVC	NVC NVC		
Sealing Materials Butyl caulk Polyurethane caulk Polysulfide caulk Teflon sponge rod	• •	63 64 66 68	NVC <u>c/</u> NVC NVC	NVC R SFT1&2 REV NVC	NVC SFT1&2 SCR NVC	NVC NVC NVC NVC		
Neoprene sponge		3	NVC	SCR [sic]	SHR	NVC		

<sup>a</sup>Adapted from Haxo (1976). <sup>b</sup>Hydrofluoric (HF1), acetic (CH<sub>3</sub>COOH), and nitric (HNO<sub>3</sub>) acids. <sup>c</sup>Material not tested in the waste noted. <sup>d</sup>Materials incorporated in cells. <sup>e</sup>O.10 in swell each direction, curled, and delaminated. <sup>f</sup>Neoprene OK, but reinforcing fabric (polyester) dissolved. <sup>g</sup>Black rubs off; indicating possible dissolving. Abbreviations: R - Removed specimen from waste because of excessive swelling or disintegration, NVC - No visible change, SCR - Surface cracking and hardening, HDS - Hardened and shrank, SHD -slightly hardened, BLS - Blistering of surface, SFT-1 - Softened above waste, SFT-2 - Softened in waste, CC - Color change, and REV - Reverted.

	Time of first passage of wastes or fraction of waste through material (days)						
	Stron	g acid	Stro	ng base			
Admix material	HF1 (pH 4.8)	HN03 <sup>b</sup> (pH 1.5)	Slop water (pH 12)	Spent caustic (pH 11.3)			
Treated bentonite-sand mixture A - B -	17 >44	3 3	2 2	3 3			
Native soil (Mare Island)	<u>c/</u>	>19	>19	۱۱ <sup>d</sup>			
Soil-cement containing Rich Hull ash	<u>c</u> /	>19 <sup>e</sup>	>19 NVC	2 <sup>f</sup>			
Soil-cement, portland	>19	>19 <sup>g</sup>	>19 NVC	NVC			

# Table 56. Effects of Placing Wastes Above Test Specimens of Admix Materialsa

<sup>a</sup>Adapted from Haxo (1976). <sup>b</sup>Hydrofluoric (HF1), acetic (CH<sub>3</sub>COOH), and nitric (HNO<sub>3</sub>) acids. Material not tested above the waste noted. Some dampening of bottom; neutral to litmus.

eBubbling on surface. Fluid passing through is basic.

<sup>g</sup>Surface softer.

Abbreviation: NVC - no visible change to surface of specimen in 19 days.

liners. The type of liner best suited for a given pond is determined by the allowable seepage rate, the availability of various potential liner materials, the predicted durability of the liners under the expected field conditions, and cost.

<u>Compacted earth liners</u>. The surface and subsurface soil in the pond embankments basin can be compacted to form a liner. Compaction decreases porosity, which in turn decreases hydraulic conductivity. Silty or clayey soils, tuffs, loesses, alluvium, and colluvium can make some of the best compacted earth liners. Clean sands and gravels are poor because the hydraulic conductivity is only slightly decreased by compaction. Micaeous and expansive soils are difficult to compact. The greatest reduction in hydraulic conductivity is achieved when the earth is compacted in 0.15-m (6-inch) lifts to within 95% of the maximum dry density (Clark and Moyer 1974).

Other than its low cost, the biggest advantage of a compacted earth liner is its flexibility. It can withstand seismic activity and normal subgrade settlement. This liner is stable in both wet and dry conditions. Potential failure mechanisms include freezing and thawing, drying and cracking (of expansive soils), and piping. (Piping is a progressive failure which occurs when the energy in seeping water is sufficient to erode the finest particles and transport them through the pore spaces which leaves larger cavities and promotes additional erosion.)

The primary disadvantage of a compacted earth liner is its relatively high hydraulic conductivity compared to other types of liners. In regions with strict seepage regulations or where marked seepage effects are expected, this liner may not be adequate.

Clay liners. A clay liner is a special type of compacted earth liner. The clay may be borrowed from a pit near the pond site, or it may be purchased commercially. Montmorillonites, especially bentonites, are the preferred clays because of their expansive capabilities. Sodiumrich clays tend to disperse more readily than calcium- or magnesium-rich clays, and this may reduce their hydraulic conductivities. For this reason, natural clays low in sodium are often treated with sodium before final compaction into a liner.

Bentonites are naturally abundant in parts of Wyoming, South Dakota, Montana, California, and Utah. In these areas, and in other areas having a suitable source of local clay, a liner will probably consist of a 0.3- to 1-m (1- to 3-ft) layer of clay which is compacted in 15-cm

(6-inch) lifts. In areas where clay is not naturally available, a very pure commercial bentonite may be mixed with the existing soil and compacted, or placed as a 1.25-cm (0.5-inch) thick (or thicker) membrane and covered with 15 cm (6 inches) of soil (Clark and Moyer 1974).

All the advantages described for the compacted earth liners also hold for clay liners. In addition, clay liners usually have lower hydraulic conductivities. Values of  $1.7 \times 10^{-6}$  to  $5.7 \times 10^{-7}$  cm/s (1.8 to 0.6 ft per day) are reported for one clay-soil mixture, and  $9.7 \times 10^{-8}$  cm/s (0.01 ft per day) for a clay membrane (Clark and Moyer 1974).

Clay liners may not be economical for ash and sludge ponds in areas where no local clay is available. Soil mixing may be expensive, and emplacement of a continuous, thin clay membrane is difficult to achieve. Some of the dispersive properties of a clay could be lost by leaching of the sodium in an acid environment.

<u>Chemical sealants and soil additives</u>. Chemical sealants and soil additives seal the impoundment basin by filling soil interstices or by causing reactions which reduce permeability. Chemical sealants may be applied by spraying, mixing with soil, or as additions to the waste stream inflow. At present, chemical sealants are not always effective. This may be due in part to soil nonhomogeneities, and in part to the sealant itself. Additional research may produce a chemical sealant that is more effective than presently available liners.

Sodium carbonate, sodium silicate, and sodium pyrophosphate have been tested for suitability as sealants. These chemicals act by increasing the sodium-to-calcium ratio in a soil, thus dispersing the soil and decreasing its permeability. Sodium carbonate has been demonstrated to be superior to the other two chemicals in some cases; its seal may remain effective for up to five years (Clark and Moyer 1974). Polyphosphates such as tetrasodium pyrophosphate (TSPP), sodium trypolyphosphate (STPP), and sodium hexametaphosphate (SPP) give optimal results when mixed with clay soil and compacted to 90% of maximum density (Kays 1977). Soil treated with sulfuric acid followed by sodium silciate prior to compaction may provide a good sealant for ponds containing sulfuric acid (Clark and Moyer 1974).

Other possible chemical sealants include Zeogel (an attapulgite clay), sprayable polymer compounds, and rubber latex. Compatibility studies should be conducted with the waste to be ponded before any chemical sealant is selected.

<u>Stabilized wastes</u>. Engineering properties available in the literature for fly ash, bottom ash, and FGD sludge are listed in Table 57. Of these, only fly ash seems to have potential value as a liner. Bottom ash is too coarse and permeable, and FGD sludges are too difficult to dewater. The hydraulic conductivity of compacted (95% maximum dry density) fly ash varies between  $5 \times 10^{-5}$  and  $1 \times 10^{-4}$  cm/s which is higher than that usually desired in a liner. Addition of a chemical sealant to fly ash could possibly reduce the hydraulic conductivity. The biggest advantage of this method is that it maximizes the waste storage capacity by incorporating the waste in the pond embankments.

<u>Rigid liners</u>. Materials such as concrete, gunite, asphalt concrete, and soil cement are categorized as rigid liners. They provide some structural support as well as reducing pond seepage, but they are not impermeable. The major disadvantage of rigid materials as liners is their susceptibility to fracture under seismic, hydrostatic, thermal, and weathering stresses.

Portland cement concrete liners are formed by pouring panels of the concrete directly on the earthen embankments. An elastic sealant is placed in the construction joints to adsorb the shrinking and swelling of the concrete, but the joints are commonly not water resistant. Underdrains prevent the build-up of potentially damaging subsurface hydrostatic pressures, but cracking is still a major problem. Cracked concrete liners are difficult to repair.

Gunite is a concrete mixture which may be sprayed on the embankment's interior. It does not have construction joints and is thinner and less expensive to apply; otherwise, a gunite liner performs similarly to a concrete liner. Neither material is impermeable.

Asphalt concrete is less rigid than portland cement concrete and thus is less susceptible to cracking. It works best when applied in thicknesses of 3.8 to 7.5 cm (1-1/2 to 3 inches) on relatively flat slopes; on steeper slopes, asphalt concrete tends to slide (particularly soft asphalts in warm climates). The material also tends to deteriorate under sunlight. Asphalt concrete has sometimes been used as an erosion control blanket over a clay liner.

Soil cement may make a suitable liner for soils which are less than 50% silt and clay. Soil cement decreases erodibility and increases shear strength; however, transverse shrinkage cracks may develop as the soil cement dries. Therefore, soil cement is not frequently used as a liner. When it is considered, compatibility tests with the wastes should be conducted.

Property <sup>a</sup>	Value	Type of coal or sludge	Reference
	Fly Ash		********
Unified Soil Classification	ML	Western <sup>b</sup>	Srinivasan et al. (1977)
Plasticity index	Nonplastic	Western	Srinivasan et al. (1977)
Specific gravity	2.35 2.3 -2.6 2.39-2.44	Western Eastern Midwestern	Srinivasan et al. (1977) DiGioia et al. (1977) Cunningham et al. (1977)
Grain size	Silt Silt Silt	Western Eastern Midwestern	Srinivasan et al. (1977) DiGioia et al. (1977) Cunningham et al. (1977)
Maximum dry density - optimum moisture content	90 lb/ft <sup>3</sup> at 23% 77 lb/ft <sup>3</sup> at 29% to 89 lb/ft <sup>3</sup> at 19% 90 lb/ft <sup>3</sup> at 19.5%	Western Eastern Midwestern	Srinivasan et al. (1977) DiGioia et al. (1977) Cunningham et al. (1977)
Dry density (ponded), in situ	45-65 lb/ft <sup>3</sup> 65-80 lb/ft <sup>3</sup>	Eastern Midwestern	DiGioia et al. (1977) Cunningham et al. (1977)
Moisture content (ponded), in situ	35-55%	Midwestern	Cunningham et al. (1977)
Cohesion (psi); angle of internal friction; % maximum density	1.8; 35.5°; 95% 1.1; 34.5°; 90% 0; 39°; 90% 0; 35°; 84% 0; 22°; ? 0; 11.5°; ? 0; 28.4°; ?	Western Western Eastern Eastern Midwestern Midwestern Midwestern	Srinivasan et al. (1977) Srinivasan et al. (1977) Poellot and Curtis (1977 Poellot and Curtis (1977 Cunningham et al. (1977) Cunningham et al. (1977) Cunningham et al. (1977)
Hydraulic conductivity	l×10 <sup>-4</sup> to 5×10 <sup>-4</sup> cm/s l×10 <sup>-4</sup> to 2.3×10 <sup>-5</sup> cm/s	Eastern Eastern	DiGioia et al. (1977) Lamb et al. (1976)
Threshold wind erosion velocity	10 mph	Western	Srinivasan et al. (1977)
	Bottom ash		
Unified Soil Classification	SW-SM	Western	Srinivasan et al. (1977)
Plasticity index	Nonplastic	Western	Srinivasan et al. (1977)
Specific gravity	2.3-2.8	Eastern	DiGioia et al. (1977)
Grain size	Fine sand-fine gravel	Eastern	DiGioia et al. (1977)
Maximum dry density - optimum moisture content	72 lb/ft <sup>3</sup> at 37.4% 69-116 lb/ft <sup>3</sup> at ?	Western Eastern	Srinivasan et al. (1977) DiGioia et al. (1977)
Cohesion (psi); angle of internal friction; % maximum density	0; 38°-42.5°; loose 0; 31°; 86% 0; 31.5°; ?	Eastern Eastern Midwestern	DiGioia et al. (1977) Poellot and Curtis (1977) Cunningham et al. (1977)
Hvdraulic conductivity	$3 \times 10^{-2}$ to $9 \times 10^{-2}$ cm/s	Fastern	Poellot and Curtis (1977)

Table 57.	Engineering	Properties	of Fly	Ash,	Bottom	Ash,	and	Flue-Gas	Desulfurization	Sludge
	•	a	s Repor	ted in	n the L	itera	ture			

(continued)

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Table 57.	(Concluded)
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Property <sup>a</sup>	Type of coal Value or sludge		Reference	
	FGD slude	<u>je</u>	· · · · · · · · · · · · · · · · · · ·	
Unified Soil Classification	ML SM	Sulfite Sulfate	Hagerty et al. (1977) Hagerty et al. (1977)	
Grain size	Silt Fine sand	Sulfite Sulfate	Hagerty et al. (1977) Hagerty et al. (1977)	
Moisture content (ponded), in situ	65-70% 35-40%	Sulfite Sulfate	Hagerty et al. (1977) Hagerty et al. (1977)	
Cohesion (psi); angle of internal friction; % maximum density	0; 25°-35°; ?		Hagerty et al. (1977)	
Hydraulic conductivity	10 <sup>-4</sup> to 10 <sup>-6</sup> cm/s	Sulfite and sulfate (sulfate more permeable)	Hagerty et al. (1977)	

<sup>a</sup>Terminology [adapted for use in this report--more precise definitions may be found in Lambe and Whitman (1969)]:

The Unified Soil Classification is a system of describing soils by grain size, gradation, plasticity, and the presence or absence of organic material. A soil classified as ML is an inorganic silt, a very fine sand, or a silty or clayey fine sand and has little plasticity. A soil classified as SM is a silty sand or a poorly graded sand-silt mixture. A soil classified as SW is a well-graded sand or a gravelly sand having little or no fines.

The plasticity index is the difference between the water content of a soil at its liquid and its plastic limits as determined by a standard Atterberg limits test. A soil is nonplastic when the liquid and plastic limits occur at the same water content or when the soil cannot be made to stick together well enough to perform an Atterberg limits test.

The maximum dry density is the highest density that can be obtained using a standard compactive procedure by varing the moisture content of the soil. This density is a measure of the weight of dry soil per volume of compacted soil and the accompanying voids. The dry density will maximize at one water content. This data is important for any construction on, or with, the sediment.

The in situ dry density is the density the ponded sediment has attained by natural drainage and evaporation. The densities of the ponded ash are lower than the maximum dry densities because of the greater amount of void space containing water. The moisture contents of the ponded ash are generally larger than the optimum moisture contents.

The cohesion intercept and angle of internal friction are soil characteristics determined by failing (shearing) samples and plotting the Mohr circles on a graph. A tangent drawn through their perimeters is called the failure envelope. The point at which the failure envelope crosses the y axis (representing shear strength) is called the cohesion. Cohesion is the strength given a soil by the surface forces of each particle. Silts and sands have little or no cohesion. Their strength is primarily due to friction between the particles. The slope of the Mohr envelope is the angle of internal friction. The cohesion and angle of internal friction are specified at a particular density or percentage of the maximum dry density because the Mohr envelope only approximates a straight line. Both will vary with extremes in moisture content.

The hydraulic conductivity is the rate at which water may seep through the sediment.

The threshold wind velocity is the minimum wind speed at which sediment particles of a particular size, and shape, and weight are likely to be transported by the wind. bLow-sulfur coal. <u>Flexible synthetic liners</u>. Flexible synthetic liners are the only impermeable liners. They are manufactured as long continuous sheets which can be sealed at the edges so that each liner exactly fits the pond. Flexible liners rely upon the earthen structure for support. Most are conditionally guaranteed by their manufacturer for 20 years. Flexible liners may be vulnerable to puncture (especially during installation), aging with exposure to sun or temperature extremes, reaction with ponded wastes, and stresses from trapped gases or groundwater. A cover of 15 to 30 cm (6 to 12 inches) of soil will protect a flexible liner from puncture by traffic.

Flexible synthetic liners vary considerably in physical properties, chemical compatibilities, installation, durability, and cost. Plastic liners are particularly popular because they are impermeable and relatively inexpensive. Polyethylene (PE) was the first material to be widely used. It has since been replaced in popularity by polyvinyl chloride (PVC) for the reasons outlined in Table 58 (Kays 1977). Chlorinated polyethylene (CPE) is less affected by sunlight. It is inert and will not readily react with wastes, but it is also little affected by adhesives. Plies of the liner and CPE seams do not bind well. Chlorinated polyethylene has been used for the sides of some PVC-lined ponds to take advantage of the best qualities of both liners.

Liner	Advantages	Disadvantages
Polyvinyl chloride	Higher strength Greater abrasion resistance Good adhesive system Larger size pieces available Greater flexibility No thickness limitation Good crease resistance	Poor sun aging Higher cost Higher shipping weight
Polyethylene	Lower first cost Lower shipping weight	Poorer sun aging No adhesive system Poor abrasion resistance Limited piece size Burial required to prevent "float out" Very stiff, except in thick- nesses under 8 mils Poor crease resistance

Table 58. Comparison of the Properties of Polyvinyl Chloride and Polyethylene Liners<sup>a</sup>

<sup>a</sup>Adapted from Kays (1977) (with permission, see credits).

Rubber liners include butyl, ethylene propylene diene monomer (EPDM), neoprene, and elasticized polyolefin (3110). Hypalon has properties of both the rubber and the plastic liners.

Butyl rubber is considerably more elastic than the plastic liners, and it resists extreme temperatures [-45° to 93°C (-50° to 200°F)] without loss of flexibility or strength. Unfortunately, it is very difficult to make seams in butyl that are stronger than 60% of the strength of the butyl (Clark and Moyer 1974). The EPDM liners are susceptible to shrinkage when exposed to sunlight. Hypalon also tends to shrink, but this is partially controlled by sandwiching Hypalon plies with a reinforcing fabric. Hypalon is one of the most inert liners and thus widely used with caustic wastes. Neoprene is not often used because of its cost and because its special properties are seldom needed. Neoprene has poor sun aging characteristics, especially in desert regions. The 3110 lining is unique because high-quality seams are formed by heat welding, even when the liner is not clean, during a drizzle or through a wide range of air temperatures. Its resistance to chemicals exceeds that of any other common lining system, and it has good resistance to sun aging. Nevertheless, the 3110 liner is relatively new and remains to be field tested. Currently, it is sold with no guarantee (Kays 1977).

#### Stabilization and Final Reclamation of Ash and Sludge Ponds

Land, water, and air quality impacts which accompany ash and sludge disposal at coal-fired power plants can be alleviated by initiation of efficient stabilization and reclamation as soon as is technically feasible. Stabilization is defined as the containment of the ash and sludge

in a manner that minimizes erosion and leaching. Reclamation can be defined as the restoration of the land to a use equal or superior to its prior use [e.g., Wyoming's land quality rules and regulations (Wyoming Land Qual. Div. Dep. Environ. Qual. 1975)].

Very few ash or sludge ponds have yet been reclaimed. A number of fly ash ponds which have reached capacity have subsequently been cleaned out and reused. (Fly ash excavated from these ponds has been used commercially in such functions as structural fills and soil additives. Excess dry fly ash is usually placed in a landfill.) The technology for the reclamation of FGD sludge ponds is under development. In the absence of direct experience with the stabilization and reclamation of ash and sludge ponds, technology can be borrowed from the waste disposal practices of other industries (Dean et al. 1974).

Waste pond stabilization involves contouring the wastes to a stable shape that will not enhance erosion, then covering the wastes with a material which will protect against erosion as well as inhibit the percolation of precipitation. The first step in stabilization is to remove the excess ponded and pore water and to maximize the bearing capacities of the wastes. Optimal moisture contents are in the range of 20-30% for fly ash and 30-60% for FGD sludges (Table 57). In some regions, the waste ponds can be sufficiently dewatered by evaporation and seepage. Ponds located in regions with net precipitative gains, especially when these ponds are lined or contain wastes with low hydraulic conductivities or unusually high capillary forces, may not dewater unless the ponds are constructed with underdrains (Fig. 26).



Fig. 26. Typical Cross Section of a Pond Underdrain Filter. From DiGioia et al. (1977) (with permission, see credits).

Dewatered ash ponds can be graded so that their shape blends with the surrounding topography. Slopes can be adjusted, flattened, and benched to minimize mass wasting (e.g., erosion, landslides, rockfalls) and divert surface water. Perhaps one of the most important functions of pond contouring is to remove all surface depressions which might trap surface water which could seep through the wastes.

Most ash and sludge ponds will probably be covered with soil and revegetated. (Exceptions to this would be the cases where the area would be built upon, paved for a parking lot, or used for some other similar purpose. Construction on an abandoned pond site would require a careful analysis of properties such as bearing capacities and liquifaction potentials. Such construction is not likley to occur except perhaps in regions where available land is extremely scarce.) The soil cover not only protects the wastes from wind and water erosion, but minimizes waste leaching by inhibiting the percolation of precipitation. Clay or other liners may be used as part of the cover in instances where regulatory agencies require the additional protection. Cover thickness depends upon the cover material and the characteristics of the expected vegetation.

The effects of plant root penetration into fly ash are poorly known; fly ash is sometimes used as an agricultural soil additive, but in that case it is mixed with soil which acts as a diluent. Plant growth in pure fly ash--with specific attention to trace-element and radionuclide uptake and subsequent effects on the vegetation, herbivores, and other components of the food chain--has yet to be even partially evaluated. The FGD sludges are often acidic and unconducive to plant growth. For this reason, soil caps may need to be somewhat thicker on sludge ponds than on ash ponds. Revegetation is best done with grasses and plants indigenous to the area; a two-stage reclamation procedure may occasionally be necessary, i.e., start with a rapidly growing, hardy species, followed by more desirable grasses and forbs. In some regions, irrigation may be necessary to aid in revegetation. Wind erosion can be controlled by mulches or chemical additives until roots proliferate.

# Wastes from Coal Cleaning

A primary concern during the evaluation of impacts of the coal slurry pond is the eventual land use of the area. Reclamation of coal-refuse piles and slurry ponds is now required by most states. Pennsylvania regulations, the most stringent in the Appalachian states, are aimed at prevention of coal-waste ignition, abatement of water pollution, and proper construction of piles and lagoons (Natl. Acad. Sci. 1975). Many states, including Kentucky (Edling 1974; Imhoff et al. 1976), have reclamation laws requiring that all toxic, acid-producing, or fire-hazardous material be covered with 1.2 m (4 ft) or more of overburden (Imhoff et al. 1976). The Illinois reclamation law requires that slurry areas must be covered with at least 1.2 m (4 ft) of soil or other suitable material. Acceptable plant cover must then be established. Slurry must be confined in depressed areas bounded by second dams which must be vegetated (Surface-mined Land Conservation and Reclamation Act-1971, as amended by House Bill 1277 and the 78th General Assembly, effective 1 July 1975).

At present, proper construction practices and revegetation seem to be the best methods for mitigating the impacts from gob and slurry areas. Compaction of the waste improves stability and reduces oxygen infiltration, thereby limiting acid production and preventing spontaneous ignition. Proper contouring helps minimize erosion and improves the appearance of the disposal area. Revegetation reduces the threat of combustion, decreases erosion and runoff, increases the stability of the pile, reduces the acid drainage (by reducing the exposure and oxidation of pyrites), and beautifies the landscape (Colgate et al. 1973; Thompson and Hutnick 1971).

Measures for mitigating aquatic impacts are in large part identical with those used to reduce terrestrial impacts. Compaction, proper contouring, and revegetation reduce erosion and runoff. Infiltration to groundwater may be minimized by providing impermeable liners and bases for slurry ponds and gob disposal areas. Mixing fly ash with gob prior to disposal has been reported to bring the pH of drainage to near neutral and to keep metal concentrations at relatively low levels (Martin 1974).

There has been some question about the necessity of 1.2 m (4 feet) of soil or overburden for the successful reclamation of gob and slurry areas. Brundage (1974) reported no visible differences between vegetative cover on gob areas from three to eleven years old covered with 0.3, 0.6, 0.9 or 1.2 m (1, 2, 3, or 4 feet) of soil. When the soil depth was less than 23 cm (9 inches), vegetative cover decreased with soil depth. Other workers are investigating the possibilities of establishing vegetation without using a soil covering. Amendments to gob and slurry such as lime (Davidson 1974, Sorrel 1974, Czapowskyj and Sowa 1976) or fly ash (Capp and Gilmore 1974) along with fertilizer and mulch are being tested with success.

#### EROSION AND DUST CONTROL

#### Wind Erosion

Dust sources at a coal-fired power plant include the coal stockpiles, all coal-handling procedures and machinery, dirt haul roads, all unprotected earth surfaces such as pond embankments, and dried ash and sludge. Protection against wind erosion follows two lines of reasoning: (1) anything the wind cannot reach will not blow, and (2) particles too heavy to be transported by the wind will not blow. The application of water is the most common dust suppression method. Other methods include compaction, surface contouring, wind breaks, mulching, vegetation, riprap, and chemical application.

<u>Coal stockpiles</u>. Coal stockpiled for future plant use not only may erode but also has the potential for spontaneous combustion if the oxygen and heat conditions are right. Chances for spontaneous combustion are reduced by compacting the coal deposits at or near the optimum water content. This technique also tends to slightly lessen the possibility of wind and water erosion of the coal. Coal stockpiles are temporary structures, and erosion protection by covering is not practical. Sprinkling with water and the proper positioning of wind breaks and "snow fences" provide the best dust control. Keeping the coal relatively moist also cuts down on the dust created during handling.

<u>Haul roads</u>. Dust due to truck traffic on dirt haul roads can be mitigated by keeping the dirt roads damp and, if necessary, by paving any roads where the dust problem is consistently severe. Sometimes even careful selection of the routes of haul roads will lessen the amount of dust created.

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<u>Embankments</u>. Dust may also be generated from unstabilized embankments of cooling-water lagoons and waste-disposal ponds. Mitigation usually involves covering the surface, and vege-tation is the most aesthetic and probably also one of the most effective covers. Prior to the establishment of a vegetative cover, wind erosion is usually prevented by a mulch of straw, bark, or similar substance, or by a chemical which allows seeds to receive the water and air necessary for germination. Chemicals may be used alone as stabilizing agents, but a vegetative cover is preferred for its permanence and aesthetics.

<u>Ash and sludge surfaces</u>. Ash and sludge surfaces do not present a dust blowing hazard unless they are dry. Capillary forces in an active sludge pond are very efficient in keeping sludges moist even when they are not covered by free water. Usually the most efficient mitigative procedure is to spray water over these wastes. The only exception comes upon abandonment, when dewatering and permanent stabilization is the goal. During the dewatering period, the ash or sludge waste may be covered with a thin layer of gravel, coarse sand, or other permeable material which allows surface evaporation but prevents dust blowing.

#### Water Erosion

Water erosion may occur by sheet, gully, or stream erosion on the coal stockpiles, dirt roads, cooling-lagoon embankments, waste-pond embankments, or anywhere around the power plant where the energy of moving water is great enough to transport sediment. Water may also cause internal erosion of the lagoons and ponds if care isn't taken to prevent piping. Mitigation of surface erosion involves decreasing the likelihood of large volumes of rapidly moving water from coming into contact with highly erodable surfaces. This can be done by proper routing of runoff and drainage, reducing slopes, covering the erodible sediment, or increasing the particle size on the erodible surface (Beasley 1972; USEPA 1973; U.S. Nucl. Reg. Comm. 1977). Original site selection is important in determining the ease with which protection against water erosion can be accomplished. Riprap, filters, mulches, vegetation, and chemical additives (including all the cover materials which inhibit wind erosion) are all good covers for short-term erosion protection. A self-perpetuating vegetation is expected to provide the most efficient long-term erosion protection. Most chemical additives currently available are effective for only a few years.

Granular filters are the best protection against internal erosion and piping failure in ponds and lagoons. They are particularly well suited for preventing piping in embankments that are constructed of fine-grained, low-cohesion soils, or which contain an interface between a fine- and coarse-grained material. A filter consists of a granular soil of a known particle-size distribution. It is more coarse and pervious than the fine-grained soil it is placed next to to protect, but it is not so pervious that it will permit the fine-grained particles of the adjacent soil to be transported through it. Filters are designed according to the grain-size distribution of the soil to be protected. [According to accepted soil mechanics practices, grain-size distributions are commonly displayed on cumulative curves which correlate grain sizes (particle diameters) with the percentage of that soil (by weight) which is finer than those sizes. The curves are used by identifying grain sizes corresponding to various predetermined percentages. The term D<sub>n</sub> identifies the grain diameter at which n% of the particular soil is finer and (100-n)% of the soil is coarser.] Design criteria are listed below (Williams 1975). In instances where the grain-size differences between adjacent soils are large, a series of several filters, each protecting the adjacent filter, may be necessary.

- 1.  $\frac{D_{15} \text{ filter}}{D_{85} \text{ protected soil}} \leq 5$ . This assures that the filter will contain enough finegrained particles to keep the pore sizes small enough to prevent any significant volume of the soil to be protected to be transported through the filter.
- 2.  $\frac{D_{50} \text{ filter}}{D_{50} \text{ protected soil}} \le 25$ . This, in conjunction with the first criterion, assures that the filter is not too coarse to protect the other soil.
- 3.  $\frac{D_{15} \text{ filter}}{D_{15} \text{ protected soil}} \ge 5$ . This assures that the fine-grained particles of the filter are not as fine-grained as those of the soil to be protected. It helps assure that the filter is more coarse than the protected soil.
- 4. The filter should not be gap graded. In other words, each of the grain sizes incorporated in the filter should be relatively equally represented. This assures that no critical grain size will be missing from the filter.

- 5.  $D_5$  filter > 0.074 mm (this is the 200 mesh screen-hole size). Fines should be cohesionless. This assures that the filter will be permeable, not a seepage barrier.
- 6.  $\frac{D_{6.0} \text{ filter}}{D_{1.0} \text{ filter}} \leq 20$ . This puts an upper limit on the allowable range in grain

sizes within the filter.

Ponds and lagoons may also have a surface erosion problem due to wave action on the embankments. A riprap surface is known to be very effective in alleviating this problem. It is better than vegetation because plant growth is difficult to establish in a wave zone; also, vegetation may produce a zone of weakness if the embankment is subsequently raised by upstream construction.

### REFERENCES

- Beasley, R. P. 1972. Erosion and Sediment Pollution Control. Iowa State University Press, Ames, Iowa. 320 pp.
- Brundage, S. S. 1974. Depth of soil covering refuse (gob) vs. quality of vegetation, pp. 183-185. In F. J. Wobber et al., Survey of Coal Refuse Banks and Slurry Ponds for the Indiana State Legislature Using Aerial and Orbital Inventory Techniques. First Symposium on Mine and Preparation Plant Refuse Disposal, National Coal Association, Washington, D. C.
- Capp, J. P., and D. W. Gilmore. 1974. Fly ash from coal burning power plants: an aid in revegetating coal mine refuse and spoil banks, pp. 200-211. In F. J. Wobber et al., Survey of Coal Refuse Banks and Slurry Ponds for the Indiana State Legislature Using Aerial and Orbital Inventory Techniques. First Symposium on Mine and Preparation Plant Refuse Disposal, National Coal Association, Washington D. C.
- Cavallaro, J. A., M. T. Johnson, and A. W. Deurbrouck. 1976. Sulfur reduction potential of the coals of the United States. U.S. Bur. Mines Rep. Invest. 8118. 323 pp.
- Clark, D. A., and J. E. Moyer. 1974. An Evaluation of Tailings Ponds Sealants. EPA-660/2-74-065; PB-235 929. Prepared by Robert S. Kerr Environmental Research Lab., Ada, Oklahoma, for U.S. Environmental Protection Agency, Washington, D. C. 35 pp.
- Colgate, J. L., D. J. Akers, and R. W. Frum. 1973. Gob Pile Stabilization, Reclamation and JUtilization. Rep. No. 75, Interim Rep. No. 1. Office of Coal Research, U.S. Department of the Interior, Washington, D. C. 127 pp.
- Cunningham, J. A., R. G. Lukas, and T. C. Anderson. 1977. Impoundment of fly ash and slag--a case study, pp. 227-245. In Geotechnical Practice for Disposal of Solid Waste Materials. ASCE Specialty Conference of the Geotechnical Engineering Division, American Society of Civil Engineers, New York.
- Czapowskyj, M. M., and E. A. Sowa. 1976. Lime helps establish crown-vetch on coal-breaker refuse. U.S. For. Serv. Res. Pap. No. NE-348. Northeastern Forest Experimental Station, Upper Darby, Pa. 6 pp.
- Davidson, W. H. 1974. Reclaiming refuse banks from underground bituminous mines in Pennsylvania, pp. 186-199. In F. J. Wobber et al., Survey of Coal Refuse Banks and Slurry Ponds for the Indiana State Legislature Using Aerial and Orbital Inventory Techniques. First Symposium on Mine and Preparation Plant Refuse Disposal, National Coal Association, Washington D. C.
- Dean, K. C., R. Havens, and M. W. Glantz. 1974. Methods and costs for stabilizing fine-sized mineral wastes. U.S. Bur. Mines Rep. Invest. 7896. 26 pp.
- DiGioia, A. M., J. F. Meyers, and J. E. Niece. 1977. Design and construction of bituminous fly ash disposal sites, pp. 267-284. <u>In</u> Geotechnical Practice for Disposal of Solid Waste Materials. ASCE Specialty Conference of the Geotechnical Engineering Division, American Society of Civil Engineers, New York.

Edling, R. J. 1974. Kentucky (western), pp. IV-1 to IV-130. In R. P. Carter et al., Surface Mined Land in the Midwest: A Regional Perspective for Reclamation Planning. ANL/ES-43. Argonne National Laboratory, Argonne, Ill.

- Hagerty, D. J., C. R. Ullrich, and B. K. Thacker. 1977. Engineering properties of FGD sludges, pp. 23-40. In Geotechnical Practice for Disposal of Solid Waste Materials. ASCE Specialty Conference of the Geotechnical Engineering Division, American Society of Civil Engineers, New York.
- Haxo, H. E., Jr. 1976. Evaluation of selected liners when exposed to hazardous wastes, pp. 102-111. <u>In</u> Residual Management by Land Disposal, Proceedings of the Hazardous Waste Research Symposium. PB-256 768. University of Arizona, Tuscon.
- Heitner, K. L. 1977. Air pollution assessments of new fossil energy technologies. J. Air Pollut. Control Assoc. 27(12):1173-1177.
- Imhoff, E. A., T. O. Friz, and J. R. LaFevers. 1976. A guide to state programs for the reclamation of surface mined areas. U.S. Geol. Surv. Circ. No. 731. 33 pp.
- Jones, J. W. 1976. Research and development for control of waste and water pollution from flue gas cleaning systems, pp. 579-604. <u>In</u> Proceedings of the Symposium on Flue Gas Desulfurization--New Orleans, Vol. II.
- Kays, W. B. 1977. Construction of Linings for Reservoirs, Tanks, and Pollution Control Facilities. John Wiley & Sons, New York. 379 pp.
- Lamb, D. W., W. Herrmann, and J. Pizzella. 1976. Fly ash as construction material for water retaining structures, pp. 369-379. <u>In</u> Ash Utilization, Proceedings of the Fourth International Ash Utilization Symposium, St. Louis, Mo., March 24-25. MERC/SP-76/4. U.S. Energy Research and Development Administration, Morgantown Energy Research Center, Morgantown, W. Va.
- Lambe, T. W., and R. V. Whitman. 1969. Soil Mechanics. John Wiley and Sons, Inc., New York. 553 pp.
- Leavitt, J. M., L. A. George, and R. E. Clark. 1976. Sulfur dioxide emission limitation (SDEL) program at TVA power plants. J. Air Pollut. Control Assoc. 26(12):1133-1140.
- Martin, J. F. 1974. Coal refuse disposal in the eastern United States. <u>In</u> News of Environmental Research in Cincinnati/Industrial Waste Treatment Research. U.S. Environmental Protection Agency. 4 pp.
- National Academy of Sciences. 1975. Underground Disposal of Coal-Mine Wastes: A Report to the National Science Foundation. Study Committee to Assess the Feasbility of Returning Underground Coal Mine Wastes to Mined-Out Areas, Washington, D. C. 172 pp.
- Poellot, J. H., and W. J. Curtis. 1977. Jarrett Branch industrial waste landfill--a case history, pp. 283-300. <u>In</u> Geotechnical Practice for Disposal of Solid Waste Materials. ASCE Specialty Conference of the Geotechnical Engineering Division, American Society of Civil Engineers, New York.
- Sorrell, S. T. 1974. Establishing vegetation on acidic coal refuse materials without use of topsoil cover, pp. 228-236. <u>In</u> F. J. Wobber et al., Survey of Coal Refuse Banks and Slurry Ponds for the Indiana State Legislature Using Aerial and Orbital Inventory Techniques. First Symposium on Mine and Preparation Plant Refuse Disposal, National Coal Association, Washington, D. C.
- Srinivasan, V., G. H. Beckwith, and H. H. Burke. 1977. Geotechnical investigations of power plant wastes, pp. 169-187. <u>In</u> Geotechnical Practice for Disposal of Solid Waste Materials. ASCE Specialty Conference of the Geotechnical Engineering Division, American Society of Civil Engineers, New York.
- Strom, G. H. 1976. Transport and diffusion of stack effluents, pp. 401-501. <u>In</u> A. C. Stern (ed.), Air Pollution, 3rd ed. Vol. 1, Air Pollutants, Their Transformation and Transport. Academic Press, New York.
- Thompson, D. N., and R. J. Hutnick. 1971. Environmental Characteristics Affecting Plant Growth on Deep-mine Coal Refuse Banks. Spec. Res. Rep. No. SR-88. College of Agriculture, Pennsylvania State University, University Park, Pa. 81 pp.
- U.S. Environmental Protection Agency. 1973. Processes, Procedures and Methods to Control Pollution Resulting from All Construction Activity. EPA 430/9-73-007. Washington, D.C. 234 pp.

- U.S. Nuclear Regulatory Commission. 1977. Draft Environmental Standard Review Plans for Environmental Review of Construction Permit Applications for Nuclear Power Plants, Parts I, II, III. NUREG-0158. Office of Nuclear Reactor Regulation. 3 v. (various pagings).
- Walker, F. E., and F. E. Hartner. 1966. Forms of sulfur in U.S. coals. U.S. Bur. Mines Inf. Circ. 8301. 51 pp.
- Williams, R. E. 1975. Waste Production and Disposal. Miller Freeman Publications, Inc., San Francisco. 489 pp.
- Wyoming, Land Quality Division, Department of Environmental Quality. 1975. Land Quality Rules and Regulations. Cheyenne.

# CONVERSION OF OIL- OR GAS-FIRED ELECTRIC GENERATING STATIONS

Previous chapters have addressed the features and impacts which are specific to operating coal-fired electric generating plants. Existing oil- or gas-fired electric generating stations may be prohibited from burning petroleum products or natural gas as required by the Energy Supply and Environmental Coordination Act of 1974 (ESECA), 15 U.S.C. § 791 et seq., as amended by the Energy Policy and Conservation Act of 1975 (EPCA), PL 94-163 (Fed. Energy Admin. 1977c). The fuel substitute in most cases would be coal. Before prohibiting power plants from burning petroleum products or natural gas, it must be first found that:

1. The power plant had on 22 June 1974, or thereafter, acquired or was designed with the necessary plant equipment and capability to burn coal, or has been required to meet a design and construction requirement under ESECA.

2. Issuance of a prohibition order is practicable and consistent with the purposes of ESECA.

3. Coal and coal transportation facilities will be available during the period the prohibition order will be in effect.

4. The prohibition order will not impair the reliability of service in the area served by the power plant.

It seems apparent that in the near future certain existing power plants will convert from burning oil or gas to coal. This chapter addresses the unique impacts of conversion by (1) presenting a general description of both oil- and gas-fired power plants, (2) delineating those features of each which are different from coal combustion, (3) briefly discussing the major impacts associated with those contrasting features, (4) identifying the major power plant changes required to convert to coal, and (5) discussing the impacts that are specific to conversion.

# DESCRIPTION OF A TYPICAL OIL-FIRED PLANT

The energy flow and the water/steam cycle in an oil-fired plant are the same as in a coalfired plant (Figs. 1 and 3, respectively), with the exception that oil, rather than coal, supplies the chemical energy that is converted into heat by combustion in the boiler. Oil arrives at an oil-burning plant by barge or pipeline and is pumped into onsite storage tanks. To overcome the serious hazard from oil storage-tank failure, the oil is stored in underground tanks or in cofferdam-surrounded tanks on the surface.

### Fuel Oil Requirements

Typically, oil-burning electric power plants burn No. 6 oil--the heaviest of the fuel oils--due to its low cost relative to the lighter oils. Number 6 oil is fairly viscous. To facilitate pumping the oil, storage and transportation facilities are usually equipped with heating equipment. The heaters, storage tanks, and piping for heavy oils need to be periodically cleaned due to fouling and sludge formation.

The amount of fuel oil consumed per day by an oil-burning plant, i.e., its daily fuel oil requirement (DFOR), is given by the formula:

$$DFOR \left(\frac{gallon}{day}\right) = \left(\frac{P}{100}\right) C(MW) \times 10^3 \frac{kW}{MW} \times 24 \frac{hr}{day} \times 3412 \frac{Btu}{kW \cdot h} \times \frac{100}{E} \times \frac{1}{B_{fo}} \frac{gal}{(Btu)}$$
(22)

where P is the capacity or plant factor in %, C is the capacity of the plant in megawatts (MW), and E is the efficiency of the plant in % (see p. 13 for more complete definitions).  $B_{fo}$  is the heat content, in Btu, of one gallon of fuel oil.

DFOR (in gallons/day) is presented in Table 59 for various plant capacities. [The quantities in gallons/day can be converted to barrels/day by using the conversion factor: 1 gallon = (1/42) barrel.] The table assumes the use of a No. 6 fuel oil having a relatively high sulfur content (3.5% by weight). The sulfur content of No. 6 oil varies from 0.7 to 3.5% (Babcock and Wilcox Co. 1972).

Plant size	Fuel oil c	onsumed <sup>b</sup>		Lime or limeston		ne required	(MT/day) <sup>C</sup>
(MWe)	(liters/day)	(gal/day)			Lime	Limestone	•
100	390,000	103,000	· · · · · · · · · · · · · · · · · · ·		23.7	52.8	
350	1,370,000	362,000			83.1	185	
700	2,740,000	724,000			166	371	
2100	8,215,000	2,170,000			498	1116	

Table 59. Estimated Fuel Oil and Lime or Limestone Requirements for Oil-Burning Power Plants of Various Sizes<sup>a</sup>

 $^{a}_{L}$ The plants are assumed to have a 38% efficiency and to operate at 70% capacity.

No. 6 fuel oil with 145,800 Btu/gal, 0.3% ash, 1% water, 3.5% sulfur, and a density of 8.1 lb/gal. Determined from the corresponding daily fuel-oil requirements. The scrubber is assumed to

have an 85% SO<sub>2</sub> removal efficiency, and No. 6 fuel with a 3.5% (by weight) sulfur content is assumed.

#### Lime Requirements

With lime scrubbing, typically 1.2 atoms of calcium are supplied to the scrubber for each sulfur atom removed from the stack gas. Using this number, and assuming that the scrubber removes 85% of the SO<sub>2</sub> passing through it, the quantity of lime/day required by the scrubber, i.e., the daily lime requirement (DLR<sub>fo</sub>) for a fuel-oil-fired plant, is given by:

$$DLR_{fo} (tons/day) = DFOR \left(\frac{gallons}{day}\right) \times 8.1 \frac{1b}{gal} \times \frac{1 ton}{2000 lb} \times \frac{(\% sulfur in oil)}{100} \times \frac{85}{100} \times \frac{56 (mol. wt. Ca0)}{32 (at. wt. S)} \times 1.2 = 7.23 \times 10^{-3} DFOR \left(\frac{gallons}{day}\right) \times \frac{(\% sulfur in oil)}{100} .$$
(23)

 $DLR_{fo}$  values are presented in Table 59 for an oil having a sulfur content of 3.5% by weight.

#### Limestone Requirements

In limestone scrubbing, the removal of one S atom from the flue gas typically requires an input of 1.5 Ca atoms into the scrubber. With this number, and again with the scrubber having an 85% SO<sub>2</sub> removal efficiency, the amount of limestone required by the scrubber per day, i.e., the daily limestone requirement (DLSR<sub>fo</sub>) for a fuel oil-fired plant, is given by:

$$DLSR_{fo} (tons/day) = DFOR (\frac{gallons}{day}) \times 8.1 \frac{1b}{gal} \times \frac{1 ton}{2000 lb} \times \frac{(\% sulfur in oil)}{100} \times \frac{85}{100} \times \frac{100 (mol. wt. CaCO_3)}{32 (at. wt. S)} \times 1.5 = 16.14 \times 10^{-3} DFOR (\frac{gallons}{day}) \frac{(\% sulfur in oil)}{100} .$$
 (24)

Values of  $\text{DLSR}_{fo}$  are also presented in Table 59 for a sulfur content of 3.5% by weight.

#### Water Requirements

Water is needed for cooling in the lime/limestone scrubbing system and, possibly, for the conversion of combustion ash into a slurry. The amount of cooling water needed is essentially independent of the fuel burned, provided that plant power output, plant efficiency, type of cooling system, and temperature of the cooling water are held constant and assuming zero moisture content in the fuel.

#### Boilers in an Oil-Fired Plant

The oil is injected into the boiler by burners located in side walls of the boiler combustion chamber (furnace). Each burner also injects air, and the air and oil streams become thoroughly mixed within the furnace. In modern boilers the oil must be introduced at high rates. To accomplish this, each burner contains an atomizer which sprays the oil into the furnace as a fine mist. The atomizing process yields a high surface/volume ratio, allowing extensive contact with the combustion air and thereby promoting prompt ignition and rapid combustion. For proper atomization, No. 6 oil must be heated to 95-105°C (200-220°F).

The two most widely utilized systems for atomizing the oil are steam or air atomizers and mechanical atomizers. A steam (or air) atomizer operates by creating a steam-fuel (or air-fuel) emulsion, which upon release into the furnace atomizes the oil by the rapid expansion of the steam (or air). In mechanical atomizers, the pressure of the fuel itself causes the oil to atomize

As with coal-fired units, oil-fired boilers utilize superheaters, reheaters, etc., to increase thermal efficiency.

# Stack-Gas Cleaning in an Oil-Fired Plant

The percentage, by weight, of sulfur in No. 6 fuel oil can range up to 3.5 (Babcock and Wilcox Co. 1972). This percentage is identical to that of high-sulfur Illinois coal. Because of this, oil-fired plants may have SO<sub>2</sub> scrubbing systems.

The problem of  $NO_x$  emissions is controlled most effectively by modifying the combustion process, similarly to that discussed for coal combustion.

The ash content of No. 6 fuel oil (0.01-0.5%) may require the use of particulate removal equipment such as electrostatic precipitators.

Stack-gas emissions for oil-fired plants of various sizes are presented in Table 60.

		Emissions (MT/day)							
Plant ciro	Partic	Particulates		02		N	D <sub>X</sub>		
(MWe)	0i1 <sup>b</sup>	Gas	0il <sup>c</sup>	Gas <sup>d</sup>	•	0il <sup>e</sup>	Gas <sup>f</sup>		
100	0.7	0	2.3	0		2.4	2.0		
350	2.6	0	8.0	0		8.4	6.9		
700	5.4	0	16.0	0		16.8	13.6		
2100	16.0	0	47.9	0		50.8	40.8		

Table 60. Stack-Gas Emissions from Oil- and Gas-Fired Power Plants of Various Sizes<sup>a</sup>

<sup>a</sup>Assumes a plant having a 38% efficiency and operating at 70% capacity.

Assumes an ash content of 0.2% and no particulate removal.

Assumes a sulfur content of 2%, by weight, and an 85% scrubber removal efficiency. Assumes Ohio gas which has 0.34% sulfur, by weight, is not used. Based on 700 lb NO<sub>X</sub> per 10<sup>9</sup> Btu heat input (Brown et al. 1974), plus combustion modifications which reduce NOx formation by a factor of two.

Based on 574 lb  $NO_X$  per 10<sup>9</sup> Btu heat input (Brown et al. 1974), plus combustion modifications which reduce  $NO_X$  formation by a factor of two.

# DESCRIPTION OF A TYPICAL NATURAL-GAS-FIRED PLANT

The energy flow and the water/steam cycle for a natural-gas-fired power plant are the same as in a coal-fired plant (Figs. 1 and 3, respectively), except that natural gas, rather than coal, supplies the chemical energy that is converted into heat. Natural gas typically arrives at the power plant by pipeline and is fed by the onsite piping system to the boilers. Fluctuations in boiler demand can be accommodated by controlling the gas pressure in the boiler supply pipeline. Gas storage tanks are unnecessary (Babcock and Wilcox Co. 1972).

#### Natural Gas Requirements

The quantity of natural gas consumed per day by a natural-gas-burning plant, i.e., its daily natural gas requirement (DNGR), is given by the expression:

DNGR (cubic feet/day) =

$$\left(\frac{P}{100}\right) C(MW) \times 10^3 \frac{kW}{MW} \times 24 \frac{hr}{day} \times 3412 \frac{Btu}{kW \cdot h} \times \frac{100}{E} \times \frac{1 \text{ cubic foot nat. gas}}{B_{ng} (Btu)}$$
 (25)

where P, C, and E are the same as defined above and on page 13. B<sub>ng</sub> is the Btu content of one cubic foot of natural gas. Generally, natural gas contains negligible quantities of sulfur and no cubic force of natural gas. ash; hence, emission control devices are unnecessary. The DNGR's (in cubic feet/day) for various

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plant sizes are  $15.1 \times 10^6$  (100 MWe),  $52.8 \times 10^6$  (350 MWe), 106 (700 MWe), and  $317 \times 10^6$  (2100 MWe). [These data are for natural gas with 1000 Btu/ft<sup>3</sup> (at 60°F and 30 inches Hg) and 0% sulfur.]

#### Water Requirements

With a natural-gas-fired plant, water is needed only for cooling. The quantity required is essentially the same as for a coal- or fuel-oil-fired plant having the same power output, plant efficiency, type of cooling system, and cooling water temperature.

#### Boilers in a Natural-Gas-Fired Plant

Gas and air are introduced into the boiler combustion chamber by the burner, which provides the turbulence necessary to ensure complete mixing of the gas with the air.

Above the combustion chamber, the boiler contains the same components (superheaters and reheaters, etc.) as a pulverized-coal-fired boiler.

#### Stack-Gas Cleaning in a Natural-Gas-Fired Plant

Natural gas is "clean burning," that is, does not produce particles (fly ash) or  $SO_X$ . It does produce  $NO_X$ , however, but no process for removing  $NO_X$  from the stack gas has yet been fully developed (Shimizu et al. 1975). Stack-gas emissions for gas-fired power plants of various sizes are presented in Table 60.

# FEATURES OF OIL- OR GAS-FIRED ELECTRIC GENERATING PLANTS THAT ARE DIFFERENT FROM A COAL-FIRED PLANT

Differences between coal-fired and oil- or gas-fired electric generating plants occur mainly in (1) handling and storage of the fuel, (2) boiler size, and (3) quantity and type of combustion products. There are usually no major differences in other environmentally important aspects of power stations. For example, siting requirements are, in general, similar for all three types of power plants because all require a source of cooling water; land for power plant facilities, fuel storage, and waste disposal (the latter with the exception of gas-fired stations); proximity to major transportation routes; and electric-power transmission lines. The following discussion, therefore, concerns only the three major differences enumerated above.

## Fuel Handling

The Collins Generating Station near Chicago provides an illustration of how fuel oil is handled (Fig. 27). Oil arriving by barge at the 2500 MWe (proposed) oil-burning Collins Station is heated to reduce its viscosity and then pumped from the barges to a floating roof-type surge tank (U.S. Army Engineer District 1975). From the surge tank the oil is pumped by another set of pumps from the main storage tanks to the boilers. The oil is also heated in the surge tank, in the storage-tank-to-storage-tank piping, and in the storage-tank-to-boiler piping (U.S. Army Engineer District 1975).

Natural gas arrives at a gas-burning plant by pipe and is fed by the onsite piping system to the boilers at a controlled rate.

In comparison, at a large coal-burning plant, the coal is moved by conveyor from the plant's receiving facility to live storage, and again by conveyor from live storage to crusher to surge bin and thence to the silos feeding the boiler (Fig. 4). With pulverized-coal firing, the coal from the silos is pulverized, mixed with air (the primary air), and pumped as a fluid to the boiler burners. Dust, an important feature of coal-burning plants, is removed from the coal in the surge bin. Due mainly to coal dust, coal-fired plants are relatively dirty compared to their oil- or gas-burning equivalents.

#### Fuel Storage

Fuel oil is stored in large aboveground or underground tanks at the plant site. Natural gas is similarly stored, although many gas-burning plants do not have storage tanks, but rely instead on the storage capabilities of the pipeline system which delivers gas to the plant. Coal is stored in a large pile, sometimes 15 m (50 ft) high and extending over many acres. The approximate area required for storage and handling of coal, fuel oil, and natural gas is shown in Table 61 for three 700-MWe power plants fired respectively by the three fuels.

If only the Btu content of coal (e.g., subbituminous coal) vs. that of fuel oil (11,400 Btu/lb vs. 18,000 Btu/lb) is considered, the oil storage/handling area for an oil-burning plant would be expected to be smaller than the coal storage/handling area for a coal-burning plant. This is not the case, however, because each oil tank must be surrounded by a large open space bounded by a cofferdam. Thus, the fuel storage/handling area is actually larger for the oil-fired plant than for the coal-fired one, as seen in Table 61.

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Figure 27. Proposed Layout of an Oil-Fired Generating Station and Ancillary Facilities (Collins Station, Illinois). Modified from U.S. Army Engineer District (1975).

	Area requirements							
	Coal-fired plant		Fue fire	l-oil- d plant_	Natural-gas- fired plant			
Components	(ha)	(acres)	(ha)	(acres)	(ha)	(acres)		
Fuel storage, handling	3.6	8.9	5.1	12.6	0.3	0.8		
Power generation	0.8	2.0	0.6	1.6	0.6	1.5		
Waste heat dispersal (Cooling towers)	6.5	16	6.5	16	6.5	16		
Waste handling	3.1	7.6	1.3	3.2	0	0		
Total	14.0	34.5	13.5	33.4	7.4	18.3		
Area permanently disturbed <sup>b</sup>	101	250	97	240	89	220		

Table 61. Approximate Area Requirements for Three 700-MWe Power Plants--One Fired by Coal, One by Fuel Oil, and One by Natural Gas<sup>a</sup>

<sup>a</sup>Data are based on Table 4 (for the coal-fired plant); Federal Energy Administration (1977a, 1977b); and on staff communications with personnel of the Commonwealth Edison Company, Chicago.

Commonwealth Edison Company, Chicago. <sup>D</sup>Includes roads, parking areas, switchyards, landscaping, etc., not included in the rest of the table.

#### Boiler Design

Fuel--whether oil, gas, or pulverized coal--enters the furnace via the burner. Circular and cell burners, the most widely used types, can be equipped to fire any one, any two, or all three of these fuels.

For the same output in kilograms per hour of hot steam at a given temperature per hour, a pulverized-coal boiler must be significantly larger than an oil- or gas-fired unit (Witkowski 1977), as shown in Figure 28.

Sootblowing equipment is unnecessary in gas-fired boilers, but must be utilized in boilers fired with oil or pulverized coal (Babcock and Wilcox Co. 1972). The spacing of the superheater tubes may be greater in a pulverized-coal boiler than in an oil- or gas-fired unit (Witkowski 1977).



Figure 28. Re

 Relative Comparison of Furnace Sizes for Gas, Oil, Bituminous Pulverized Coal, and Lignite Pulverized Coal. From Witkowski (1977).

#### **Combustion Products**

Ash. Natural-gas burning does not produce ash. Ash hoppers, ash handling equipment, ash pits, and fly ash control systems are thus unnecessary using this fuel.

The ash content in residual fuel oil is usually 0.2% or less, compared to 6 to 10% in coal (Babcock and Wilcox Co. 1972). As a result, oil-fired boilers do not require ash hoppers and ash pits. Fly ash removal equipment is not generally required (Witkowski 1977), although such equipment is utilized at some oil-burning plants (Miller 1977, personal communication).

In contrast, coal-burning power plants produce large quantities of bottom ash (withdrawn at the bottom of the furnace) and fly ash (entrained in the flue gas). The fly ash must be extracted from the flue gas by a particulate control device, usually an electrostatic precipitator or wet scrubber. The bottom ash is converted to a slurry and the fly ash removed from the control device in dry form, or both types of ash can be slurried. The ash slurry is piped to a settling pond, which requires considerable land.

<u>Nitrogen oxides</u>. Oxides of nitrogen are produced by gas-, oil-, and coal-fired power plants, with the NO<sub>X</sub> emission rate being lowest for gas and highest for coal (Shimizu et al. 1975). Gaseous emission products from oil, gas, and coal combustion are presented in Table 62.

<u>Sulfur dioxide</u>. Generally, natural gas from U.S. wells contains negligible sulfur (Babcock and Wilcox Co. 1972). Hence, gas-fired plants do not produce  $SO_2$ .

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	Products released (1b/10 <sup>6</sup> Btu)						
Emission product	Fuel oil <sup>b</sup>	Natural gas <sup>C</sup>	Bituminous coal <sup>d</sup>				
Particulates	0.06	0.015	2.86				
Carbon monoxide	0.02	0.017	0.04				
Sulfur dioxide	3.81	0.0006	1.36				
Sulfur trioxide	0.05	ante d'al la companya de la company Reference de la companya de la compa	-				
Nitrogen oxides	0.73	0.6	0.64				
Hydrocarbons	0.01	0.001	0.01				
Aldehydes	0.007	<del>.</del>	0.00018				

Table 62. Gaseous Emission Products from Oil, Natural Gas, and Coal Combustion<sup>a</sup>

<sup>a</sup>Data derived from USEPA (1973a) and represent emission products in the absence of pollution abatement equipment. A hyphen indicates data not provided. <sup>b</sup>Assumed heat content = 18,000 Btu/1b, 8 lb oil/gal oil, sulfur content = 3.5%. <sup>c</sup>Assumed 1000 Btu/ft<sup>3</sup>.

Assumed 14,000 Btu/1b ( $30.8 \times 10^6$  Btu/MT), 5% ash, sulfur content = 1%.

The No. 6 fuel oil can have a fairly high sulfur content--up to 3.5%. (High-sulfur Illinois coal has typically a 3.5% sulfur content.) Oil-fired plants must either burn oil with a low sulfur content or utilize flue-gas desulfurization (FGD) systems. The most widely used FGD systems require lime or limestone as input and produce lime or limestone sludge as an output. Such systems require both a storage area for the input lime or limestone and landfill area for the output sludge.

Coal-fired plants must either burn low-sulfur coal or use an FGD process. Lime or limestone scrubbing systems in coal-burning plants can produce large quantities of sludge, requiring a sizable area for landfill (see Table 48).

# GENERAL DISCUSSION OF IMPACTS ASSOCIATED WITH FEATURES OF OIL- OR GAS-FIRED ELECTRIC GENERATING PLANTS THAT ARE DIFFERENT FROM A COAL-FIRED PLANT

Impacts to the natural environment associated with the handling and storage of oil or natural gas, and by-products of their combustion, are briefly described below.

#### Fuel Handling and Storage

Although an oil storage/handling area for an oil-burning plant is essentially the same size as the coal storage/handling facility for a coal-fired station, the impacts to biota are expected to be less severe from the former than from the latter. An oil storage facility is surrounded by open space bounded by a cofferdam; for example, at the oil-fired station shown in Figure 27, each oil storage tank is situated in the center of about 2.3 ha of land (the total oil storage area for four tanks of No. 6 oil and two tanks of No. 2 oil was about 14 ha or 35 acres). This open area around the oil storage tanks is available for the establishment of herbaceous vegetation and wildlife habitation. On the other hand, coal storage yards encompass several hectares of land which are precluded from vegetation and wildlife use. Additional land at oil-fired stations is usually required for retention basins to catch oil from spills and leaks as well as other runoff from the immediate vicinity of the storage tanks.

At oil-fired power plants, the potential exists for impacts from oil spills during transfer and storage of the oil. Leaks from lines, storage-tank levees, and/or barge washing can result in oil contamination of land and water. Lighter fractions are likely to become aerosolized whereas heavier portions penetrate the soil surface.

The impacts of oil contamination (spills) on terrestrial ecosystems are not expected to be long-term. The actions of more than 100 species of bacteria, yeasts, and molds which are known to attack hydrocarbons (Wein and Bliss 1973) will improve oil-contaminated soil within a few years so that normal vegetative production can occur. Although such compounds as iron and aluminum may accumulate in the soil due to increased microbial activity, nutrients may be released resulting in stimulated plant growth (Wein and Bliss 1973). Straight-chain hydrocarbons tend to be less toxic to vegetation than are olefins, naphthalenes, and aromatic compounds. In general, the smaller molecules within these groups tend to be the most phytotoxic (Van Overbeek and Blondeau 1954). Baker (1970) has summarized the literature on physiological effects of various oils on plants. Methods utilized to reclaim oil-spill areas on land include increasing the soil microbiota by cultivation and fertilization, "seeding" with the appropriate micro-organisms, and burning the oil (Schwendinger 1968).

Aquatic ecosystems can be severely affected by oil spills. During an oil spill accident, oil is released and initially floats on the water surface. Volatile components evaporate, but other components of oil or products of oil degradation are soluble in water. Some of these soluble components can coat fish gills and interfere or prohibit oxygen exchange (Battelle Northwest Lab. 1967). In water with marginal oxygen content (much below saturation), both the gill-coating effect and increased biological oxygen demand may cause fish kills by suffocation. The heavier components of oil sink. On the river bottom, an oily sludge may smother benthos or adversely affect invertebrates due to reductions in food sources (McCauley 1966). Algae are destroyed by oil due to interference with photosynthesis and the direct toxic effects of some oil components, including naphthenic acids, mercaptans, and phenols (U.S. Army Engineer District 1975).

# Combustion Byproducts

Until the advent of electrostatic precipitators, greater amounts of particulates were emitted from coal combustion than from oil combustion. Nitrogen oxide emissions, however, are higher for an oil-fired than for a coal-fired power plant (see Table 62). Stack emissions from gas- and oil-fired power plants are regulated, as are those from coal-fired power plants, and impacts should be similar.

Solid-waste generation is a feature of oil- or gas-fired power plants that differs markedly from coal-burning plants. Gas-fired power plants do not produce solid wastes. The amount of scrubber sludge or ash produced at an oil-fired power plant will depend on the type of oil burned and its sulfur and ash content. In general, except when high-sulfur oil is used, oil-fired plants will have smaller land area requirements for waste disposal than a coal-fired plant. Impacts to the aquatic environment due to seepage from these waste-disposal sites will be quantitatively similar, but the potential for an adverse effect to occur will be greater from a coal-fired plant.

# GENERAL DESCRIPTION OF CONVERTING OIL- OR GAS-FIRED POWER PLANTS TO COAL

The possibility of modifying an existing oil- or gas-fired unit to burn coal may be simple, complex, or perhaps impossible (Witkowski 1977). If conversion is undertaken because the utility has received a prohibition order pursuant to the coal utilization provisions of ESCA, the task of modifying may be simple because the issuance of the prohibition order means the power plant possesses the necessary equipment and capability to burn coal. If the decision to convert is made internally by the utility, because of fuel unavailability or high fuel costs, conversion may be complex.

The conversion of a boiler from oil- and/or gas-firing to coal involves many engineering aspects, e.g., steam capacity, furnace exit gas, gas temperature, furnace size, boiler circulation, superheater, tube spacing, performance, tube metals, etc. (Witkowski 1977). A detailed discussion of the possible internal boiler modifications required are not within the scope of this document. Those aspects of conversion that need to be considered are the requirements for new and/or rejuvenated ancillary facilities, i.e., coal storage areas, coal handling and fuel preparation equipment, equipment to collect and dispose of combustion wastes, and waste disposal sites. All of these have been discussed in detail in earlier chapters but will be briefly presented here.

#### Retrofitting for Control Technologies

Particulate control technologies. Natural gas contains no ash and so, when burned, produces no fly ash (particulates). Fuel oil contains relatively little ash compared to coal. Consequently, oil-burning power plants generally do not need to control particulate emissions. Coalburning plants do need to control such emissions, however. Thus, converting a plant to coal requires the installation of a device, usually an electrostatic precipitator or a wet scrubber, for removing fly ash from the stack gas. In addition, the plant must be provided with a system for disposing of the captured ash. Such a system usually involves sluicing the ash to a settling pond (Fed. Energy Admin. 1977b). The settled ash can be allowed to fill the pond or be periodically dredged out for dumping at a landfill site. Furnace bottom ash must also be disposed of.

<u>Nitrogen oxides control technologies</u>. Coal-fired plants have a higher  $NO_X$  emission rate than either gas- or oil-fired plants (Shimizu et al. 1975). Hence, when converting to coal, modifications should probably be made in the combustion process to meet the  $NO_X$  New Source Performance Standards (see Table A.1, Appendix A).

<u>Sulfur dioxide control technologies</u>. Natural gas is "clean burning" and does not produce  $SO_2$  [with the exception of gas from Ohio fields which contains a minor amount of sulfur (Babcock and Wilcox Co. 1972)]. The conversion of a gas-fired plant to coal firing will require the retrofitting of an  $SO_2$  scrubber, unless the plant burns coal of low sulfur content to meet the New Source Performance Standards (see Table A.1, Appendix A).

The conversion of an oil-fired plant to coal firing may or may not require the installation of an  $SO_2$  scrubber, depending on the sulfur content of the coal that is to be burned.

If conversion from gas or oil to coal does require the retrofitting of a scrubber, and if the scrubber produces a lime or limestone sludge, then the plant must be provided with means for disposing of the sludge--perhaps by dewatering followed by landfilling.

#### New Ancillary Facilities

<u>Coal storage area</u>. Coal storage requires an area for reserve- and live-storage stockpiles. The hectares (acreages) typically required for these uses are indicated in Table 4. Also, a wastewater treatment system for coal-pile runoff may be needed.

<u>Coal handling facilities</u>. Coal handling facilities include: mechanisms for unloading the coal brought to the plant site by rail, barge, or truck; conveyors to move the coal; a coal crusher and surge bin; boiler-feed bunkers; and pulverizers which transform the coal into a powder and mix it with the primary air for delivery to the burners. Figure 29 shows (in dashed lines) the bunker, scales, feeder, and pulverizer which must be added to convert an oil- or gasburning unit to coal firing.

Lime/limestone storage and handling facilities. If a lime/limestone consuming scrubber is to be installed to serve the converted plant, an onsite area is required for the storage of the lime or limestone. The conversion of the lime or limestone into scrubber-feed slurry requires a conveyor, a pulverizer, a pulverizer-feed silo, and a classifier.

<u>Waste disposal sites</u>. Converting to coal will require waste disposal sites for bottom ash, collected fly ash, and possible scrubber sludge. It is logical to assume that a power plant converting to coal will not be found in association with an active coal mining operation. Therefore, disposal of wastes in the mine pits, as discussed earlier, will not be an alternative as a disposal site. Additional land area, either onsite or offsite, will be required.

IMPACTS ASSOCIATED WITH OIL- OR GAS-FIRED POWER PLANTS CONVERTED TO COAL

#### Introduction

Previous chapters have presented in detail the impacts of burning coal in an existing or newly constructed electrical generating station. When the engineering aspects of conversion to coal are complete, the impacts of operation are not anticipated to be different from those discussed for a plant originally designed and constructed to burn coal. Areas for coal, and possibly limestone, storage and for disposal of combustion and emission control wastes will be required. The potential impacts from these areas and from the gaseous and particulate combustion emissions will be specific for each site assessed.

There are some impacts to fish and wildlife which may occur in the process of converting an oil- or gas-fired plant to coal. Some support facilities for oil-fired power plants may be dismantled. When such facilities are dismantled, construction-type impacts due to movement of men and machines will occur. These include dust, noise, soil erosion, etc.; but with sufficient forethought and proper controls, such impacts can be minimized and rendered fairly insignificant (U.S. Nucl. Reg. Comm. 1977; USEPA 1973b; Beasley 1972; Emerson et al. 1974). It is improbable that such activities would occur at a gas-fired power plant.

#### Fuel Oil Handling Facilities

Oil handling facilities, storage tanks, and pipes and pumping facilities may be dismantled, leading to adverse impacts to fish and wildlife if residual oil contaminates land and water. Careful sequencing of dismantling operations and control of surface runoff can minimize potential adverse impacts.

If the above-mentioned facilities are dismantled, the land can be used for facilities such as coal storage piles or combustion waste landfill. However, if it is uneconomical to dismantle, the land may effectively be unusable for other purposes. Therefore, the total land requirements for the converted coal power plant may be greater than for a power plant originally designed for coal.



Figure 29. Components (dashed lines) That Must be Added to an Oil- or Gas-Burning Boiler to Provide for the Burning of Pulverized Coal. Redrawn from Heil and Leatham (1977).

Barge facilities designed for oil power plants may have to be modified to handle coal. This may require dredging and associated work in the waterway, leading to potential impacts to fish and wildlife. The extent of these impacts will be site-specific and can range from temporary disturbance of biota and habitat to permanent modification or elimination of biota and habitat. Judicious planning and tight controls can minimize impacts (U.S. Nucl. Reg. Comm. 1977; Krenkel et al. 1976).

If it is uneconomical to modify or dismantle barge facilities, the new coal power plant will need new barge or railroad facilities. This results in a commitment of additional land and intrusion on the waterway that is greater for the converted coal power plant than for a plant originally designed for coal.

# REFERENCES

Babcock and Wilcox Co. 1972. Steam, Its Generation and Use, 38th ed. New York. 1 v. (various pagings).

Baker, J. M. 1970. The effects of oils on plants. Environ. Pollut. 1:27-44.

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- Battelle Northwest Laboratories. 1967. Oil Spillage Study. AD 666 289. Battelle Memorial Foundation, Richland, Wash. U. S. Dept. of Commerce.
- Beasley, R. P. 1972. Erosion and Sediment Pollution Control. Iowa State University Press, Ames, Iowa. 320 pp.
- Brown, R. A., H. B. Mason, and R. J. Schreiber. 1974. Systems analysis requirements for nitrogen oxide control of stationary sources. EPA-650-2-74-091; PB 237367. Prepared by Aerotherm/ Accurex Corp. for the U.S. Environmental Protection Agency, Office of Research and Development. 165 pp.
- Emerson, D. B., et al. 1974. General Environmental Guidelines for Evaluating and Reporting the Effects of Nuclear Power Plant Site Preparation, Plant and Transmission Facilities Construction. AIF/NESP-003. Atomic Industrial Forum, Inc.
- Federal Energy Administration. 1977a. Environmental Assessment, Lawrence Generating Station, Kansas Power and Light Company, Power Plants 3, 4 and 5. Report No. FEA/G-77-150. 99 pp.
- Federal Energy Administration. 1977b. Draft Environmental Impact Statement, McManus Generating Station, Georgia Power Company, Power Plants 1 and 2. Report No. FEA/G-77-147. 202 pp.
- Federal Energy Administration. 1977c. Coal Conversion Program: Energy Supply and Environmental Coordination Act (As Amended), Sec. 2, Vol. 1, Final Revised Environmental Impact Statement. FEA/G-77-145. Office of Coal Utilization.
- Heil, T. J., and C. H. Leatham, Jr. 1977. Principal aspects of converting steam generators back to coal, pp. 149-176. <u>In</u> Proceedings of the Fuel Switching Forum, Pittsburgh, Pa., June 6-7, 1977. CONF-770658. U.S. Energy Research and Development Administration, Washington, D. C.
- Krenkel, P. A., J. Harrison, and J. C. Burdick (eds.). 1976. Dredging and its environmental effects. Proceedings of the Specialty Conference, Mobile, Alabama, Jan. 26-28, 1976. American Society of Civil Engineers, New York. 1,037 pp.
- McCauley, R. N. 1966. The biological effects of oil pollution in a river. Limnol. Oceanogr. 11:475-486.
- Miller, W. 1977. Personal communication (Commonwealth Edison Company, Chicago).
- Schwendinger, R. B. 1968. Reclamation of soil contaminated with oil. J. Inst. Petrol. 54:182-197.
- Shimizu, A. B., R. J. Schreiber, H. B. Mason, G. G. Poe, and S. B. Youngblood. 1975. NO<sub>x</sub> Combustion Control Methods and Costs for Stationary Sources, Summary Study. EPA-600/2-75-046; PB 246730. U.S. Environmental Protection Agency, Washington, D.C. 104 pp.
- U.S. Army Engineer District. 1975. Final Environmental Impact Statement Relating to the Commonwealth Edison Company Collins Generating Station. Chicago, Ill. 1 v. (various pagings).
- U.S. Environmental Protection Agency. 1973a. Compilation of Air Pollutant Emission Factors, 2nd ed. Publ. No. AP-42; PB-223 996. Office of Air and Water Programs, Research Triangle Park, N.C. 288 pp.
- U.S. Environmental Protection Agency. 1973b. Processes, Procedures and Methods to Control Pollution Resulting from All Construction Activity. EPA 430/9-73-007; PB-257 318. Office of Air and Water Programs, Washington, D.C. 234 pp.
- U.S. Nuclear Regulatory Commission. 1977. Draft Environmental Standard Review Plans for Environmental Review of Construction Permit Applications for Nuclear Power Plants, Parts I, II, III. NUREG-0158. Office of Nuclear Reactor Regulation. 3 v. (various pagings).

Van Overbeek, J., and R. Blondeau. 1954. Mode of action of phytotoxic oils. Weeds 3:55-65.

- Wein, R. W., and L. C. Bliss. 1973. Experimental crude oil spills on arctic plant communities. J. Appl. Ecol. 10:671-682.
- Witkowski, S. J. 1977. Conversion of oil- and gas-fired units to coal firing, pp. 252-262. <u>In</u> Fourth Symposium on Coal Utilization. National Coal Association/Bituminous Coal Research, Inc.

# RESEARCH NEEDED

It is obvious from the preceding sections of this report that there is insufficient knowledge to accurately predict the environmental effects and impacts of coal-fired electric power generation on terrestrial and aquatic ecosystems. In particular, next to nothing is known of the effects of long-term exposure to very low concentrations of gaseous and trace-element environmental contaminants. At present, impact assessments can be made only qualitatively, based primarily on general physical, chemical, and biological knowledge. The following is a list of research needs, arranged under broad topical headings; if undertaken, these research topics would provide information that would move impact assessment toward a more quantitative evaluation. The list is not by any means exhaustive, but includes some of the most urgent needs that are identified within the various sections of this report.

Undoubtedly, some of the research needs identified here are presently being conducted. For example, the USEPA is sponsoring two large integrated studies on the impacts of coal-fired power plants on the environment. One study involves the 527-MWe Columbia Electric Generating Station located 6.4 km (4 mi) south of the city of Portage, Wisconsin (Inst. Environ. Stud. 1976). The other study involves the Colstrip Power Plant project near Colstrip, Montana (Preston and Lewis 1977). The Columbia study began in 1971 with the objective to document the environmental changes caused by the construction and operation of the station. The generating station came on line in March 1975. Eleven semi-annual reports have been produced to date, some of which have been cited within this report. The Colstrip project began in the summer of 1974, and two years of baseline field season data were collected prior to the stat-up of the first of two 360-MWe generating stations in September 1975. The objective for this study is to develop methods to predict the bioenvironmental effects of air pollution originating from coal combustion. The third interim report, recently released, covers primarily the baseline monitoring. Future reports should provide additional insight into assessment of the ecological impacts of coal combustion in the Northern Great Plains.

#### GASEOUS AND PARTICULATE EMISSIONS

1. Effects on wildlife species from chronic, low concentrations of sulfur oxides and nitrogen oxides.

2. Effects on wildlife of secondary pollutants derived from sulfur or nitrogen oxides, and the environmental conditions under which the secondary pollutants can reach harmful levels.

3. Interactions and synergistic effects of sulfur oxides, nitrogen oxides, particulates, and other atmospheric pollutants upon biota.

4. Effects of sulfur oxides and nitrogen oxides upon the soil microflora and microfauna involved in nutrient recycling.

5. Dose-response curves for sulfur oxide effects on vegetation.

6. Measurements of quantities and chemical forms of trace and other elements emitted from power plant stacks, transformations of these elements during atmospheric transport, and deposition rates.

#### ACID PRECIPITATION

1. Direct and indirect effects on vegetation, the biogeochemistry of the soil, soil microflora and microfauna, terrestrial animals, and aquatic biota.

2. Effects of persistent, low-level acidification on aquatic systems.

3. Analysis of the extent to which a given project may exacerbate regional and global effects of acid precipitation.

4. Biochemical, physiological, and ecological bases for tolerance of acidic habitats (it may be possible to develop tolerant strains of fish for restocking of acidified waters).

5. Relative contributions of direct acid fallout and contaminants in watershed runoff to aquatic systems.

6. Interactions of acid waters with pesticides, metals, and fertilizers, and synergistic effects of these components upon aquatic biota.

# TRACE ELEMENT BEHAVIOR

#### Terrestrial

1. Changes in soil concentrations of trace elements deposited from coal combustion with distance, soil depth, and time, including amounts lost through wind erosion, surface runoff, or leaching to groundwater.

2. Trace-element transformations and solubilization rates in soil, and the chemical and biological factors involved in these transformations.

3. Methods for determination of available concentrations of trace elements in soil, and correlation with plant uptake.

4. Effects of trace elements on soil microorganisms and their processes, including release of trace elements from decomposing organic matter, and comparison of trace elements derived from organic matter and those solubilized from the soil mineral fraction or coal-combustion particulates, in terms of availability to plants.

5. Trace-element cycling in various vegetation communities, and accumulation rates in soil.

6. Plant uptake and accumulation of trace elements under natural soil conditions, biochemistry of trace elements within various plant species, and distribution of trace elements within the plant at various growth stages under a variety of climatic conditions.

7. Tolerance limits of various plant and wildlife species to increased concentrations of trace elements, and effects of other environmental parameters on such tolerance (primarily field studies).

8. Effects of long-term, low-level exposure to trace elements on livestock and wildlife-including invertebrates, reptiles, and amphibians.

9. Biological half-lives of trace elements in animals, including rates of assimilation and elimination, and identification of target organs or tissues that accumulate specific trace elements.

10. Pathways of trace elements through food chains, including accumulation rates at each trophic level.

11. Trace-element accumulation in animals that interface terrestrial and aquatic systems.

#### Aquatic

1. Field data on trace element toxicities to aquatic organisms (most current standards have been obtained from laboratory bioassays).

2. Trace-element transformations and reactions in surface waters and groundwaters.

3. Trace-element cycling in aquatic ecosystems, including differential uptake of ionic and chelated forms, biomagnification factors, bioaccumulation-elimination and turnover rates, and determination of final sinks where trace elements are no longer available to biota.

4. Synergistic effects of heat and other contaminants on trace-element toxicities, and sublethal effects on aquatic organisms.

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# COMBUSTION WASTE DISPOSAL

1. Chemical transformations and solubilization of sludge and fly ash constituents from active and inactive disposal sites.

2. Validation of seepage transport models and determination of necessary coefficients for site-specific application.

3. Effects of ash and sludge pond seepage on wetland communities such as bogs and marshes.

4. Long-term cumulative effects of seepage constituents on soils, vegetation, and herbivores.

5. Compatibility and long-term durability of various natural and synthetic liners for ash and sludge waste impoundments.

6. Ash and sludge stabilization against wind and water erosion, including the use of various soil additives and mulches as temporary erosion-preventive materials under a variety of climatic and soil conditions.

7. Reclamation procedures for ash and sludge disposal sites, with regional and sitespecific adaptations. Information is needed on fast-growing vegetation species adapted to given areas, and fertilizer, amendment, and possibly irrigation requirements.

8. Effects of fly ash and flue-gas desulfurization sludge, and/or mixtures, as a medium for plant growth, including effects of trace-element and radionuclide uptake from fly ash by vegetation and transport through the food chain.

# COAL PREPARATION AND STORAGE

1. Measurements of dust quantities deposited on vegetation adjacent to and downwind of coal storage piles, coal slurry ponds, and preparation facilities, and effects of such dust on primary production.

2. Measurements of noise from coal storage and handling facilities, and effects on wildlife behavior.

3. Wildlife use of catch basins receiving runoff from coal storage areas, and effects of such usage.

4. Efficient and economical methods for controlling windblown dust from coal storage piles.

#### LIMESTONE PREPARATION AND STORAGE

1. Measurement of lime and limestone dust quantities released from storage and preparation facilities, including modeling of deposition patterns and measurement of deposition rates.

2. Effects of lime and limestone dust deposition on vegetation adjacent to the storage and preparation areas.

3. Effects of runoff from lime and limestone storage areas on aquatic systems.

### REFERENCES

- Institute for Environmental Studies, Environmental Monitoring and Data Acquisition Group. 1976. Documentation of Environmental Change Related to the Columbia Electric Generating Station, Seventh Semi-Annual Report, Spring-Summer 1975. IES Rep. 62. University of Wisconsin--Madison. 135 pp.
- Preston, E. M., and R. A. Lewis (eds.). 1977. The Bioenvironmental Impact of a Coal-Fired Power Plant, Third Interim Report, Colstrip, Montana, December 1977. U.S. Environmental Protection Agency, Corvallis Environmental Research Laboratory, Corvallis, Oregon. 531 pp.

# ACKNOWLEDGEMENTS

The authors acknowledge with gratitude the support of the U.S. Fish and Wildlife Service, Office of Biological Services, National Power Plant Team, which is financing this project. We particularly appreciate the assistance of Dr. Ken Hoover, Team Leader, and the helpful comments provided by Dr. Kent Schreiber, Terrestrial Ecologist, and Ms. Beth Fodor, Information Transfer Specialist. We also acknowledge the comments from the six Regional Offices of the U.S. Fish and Wildlife Service.

We express appreciation to those staff members of the Division of Environmental Impact Studies--Mr. John Martens, Ms. Shari Zussman, and Ms. Guynn Waggoner--who assisted in the preparation of this report. Portions of the report were reviewed by Mr. William Hallett, Dr. Robert Flynn, Dr. W. S. White, Dr. Gary Marmer, and Dr. Ed Daniels, whose suggestions are gratefully acknowledged. Particular thanks are due to Mrs. Dee Wyman for editorial assistance during all stages of report preparation.

# APPENDIX A. FEDERAL EFFLUENT STANDARDS FOR AIR EMISSIONS. ASH TRANSPORT WATER, AND MATERIAL STORAGE RUNOFF

# AIR EMISSIONS

# New Source Performance Standards and Ambient Air Quality Standards

Emission standards from power plants have been set by the U.S. Environmental Protection Agency (USEPA) to protect the public health and welfare. New Source Performance Standards (NSPS) set limits for the amount of pollutants emitted by a facility. Ambient standards set limits on the amount of pollution permitted at ground level. Additionally, areas of the country have been placed into classes based on air quality criteria. These classes are designed to prevent significant deterioration (PSD areas) and to maintain present air quality. Specific rulings, limits, and permits may be required from the USEPA or individual states to construct a new facility or modify an existing facility.

New Source Performance Standards set limits for particulates, oxides of sulfur and nitrogen, as well as visible emissions. The standards are given in Table A.1. Recent rulings by the courts have questioned the validity of the NSPS (Anon. 1977), but it is assumed that new facilities must be in compliance. Due to the concern over increased emissions from fossil-fired power plants, it is likely that emission limits will be decreased for new sources, making the use of Best Available Control Technology (BACT) necessary (see the following discussion of 1977 Clean Air Act Amendments).

Pollutant	Emissions (1b/10 <sup>6</sup> Btu) <sup>b</sup>	Fuel type
Particulates	0.1 (also 20% opacity limit)	A11
\$0 <sub>2</sub>	0.8 1.2	Liquid fuel Solid fuel
NO <sub>X</sub>	0.2 0.3 0.7	Gaseous fuel Liquid fuel Solid fuel

Table A.1. Federal Emission Standards for New Fossil-Fuel-Fired Steam Generatorsa

<sup>a</sup>From USEPA (1971b). Data are for units of more than  $250 \times 10^6$  Btu/hr heat input. Maximum 2-hr average.

Ambient air quality standards are established to protect the public health (primary standards) and to protect the public welfare (secondary standards). These standards are listed in Table A.2 and are established with a margin of safety (USEPA 1971a). Individual states may establish ambient standards in addition to the federal standards, but state standards must be as restrictive or more so than the federal standards. Ambient concentrations are found by adding calculated concentrations, using applicable meteorological data and realistic plant emissions, to the measured background concentrations. Short-term concentrations can be calculated by adding conservative values (those input values leading to the highest predicted values) to background concentrations.

Proper measuring and sampling techniques, approved by the USEPA, have been developed for stack monitoring to determine compliance with NSPS and for ambient monitoring to determine compliance with ambient standards (USEPA 1971a). Ambient air quality monitoring has been done at a number of locations, and the data are available from the USEPA, responsible state agencies. and/or facilities requiring air quality permits from those agencies.
	Sta <b>nda</b> rds (µg/m <sup>3</sup> )			
Material	Primary	Secondary		
Suspended particulates Annual average 24-hr average <sup>b</sup>	75 260	60 150		
Sulfur dioxide Annual average 24-hr average <sup>b</sup> 3-hr average <sup>b</sup>	80 365 none	60 260 1,300		
Nitrogen dioxide Annual average	100	100		
Carbon monoxide 8-hr average <sup>b</sup> 1-hr average <sup>b</sup>	10 40	10 40		
Photochemical oxidants l-hr average <sup>b</sup>	160	160		
Hydrocarbons 3-hr average <sup>b</sup>	160	160		

# Table A.2. Federal Ambient Air Quality Standards<sup>a</sup>

<sup>a</sup>Data from USEPA (1971a).

Not to be exceeded more than once per year.

In addition to the NSPS and ambient standards, certain areas in the country are designated by the USEPA as Class I, II, or III PSD areas. Class I areas presently encompass national monuments, primitive areas, preserves, recreation areas, and wild and scenic rivers exceeding 10,000 acres. Class II and Class III are less pristine areas. Maximum allowable pollutant increases for each class are given in Table A.3 (U.S. Government 1977). These additions must also meet NSPS and ambient standards.

### Table A.3. Maximum Allowable Increase in Pollutant Concentrations for PSD Areas<sup>a</sup>

	Maximum	allowable	increase (µ	g/m <sup>3</sup> )
Pollutant	Class I	Class	II	Class III
Particulates Annual geometric mean 24-hr maximum	5 10	19 37		37 75
Sulfur dioxide Annual arithmetic mean 24-hr maximum 3-hr maximum	2 5 25	20 91 512		40 182 700

<sup>a</sup>Data from U.S. Government (1977).

Due to the changing standards for emissions and air quality concentrations, as well as the variety of different regulatory agencies--either federal, state, or local--having jurisdiction over power plants, the regional USEPA office, the state department of air quality, and all local agencies must be consulted before any licenses are granted and plants constructed.

## 1977 Clean Air Act Amendments

The Clean Air Act Amendments (U.S. Government 1977) were signed into law on 7 August 1977. Major changes were made in the regulations concerning Air Quality Control Regions (AQCR's) and State Implementation Plans (SIP's) to ensure compliance with the Clean Air Act and emission standards for new or modified stationary sources. By 6 December 1978, each state is to notify the administrator of the USEPA of those AQCR's within the state which are in violation of the ambient air quality standards or for which insufficient data are available to make a judgment of the air quality. Also, any source which will contribute significant amounts of pollutants to AQCR's across state boundaries must notify all nearby states of the concentrations of pollutants resulting from the emissions of a new or modified source.

States may also redesignate Class I PSD areas to Class II or Class III. However, mandatory Class I areas (international parks, national wilderness areas and national memorial parks exceeding 5,000 acres in size, and national parks exceeding 6,000 acres in size) and certain others (national monuments, national primitive areas, and wild and scenic rivers exceeding 10,000 acres in size) can be designated Class I or Class II areas only.

If an area is not in compliance with the ambient air quality standards, no permits for sources can be issued in the area unless additional emissions from the source will be offset by reduced emissions from existing sources within the area. Lowest achievable emissions from a new or modified source in such a nonattainment area is required. To better quantify existing air quality, the USEPA will establish an air quality monitoring system across the nation.

In the past, New Source Performance Standards have limited the amounts of various pollutants a new source may emit. In addition to these standards, the new Clean Air Act Amendments will require "the achievement of a percentage reduction in the emissions from such category of sources from the emissions which would have resulted from the use of fuels which are not subject to treatment prior to combustion." This requires "best technological system of continuous emission reduction." The use of naturally low-sulfur fuels is not in itself satisfactory. It is probable that sulfur reductions of about 90% and particulate reductions of 99.5% will be mandated. A state governor, the EPA administrator, or the President may prohibit major fuelburning sources from using any fuels "other than locally or regionally available coal or coal derivatives." The operator of the fuel-burning source may be required to enter into long-term contracts for local coal and also to contract for additional emission abatement devices required to comply with emission standards.

The Clean Air Act amendments will tighten emission standards, disallow the use of inherently low-polluting fuels as a pollution control device, provide no dispersion credit for any stack more than 2.5 times as tall as related facilities, and establish a more complete air quality monitoring system across the nation.

#### ASH TRANSPORT WATER AND MATERIAL STORAGE RUNOFF

Section 423.11 subparagraph (h) of Title 40, Code of Federal Regulations (40 CFR) states in part that "low volume wastes sources would include but are not limited to waste waters from wet scrubber air pollution control systems" (USEPA 1974). In addition, subparagraph (i) of the same section states, "The term 'ash transport water' shall mean water used in the hydraulic transport of either fly ash or bottom ash." Under guidelines established under Section 423.12 ("... best practicable control technology currently available"), the quantity of pollutants discharged from low volume sources cannot exceed the quantity determined by multiplying the flow from waste sources times the concentration listed in Table A.4.

Likewise, the quantity of pollutants discharged in ash transport water shall not exceed the quantity determined by multiplying the flow of ash transport water times the concentration listed in Table A.4.

	Concentration (mg/L)				
Effluent characteristics	Maximum for any one day	Average of daily values for 30 consecutive days cannot exceed			
Total suspended solids (TSS)	100	30			
0il and grease	20	15			

Table A.4. Federal Standards for Low-Volume Waste Effluents<sup>a</sup>

<sup>a</sup>Data from USEPA (1974).

Under Section 423.13 ("... best available technology economically achievable"), low-volume wastes standards remain the same as those described in Section 423.12 and Table A.4. In Section 423.13, ash transport water is discussed in terms of "fly ash sluicing" and "bottom ash transport water." The standards for fly ash sluicing are the same as discussed under Section 423.12 and Table A.4. The bottom ash transport product is derived using flow of bottom ash transport water and Table A.4. This product is then divided by 12.5.

Section 423.15 ("standards of performance for new sources") again sets standards for low volume wastes equal to those described under Section 423.12 and Table A.4. The product derived for bottom ash transport water as described in Section 423.13 is now divided by 20 rather than 12.5. In Section 423.15, it is further stated that "there shall be no discharge of TSS or oil and grease in fly ash transport water."

Section 423.41 subparagraph (b) of 40 CFR states: "The term 'material storage runoff' shall mean the rainfall runoff from or through any coal, ash or other material storage pile." Under guidelines set forth in 40 CFR Sections 423.42 (" ... best practicable control technology currently available"), 423.43 (" ... best available technology economically achievable"), and 423.44 ("standards of performance for new sources"), effluent standards are set at a maximum of 50 mg/L for total suspended solids (TSS) and a pH range of 6.0 to 9.0.

In addition, subparagraph (b) of these sections states that "any untreated overflow from facilities designed, constructed and operated to treat the volume of material storage runoff and construction runoff which results from a 10 year, 24 hour rainfall event shall not be subject to the limitations ... " described above.

In summary, effluent guidelines for determining ash transport water standards are as follows:

For best practicable control technology: flow × concentration\* = standard

- For best available technology economically achievable:
   fly ash sluicing
  flow × concentration\* = standard
  - bottom ash transport water  $\frac{flow \times concentration^*}{12.5} = standard$

For new source performance standards: - fly ash sluicing no discharge of TSS or oil and grease

- bottom ash transport water  $\frac{flow \times concentration^*}{20.0} = standard$ 

Effluent guidelines for determining all low-volume wastes standards, which include scrubber ash, are determined as follows:

flow × concentration\* = standard

All effluent standards relevant to material storage pile runoff are presented in Table A.5.

Table A.5. Federal Standards for Material Storage-Pile Runoff<sup>d</sup>

Effluent characteristic	Best practicable control technology	Best available technology economically available	New source performance standards
Total suspended solids (TSS)	50 mg/L	50 mg/L	50 mg/L
pH range	6.0 – 9.0	6.0 - 9.0	6.0 - 9.0

<sup>a</sup>Data from USEPA (1974).

\*For appropriate concentration, see Table A.4.

#### OTHER EFFLUENTS

At present, there are no federal standards regulating downward movement of effluents from ash or sludge disposal ponds through the substrata (seepage). However, the USEPA may have authority to investigate possible groundwater contamination under the Resource Conservation and Recovery Act of 1976 and/or the Safe Drinking Water Act. The agency is currently engaged in a study to determine the impacts of toxic pollutants in the effluents from waste-disposal ponds. Regulations controlling the discharge of these toxic pollutants are expected within a year of completion of the study.

If the discharge from an ash or sludge disposal pond flows into a stream, lake, or aquifer that is used as a drinking water source (for at least 20-25 people), the U.S. Public Health Service Drinking Water Standards apply, and may limit the quality of the seepage or discharge water allowed (Saulys 1977, personal communication).

In addition to the federal standards and regulations, various states may have regulatory authority over seepage and/or surface-water runoff through such means as state environmental impact statements and National Pollutant Discharge Elimination System permits. Possible state agencies which may be involved in regulating groundwater and/or surface-water runoff include departments of natural resources, conservation departments, pollution control boards, and state environmental protection agencies. Public law PL 92-500 stipulates that the state regulation takes precedence over the federal regulation when the former is more stringent.

#### REFERENCES

Anonymous. 1977. A new end run around EPA air standards. Bus. Week 77(2507):64.

- Saulys, V. 1977. Personal communication (U.S. Environmental Protection Agency, Region V, Chicago).
- U.S. Environmental Protection Agency. 1971a. National primary and secondary ambient air quality standards. Fed. Regist. 36(84):8186-8190.
- U.S. Environmental Protection Agency. 1971b. Standards of performance for new stationary sources. Fed. Regist. 36(247):24876-24895.
- U.S. Environmental Protection Agency. 1974. Steam electric power generating point source category, effluent guidelines and standards. Fed. Regist. 39(196):36185-36207.
- U.S. Government. 1977. Clean Air Act, 42 U.S.C. 1857 et seq., as amended by PL 90-148, PL 91-604, PL 92-157, PL 93-15, PL 93-319, and PL 95-95; Title I, Part C. Environment Reporter 71:1101-1181.

# APPENDIX B. COAL CLASSIFICATION AND COMPOSITION

# CLASSIFICATION OF COAL

Coal is composed of a highly complex and heterogeneous group of substances and possesses a wide range of chemical and physical properties. Coal is formed by the accumulation and subsequent modification of plant matter; its final properties depend on the nature of the original vegetation, the circumstances of deposition, and the subsequent events that occur during meta-morphosis into coal.

One of the most commonly accepted methods of coal characterization is the classification by rank, developed by the American Society for Testing and Materials (1973). Classification by rank, which represents the progressive response of coal to pressure and/or heat during the metamorphic process (Simon and Hopkins 1973), orders coals into a series ranging from lignite, at the lower end of the scale, through the various ranks of subbituminous and bituminous coals to the anthracites, at the upper end of the scale. This classification (Table B.1) is based upon fixed carbon, volatility content, calorific content, and agglomerating characteristics of coal.

		the second se	and the second	
Class	Moisture (%)	Fixed carbon limits (%) <sup>b</sup>	Volatile matter limits (%) <sup>b</sup>	. Calorific value limits (Btu/lb)c,d
Anthracite	< 2	86-98	2-14	14,000-16,000
Bituminous	2-15	50-86	14-50	10,500-14,000
Subbituminous	20-30	40-60	-	8,300-10,500
Lignite	30-50	< 40	-	6,300-8,300

# Table B.l. Classification of Coals<sup>a</sup>

<sup>a</sup>From Simon and Hopkins (1973). <sup>b</sup>Dry mineral-matter-free basis. <sup>c</sup>Moist mineral-matter-free basis. <sup>d</sup>To convert Btu/lb to J/kg, multiply by 2.324 × 10<sup>3</sup>.

Lignite, the parent form of all higher ranks, is often called brown coal. Lignite can contain up to 50% water and has the lowest carbon content of all the ranks of coal and therefore has a relatively low heat content, expressed as Btu output per pound. Consequently, larger quantities of lignite must be burned to equal the energy output of higher ranks of coal. Large lignite deposits are found in western North Dakota, eastern Montana, and northwestern South Dakota; smaller deposits are found in the southcentral states of Texas, Arkansas, Louisiana, Mississippi, and Alabama (Min. Inf. Serv. 1975).

Subbituminous coal has a slightly higher heat value than lignite due to lower moisture content and greater amount of carbon. Subbituminous coal deposits occur in nearly all of the Rocky Mountain states (Min. Inf. Serv. 1975).

Bituminous coal is the most widely distributed and most abundant of all the ranks of coal in the United States (Min. Inf. Serv. 1975). It has a higher heat value than the two previously mentioned lower ranks of coal (Simon and Hopkins 1973). Because of its high heat value and abundance, bituminous is the predominant form of coal used by electrical utilities. Bituminous deposits can be found in the eastern, midwestern, Rocky Mountain, and far western states (Min. Inf. Serv. 1975).

Anthracite has the lowest moisture content and the highest fixed carbon content of all ranks of coal. The largest deposits of anthracite being mined in the United States today are in eastern Pennsylvania (Min. Inf. Serv. 1975).

Coal ranking represents a multipurpose classification scheme designating general coal characteristics. The broad rank designations anthracite, bituminous, subbituminous, and lignite will be used in the following discussion, recognizing that subdivision within each of these ranks is possible. To determine a coal's suitability for a given purpose and its usage and waste production rates, more data are required. Characteristics of particular importance in electrical power generation are heat (Btu/lb), sulfur, ash, moisture, and trace-element contents.

#### IMPORTANT COAL CONSTITUENTS

Heat content (Btu/lb) is important because it dictates the amount of coal consumed annually by a given power plant. Transportation costs per unit heat output may be an important cost factor, and may affect the type of coal used in a particular plant. Sulfur content is important because of the deleterious health and environmental effects of sulfur dioxide, which is created as a combustion byproduct; these deleterious effects have lead to regulatory restrictions on sulfur dioxide emission and/or sulfur content of coals which may be burned. These restrictions often require utilization of low-sulfur coal from distant locations and/or removal of sulfur from coal before combustion or from the flue gases after combustion. The ash content determines the amount of bottom and fly ash produced by combustion of a given quantity of coal. Moisture lowers the effective heat content per unit weight of coal because of its weight and the heat expended in vaporizing the water, thus increasing transportation costs per useful Btu. Trace elements (including radionuclides) emitted in flue gases have received relatively little attention, but are considered in this report because of their potentially harmful environmental effects.

# ESTIMATES OF RESERVES FOR THE MAJOR COAL-PRODUCING REGIONS OF THE UNITED STATES

The locations of the major coal-producing regions of the United States are identified in Figure B.1. The following descriptions are based on data from the U.S. Energy Research and Development Administration (1975) and the U.S. Bureau of Mines (1975) except where indicated.



Figure B.1. Coal-Producing Regions of the United States. Adapted from Carter et al. (1974).

<u>Appalachian Region (Northern and Southern)</u>. The Appalachian Region covers an area of about 180,000 km<sup>2</sup> (70,000 mi<sup>2</sup>) and extends about 1300 km (800 mi) (north to south) from Pennsylvania to Alabama. Approximately one-fifth of the nation's identified coal reserves are found in this region. Coal reserves in the Appalachian Region can be divided into two areas of concentration, the northern and southern. The northern area includes the states of Ohio, Pennsylvania, West Virginia, eastern Kentucky, and smaller portions of Virginia and Tennessee. Reserves for this area are estimated at more than 13 billion MT (14 billion tons) of surface reserves and nearly 86 billion MT (95 billion tons) of underground reserves. The Southern Appalachian Coal Region is concentrated in Alabama, and coal reserves have been estimated at almost 2.7 billion MT (3 billion tons) of surface reserves.

Eastern Interior Region. The Eastern Interior Region, which lies within a structural basin and includes southern Illinois, southwestern Indiana, and western Kentucky, contains over 64 billion MT (71 billion tons) of underground reserves with nearly 16 billion MT (18 billion tons) of strippable reserves.

<u>Powder River Region</u>. The Powder River Region is located in southeastern Montana and northeastern Wyoming, and contains over 54 billion MT (59 billion tons) of strippable coal reserves.

Fort Union Lignite. The Fort Union Coal Field contains large lignite and subbituminous coal deposits in western North and South Dakota, eastern Montana, and northeastern Wyoming, and includes the subbituminous coals of the Powder River Region (Carlson 1977; Matson 1977). All of the coal in the North and South Dakota portions of the fields, and some of the eastern Montana coals consist of lignite. Strippable lignite reserves in the North Dakota and Montana portions of the field are approximately 14.5 billion and 13.6 billion MT (16 billion and 15 billion tons), respectively.

<u>Gulf Coast Lignite</u>. All of the coals of the Gulf Coast region are lignites. They span from the Mexican border through Texas, Louisiana, Mississippi, and Alabama (Averitt 1975; Daniel 1977). The strippable reserves [0-61 m (0-200 ft) deep] in Texas are estimated at 9.3 billion MT (10.3 billion tons) (Evans and Kaiser 1977). In Alabama, identified resources [less than 914 m (3000 ft) deep] are estimated at 1.8 billion MT (2 billion tons) (Culbertson 1964).

Four Corners Region. The Four Corners Region lies within the Colorado Plateau and includes part of the states of Arizona, Colorado, New Mexico, and Utah. Two estimates of the surface reserves of the Four Corners Region are over 3.4 billion MT (3.7 billion tons) and over 4.4 billion MT (4.8 billion tons).

#### MOISTURE, ASH, SULFUR, AND HEAT CONTENT OF REPRESENTATIVE U.S. COALS

Data on moisture, ash, sulfur, and heat content of coals for some major coal-producing states are presented in Table B.2 in order to illustrate typical values. Any given state may contain many mineable seams. In each case, however, data for only one seam was chosen, usually on the basis of its production within that state. The characteristics given for one seam may not be representative of other seams in the same state.

All of the coals listed for the northern and southern Appalachian regions are bituminous in rank, with high heat values and a wide range of sulfur contents. The coals from the No. 5 Illinois seam in the Eastern Interior Province are lower-heat-content bituminous coals with relatively high sulfur and ash contents. The western coals listed have relatively low sulfur and heat contents and high moisture values, particularly the subbituminous coals listed for the Powder River Region and the lignite listed for the Fort Union Formation.

#### TRACE ELEMENTS AND RADIONUCLIDES IN U.S. COALS

Trace elements are generally defined as those with a relative abundance in the earth's crust of 0.1% (one part per thousand) or less. Many of the trace elements in coal are enriched in coal ash, a combustion byproduct, relative to their crustal abundance, and some are elevated to toxic concentrations. The concentration of some of these elements in the ash of coals from three broad regions of the United States is compared with their crustal abundance, but the other elements show elevated concentrations in the coal ash from some regions. Figure B.2 also illustrates the regional variability in the concentration of some elements in coals.

Trace-element concentrations may vary widely with location, and even within a single seam. Germanium, for instance, concentrates locally in the top and bottom layers of a coal bed, or next to the parting layer (Averitt 1975). (The parting layer consists of non-coal materials found in abundance between two coal seams.) The concentration of a given element may vary with Table B.2. Summary of Moisture, Ash, Sulfur and Heat Content of Coal from Some Major Coal-Producing Seams in the United States<sup>a</sup>

			Moisture (%)		Ash (%)		Sulfur (%)		u/1b) <sup>b</sup>	m
Region/State	Seam	Range	Average <sup>C</sup>	Range	Average <sup>C</sup>	Range	Average <sup>C</sup>	Range	Average <sup>C</sup>	Reference
Northern Appalachian					· · ·		·		·····	
West Virginia Pennsylvania	Pittsburgh Pittsburgh	1.1-3.9	2.9 <sup>d</sup> 2.5(MR)	<b>4</b> -20 4.2-10.8	7(M) 7.5(MR)	0.6 -14 0.7 -3.3	2.2(M) 2.0(MR)	11,400-14,800 13,040-14,340	13,800(M) 13,690(MR)	Arkle et al. (1975) Edmunds (1975)
Southern Appalachian										
Eastern Kentucky	Upper Elkhorn #3 Upper Elkhorn #3	-	3.2 <sup>0,e</sup>	-	3.9	-	0.9	-	14,200	Smith and McGrain (1975)
Vénedede	(Jellico)	2.0-7.6	4.8(MR)	1.9-10.5 <sup>f</sup>	6.2(MR)	0.7 -3.2 <sup>9</sup>	2.0(MR)	12,630-14,290 <sup>h</sup>	13,460(MR)	Luther (1975)
Alabama	Mary Lee	1.2-4.0	2.6(MR)	4.9-19.8	12.4(MR)	0.5 -2.6	1.6(MR)	11,570-14,700	14,735(MR) 13,135(MR)	Calver (1975) Daniel (1977)
Eastern Interior		•								
Illinois	(No. 5) Harrisburg-	4 -18	11/MP)	8 -12	10(MR)	2 -5	3.5(MR)	10 100 12 700	11 400(MD)	Simon of al (1075)
Indiana Western Kentucky	(No. 5) Springfield (No. 9)(No. 5 111.)	-	5.0	5 -30	12 10.5	0.7 -7.3	3.3 3.15	9,100-14,000	12,800 12,940	Wier and Hutchinson (1975) Smith and McGrain (1975)
Powder River Region		·								
Montana	Anderson-Dietz 1 & 2	_		4 0-5 3	4 6	0 29-0 5	0.37	7 925-9 652	8 633	Matcon (1075)
Wyoming	Anderson & Canyon &	21 1 26 0	20.7	2 1 10 2	6.0	0 14 1 2	0.49	7,325-5,052	0,000	Macson (1975)
	wyodak-Anderson	21.1-30.9	29.1	3.1-12.2	0.0	0.14-1.2	0.40	7,128-9,000	8,203	GIASS (19/5)
Fort Union Lignite	. Hadaffaad	22 5 42 0	27.0		6.2	0 2 1 4	0.6	E 060 7 407	6 700	(1077)
NOTIN DAKOLA	Under med	33.3-43.0	37.9	4.4-0.0	0.2	0.2 -1.4	0.0	5,900-7,487	0,/83	Carison (1977)
Gulf Coast Lignite	Wilcox Choup		27 5		10 0	_	0.8		7 705 >	France and Katana (1077)
lexas	writes droup	-	27.5	-	10.0	. –	0.0	-	7,705	Evans and Kalser (1977)
Four Corners	Mana	70174	10.25	2 4 5 7	F 2	0400	0.6	10 450 12 000	11 (17	Dises
New Mexico	Navajo		13.2		20.4	-	0.72	10,400-12,000	9,200	Kottlowski (1975)

Adapted from Dvorak et al. (1977). Hyphens indicate no data available in the references used for this table. To convert Btu/lb to J/kg, multiply by 2.324 × 10<sup>3</sup>. Yalues are averages unless otherwise noted (MR = midrange; M = median). Halker and Hartner (1966). Synder and Aresco (1953). Excluding a value of 18.2. Excluding a value of 4.8. Excluding a value of 11,690. Excluding a value of 6.7.





location by more than two orders of magnitude. High concentrations of a specific trace element may be associated with proximity to ore beds for that element, and such anomalies in the concentration of some elements in coal are used as indicators of possible mineral deposits (Magee et al. 1973). The question of high variability was explored by Magee et al. (1973), who concluded that when coal is averaged within regions, the extreme variability observed on a local scale is not paralleled by similar variations among other regions. In Magee et al. (1973), data were averaged for groups of about three states, and variations of the order of a factor of 2-3 were found among regions for most elements. Sulfur varied by a factor of 8, and of the 18 trace elements examined, only Ge, B, Be, Ga, Zn, Sn, and Mo varied by more than a factor of 4 on this basis.

Trace-element concentrations in coal for the regions and states described in the previous section are presented in Table B.3. The entries for the Powder River and Four Corners regions are based on particularly small numbers of samples (1-14 per state), severely limiting the statistical significance of these data. The data entries for the Eastern Interior and Southern Appalachian states are based on between 25 and 51 samples per state. There are 117 samples for Pennsylvania and 247 for West Virginia.

Comparison of these data reveals higher values of barium in the Powder River Region and in New Mexico than elsewhere, and elevated boron levels in the Powder River Region, Four Corners Region, and, particularly, the Eastern Interior Region. Chromium, cobalt, copper, and vanadium content appear to be lower in the Powder River Region than elsewhere. Molybdenum and nickel concentrations are lower in Powder River and Four Corners coals than in other regions. Uranium concentrations are reported as ranges, not averages, and are seen to be highly variable, particularly in the Powder River and Four Corners regions. The value for lead in Illinois coals is significantly higher than in other regions, as is the value for manganese. The zinc content of Eastern Interior coals is high, and particularly so in Illinois. The lithium content of Appalachian coals is higher than that of other regions.

Uranium and thorium content of coal samples from various regions of the United States are listed in Table B.4. An additional radionuclide found in coal is Potassium-40 (K-40), comprising about 0.012% of the total potassium in natural materials. Coal contains an average of about 400 ppm K (calculated from data of O'Gorman and Walker 1972) and, therefore, about 0.05 ppm K-40.

Northe Appalac		nern Achian	Southern Appalachian			Eastern Interior			Powder River Region		Four Corners		
Element	W. Va.	Penn.	Eastern Ky.	Ala.	Va.	Tenn.	111.	Western Ky.	Ind.	Mont.	Wyo.	New Mexico	Ariz.
Arsenic	9	16	6	13	10	9	6	7	7	<6	1 <sup>b</sup>	2 <sup>b</sup>	2 <sup>b</sup>
Barium	77	70	79	110	99	120	49	44	31	380	170	270	39 <sup>h</sup>
Beryllium	1.2	0.8	1.5	0.74	1.1	0.58	1.3	1.4	1.7	1.5	2.4	0.94	0.97 <sup>h</sup>
Boron	20	15	19	30	13	24	81	70	85	60	36	43	49 <sup>h</sup>
Cadmium	-		-	-	-	-	2.9 <sup>C</sup>		-	<0.1 <sup>9</sup>	0.46 <sup>b</sup>	<2.6 <sup>b</sup>	<0.54 <sup>b</sup>
Chromium	19	24	19	19	20	19	29	18	19	3	5.8	11	9.7 <sup>h</sup>
Cobalt	17	18	15	18	14	13	15	16	24	7.7	5.2	15	-
Copper	11	13	11	14	13	11	8.3	8.8	9.7	3.2	4.4	5.9	4.9 <sup>h</sup>
Fluorine	70	90	30	90	50	120	59 <sup>C</sup>	-	50 <sup>h</sup>	70	160 <sup>b</sup>	160 <sup>b</sup>	70 <sup>5</sup>
Lead	4.9	5.2	4	3.7	6.1	4.9	33	6.4	7.2	4.8	0.61	4.7	3.9 <sup>h</sup>
Lithium	44	64	78	75	34	36	45	16	24	27	19	16	19 <sup>h</sup>
Manganese	21	21	26	19	42	23	`73	19	26	57	14	19	9.7 <sup>h</sup>
Mercury	0.12	0.20	-	-	-	-	0.18 <sup>e</sup>	-	0.08	0.07	0.05 <sup>b</sup>	0.08 <sup>b</sup>	0.05 <sup>b</sup>
Molybdenum	6.2	9.8	5.2	11	8.3	7.8	8.8	7.4	5.2	4.8	2.2	2.0	0.97 <sup>h</sup>
Nickel	18	20	16	17	22	16	25	16	33	3.3	4.1	8.1	4.9 <sup>h</sup>
Selenium	3.4 <sup>d</sup>	3.7 <sup>d</sup>	3.1 <sup>d,i</sup>	5.1 <sup>d</sup>	4.4 <sup>d</sup>	4.9 <sup>d</sup>	2 <sup>C</sup>	3.1 <sup>d,i</sup>	4 <sup>d</sup>	3 <sup>d</sup>	0.8 <sup>b</sup>	2.0 <sup>b</sup>	2.1 <sup>b</sup>
Tellurium	-	-	-	-	-	-	-	-	-	-	0.025 <sup>b</sup>	0.03 <sup>b</sup>	<0.02 <sup>b</sup>
Thallium	-	-	-	-	-	-	-	-	-	-	0.4 <sup>b</sup>	0.24 <sup>b</sup>	<0.2 <sup>b</sup>
Tin	1.5	1.1	4.6	2.2	2.3	1.8	2.6	2.5	0.74	1.1	1.4	1.9	0.97 <sup>h</sup>
Vanadium	30	33	29	31	33	34	35	32	35	12	15	25	9.7 <sup>h</sup>
Zinc	17	22	15	22	23	23	140	48	73	42	37	19	9.7 <sup>h</sup>
Zirconium -	63	68	60	56	44	45	88	77	100	77	39	110	39 <sup>h</sup>
Uranium range, not avg.	<10-30 <sup>f</sup>	20-190 <sup>f</sup>	10 <sup>f</sup>	-	<10 <sup>f</sup>	-	<10-80 <sup>f</sup>	-	10 <sup>f</sup>	10-340 <sup>f</sup>	10-1000 <sup>f</sup>	10-6200 <sup>f</sup>	-
#Samples for data from Abernethy et al. (1969)	247	117	26	47	51	25	29	50	31	8	3	14	1

# Table B.3. Average Trace-Element Concentrations (ppm) in Coal by State<sup>a</sup>

<sup>a</sup>From Dvorak et al. (1977). Except for entries marked by superscripts "b" through "g", entries in this table are based upon data in Abernethy et al. (1969). Hyphens indicate no data available. Swanson (1972). CRuch et al. (1974). Lakin (1973). <sup>e</sup>Ruch et al. (1971). <sup>f</sup>Abernethy and Gibson (1963). gU.S. Geological Survey (1974). <sup>B</sup>Based on a single sample. Mean value for all of Kentucky.

Table B.4.	Range of Uranium and Thorium Concentrations and Geometric Means	
	(expected values) for Coal Samples Taken from	
	Various Regions of the United States <sup>a</sup>	

	Coal rank	Number of samples	Uranium co (pp	ncentration n)	Thorium concentration (ppm)	
Region			Range	Geometric mean	Range	Geometric mean
Pennsylvania	Anthracite	53	0.3-25.2	1.2	2.8-14.4	4.7
Appalachia <sup>b</sup>	Bituminous	331	<0.2-10.5	1.0	2.2-47.8	2.8
Interior <sup>C</sup>	Bituminous	143	0.2-43	1.4	<3 -79	1.6
Northern Great Plains <sup>d</sup>	Subbituminous, lignite	93	<0.2-2.9	0.7	<2.0-8.0	2.4
Gulf <sup>e</sup>	Lignite	34	0.5-16.7	2.4	<3.0-28.4	3.0
Rocky Mountain <sup>f</sup>	Bituminous, subbituminous	134	<0.2-23.8	0.8	<3.0-34.8	2.0
Alaska	Subbituminous	18	0.4-5.2	1.0	<3.0-18	3.1

<sup>a</sup>From Swanson and Medlin et al. (1976). <sup>b</sup>Pennsylvania, Ohio, Maryland, West Virginia, Virginia, Kentucky, Tennessee, Alabama. <sup>c</sup>Michigan, Indiana, Iowa, Nebraska, Missouri, Kansas, Oklahoma, Arkansas. <sup>d</sup>North Dakota, Montana, Wyoming. <sup>e</sup>Alabama, Mississippi, Arkansas. <sup>f</sup>Wyoming, Colorado, Utah, Arizona, New Mexico.

Note: The analyses for uranium and thorium were performed on whole coal. The arithmetic average concentrations of thorium and uranium in ppm for all coal samples and various ranks of coal for the whole United States are as follows:

Coal rank	Samples	Thorium (ppm)	Uranium (ppm)	
All coal	799	4.7	1.8	
Anthracite	53	5.4	1.5	
Bituminous	509	5.0	1.9	
Subbituminous	183	3.3	1.3	
Lignite	54	6.3	2.5	

- Abernethy, R. F., and F. H. Gibson. 1963. Rare elements in coal. U.S. Bur. Mines Inf. Circ. 8163. 69 pp.
- Abernethy, R. F., M. J. Peterson, and F. H. Gibson. 1969. Spectrochemical analyses of coal ash for trace elements. U.S. Bur. Mines Rep. Invest. 7281. 30 pp.
- American Society for Testing and Materials. 1973. Standard specifications for classification of coals by rank, ASTM designation D388-66, reapproved 1972, pp. 54-58. <u>In</u> Gaseous Fuels, Coal and Coke: Atmospheric Analyses, Part 26.
- Arkle, T., Jr., J. A. Barlow, C. W. Lotz, and C. J. Smith. 1975. Description of seams: West Virginia, pp. 641-656. <u>In</u> Mining Informational Services, 1975 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Averitt, P. 1975. Coal resources of the United States, January 1, 1974. U.S. Geol. Surv. Bull. 1412. 131 pp.
- Calver, J. L. 1975. Description of seams: Virginia (revised), pp. 629-633. <u>In</u> Mining Informational Services, 1975 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Carlson, C. G. 1977. Description of seams: North Dakota, pp. 642-644. <u>In</u> Mining Informational Services, 1977 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Carter, R. P., J. R. LaFevers, E. J. Croke, A. S. Kennedy, and S. D. Zellmer. 1974. Surface Mined Land in the Midwest: A Regional Perspective for Reclamation Planning. ANL/ES-43. Prepared by Argonne National Laboratory, Energy and Environmental Systems Division, Argonne, Ill., for the U.S. Bureau of Mines, Washington, D.C. 1 v. (various pagings).
- Culbertson, W. C. 1964. Geology and coal resources of the coal-bearing rocks of Alabama. U.S. Geol. Surv. Bull. 1182-B. 79 pp. [As cited in Averitt (1975).]
- Daniel, T. W. 1977. Description of seams: Alabama, pp. 521-566. <u>In</u> Mining Informational Services, 1977 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Dvorak, A. J., et al. 1977. The Environmental Effects of Using Coal for Generating Electricity. NUREG-0252. Prepared by Argonne National Laboratory, Argonne, Ill., for the U.S. Nuclear Regulatory Commission. 221 pp.
- Edmunds, W. E. 1975. Description of seams: Pennsylvania, pp. 604-615. <u>In</u> Mining Informational Services, 1975 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Evans, T. J., and W. R. Kaiser. 1977. Description of seams: Texas, pp. 670-672. In Mining Informational Services, 1977 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Glass, G. B. 1975. Description of seams: Wyoming, pp. 657-669. <u>In</u> Mining Informational Services, 1975 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Kottlowski, F. E. 1975. Description of seams: New Mexico, pp. 585-593. <u>In</u> Mining Informational Services, 1975 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Lakin, H. W. 1973. Selenium in our environment, pp. 96-111. <u>In</u> R. F. Gould (ed.), Trace Elements in the Environment. Adv. Chem. Ser. 123. American Chemical Society, Washington, D.C.
- Luther, E. T. 1975. Description of seams: Tennessee (revised), pp. 616-619. <u>In</u> Mining Informational Services, 1975 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Magee, E. M., H. J. Hall, and G. M. Varga, Jr. 1973. Potential Pollutants in Fossil Fuels. EPA-R2-73-249; PB-225039. U.S. Environmental Protection Agency, Washington, D.C.
- Matson, R. E. 1975. Description of seams: Montana, pp. 577-584. <u>In</u> Mining Informational Services, 1975 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Matson, R. E. 1977. Description of seams: Montana, pp. 625-632. <u>In</u> Mining Informational Services, 1977 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.

- McBride, J. P., R. E. Moore, J. P. Witherspoon, and R. E. Blanco. 1977. Radiological Impact of Airborne Effluents of Coal-Fired and Nuclear Power Plants. ORNL-5315. Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Mining Informational Services. 1975. 1975 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- O'Gorman, J. V., and P. L. Walker, Jr. 1972. Mineral Matter and Trace Elements in U.S. Coals. Research and Development Report No. 61, Interim Report No. 2. Prepared for the Office of Coal Research, U.S. Department of the Interior, by the Coal Research Section, College of Earth and Mineral Sciences, The Pennsylvania State University.
- Pierce, H. W., S. B. Keith, and J. C. Wilt. 1970. Coal, oil, natural gas, helium, and uranium in Arizona. Ariz. Bur. Mines Bull. 182. 289 pp.
- Ruch, R. R., H. J. Gluskoter, and E. J. Kennedy. 1971. Mercury content of Illinois coals. Ill. State Geol. Surv. Environ. Geol. Notes No. 43. 15 pp.
- Ruch, R. R., H. J. Gluskoter, and N. F. Shimp. 1974. Occurrence and distribution of potentially volatile trace elements in coal. III. State Geol. Surv. Environ. Geol. Notes No. 72. 96 pp.
- Simon, J. A., and M. E. Hopkins. 1973. Geology of coal. <u>In</u> Elements of Practical Coal Mining. Ill. State Geol. Surv. Reprint.
- Simon, J. A., et al. 1975. Description of seams: Illinois, pp. 547-555. In Mining Informational Services, 1975 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Smith, G. E., and P. McGrain. 1975. Description of seams: Kentucky, pp. 566-571. In Mining Informational Services, 1975 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.
- Snyder, N. H., and S. J. Aresco. 1953. Analyses of tipple and delivered samples of coal (collected during the years 1948 to 1950). U.S. Bur. Mines Bull. 516. 133 pp.
- Swanson, V. E. 1972. Composition of Coal, Southwestern United States--Tables of Chemical Analyses. Extracted from U.S. Geological Survey Open-file Report, Southwest Energy Study, Report of the Coal Resources Work Group, Appendix J, Part II. 61 pp. (mimeo).
- Swanson, V. E., and J. H. Medlin, et al. 1976. Collection, Analysis, and Evaluation of Coal Samples in 1975. Open-file Report 76-468 (Draft). U.S. Department of the Interior, Geological Survey. [As cited in McBride et al. (1977).]
- U.S. Bureau of Mines. 1975. Demonstrated Coal Reserve Base of the U.S., by Sulfur Category on January 1, 1974. Mineral Industry Survey, Bureau of Mines, U.S. Department of the Interior.
- U.S. Energy Research and Development Administration. 1975. Synthetic Fuels Commercialization Program, Draft Environmental Statement. ERDA-1547. U.S. Department of the Interior, Washington, D.C.
- U.S. Geological Survey. 1974. Proposed Plan of Mining and Reclamation, Big Sky Mine, Peabody Coal Mine, Coal Lease M-15965, Colstrip, Montana. Final Environmental Statement. U.S. Department of the Interior.
- Walker, F. E., and F. E. Hartner. 1966. Forms of sulfur in U.S. coals. U.S. Bur. Mines Inf. Circ. 8301. 51 pp.
- Wier, C. E., and H. Hutchison. 1975. Description of seams: Indiana, pp. 556-559. <u>In</u> Mining Informational Services, 1975 Keystone Coal Industry Manual. McGraw-Hill Mining Publications, New York.

# APPENDIX C. SO<sub>2</sub> SENSITIVITY LISTS FOR VEGETATION

Plant species for which  $SO_2$  sensitivity has been determined are listed in this appendix. The plants are grouped into  $SO_2$  sensitive, intermediate, and resistant categories in each of the following separate lists:

- 1. Herbaceous Native Plants/Weeds (Table C.1)
- 2. Woody Trees, Shrubs, and Ornamentals (Table C.2)
- 3. Crop Plants (Table C.3)
- 4. Garden Plants (Table C.4)
- 5. Herbaceous Flowers and Ornamentals (Table C.5)

The list of native herbaceous plants and weeds (Table C.1) has been alphabetized by scientific name because common names of these plants vary from one region of the United States to another and most are well known by their scientific name. All of the other lists (Tables C.2-C.5) are alphabetized by common names because these are more universal in usage.

The  $SO_2$  tolerance ranking of a species or variety is often influenced by the specific criteria used for ranking. Criteria may range from cellular or physiological effects to changes in species composition. Foliar injury (leaf necrosis or chlorosis) is probably the most obvious response and can lead to other more significant effects. Most of the species listed in this appendix were ranked by the percentage of foliar injury induced by a given dose of  $SO_2$ . Rankings at the extremes of sensitivity or tolerance are the most useful and reliable; all must be used with caution and the understanding that these are compilations of relative sensitivities to  $SO_2$ .

The same genus may appear in more than one  $SO_2$  sensitivity category since the lists were compiled from the publications of numerous researchers--each of whom may have determined the sensitivity of a different species or variety, or of the same species under different environmental conditions, or using different ranking criteria.

Scientific name	Common name	Reference
	Sensitive	
Agrostis palustris	Bentgrass	USEPA (1973)
Amaranthus palmeri	Careless weed	Carrier (1977)
Amaranthus retroflexus	Pigweed	USEPA (1973)
Ambrosia artemisiifolia	Ragweed	Carrier (1977)
Ambrosia trifida	Ragweed, giant	Jones (1975per. comm.)
Aster sp.	Aster	USEPA (1973)
Brassica sp.	Mustard, black	USEPA (1973)
Bromus sp.	Bromegrass	USEPA (1973)
Chenopodium album	Lamb's quarters	USEPA (1973)
Cirsium sp.	inistle	Linzon et al. $(1972)$
Convolvulus arvensis	Bindweed	(1977)
Dactylis glomerata	Urchardgrass	USEPA (1973)
Delphinium sp.	Larkspur	Linzon et al. $(19/2)$
Erigeron canadensis	Fleadane Buolachast	Carrier (1977)
Fagopyrum sagittatum	Economic and	USEDA (1072)
restuca rupra	Veluetwood	(1973)
Halianthua SD	Sunflower	Carrier (1977)
Lactura scamiola	Prickly lettuce	Carrier $(1977)$
Lolium Sp.	Ryegrass	HSFPA (1973)
Malva parvifolia	Mallow	Carrier (1977)
Parthenocissus auinauefolia	Virginia creeper	Linzon et al. $(1972)$
Plantago major	Plantain	Carrier (1977)
Poa pratensis	Junegrass	USEPA (1973)
Poa sp.	Bluegrass	USEPA (1973)
Polygonum sp.	Smartweed	USEPA (1973)
Rumex crispus	Curly dock	Carrier (1977)
Rumex sp.	Sorrel	USEPA (1973)
Saponaria officinalis	Bouncing bet	USEPA (1973)
Sisymbrium sp.	Mustard, hedge	USEPA (1973)
Solanum sp.	Nightshade	USEPA (1973)
Solidago sp.	Goldenrod	Linzon et al. (1972)
Stellaria media	Chickweed	Benedict and Breen (1955)
Taraxacum officinale	Vandelion	Linzon et al. (1972)
Vicia sp.	Vetch Cooklohum	USEPA (1973)
kanthium sp.	LOCKIEDUr	USEPA (1973)
	Intermediate	
Asclepias sp.	Milkweed	USEPA (1973)
Aster sp.	Aster	Treshow (1970)
Brassica arvensis	Mustard	Benedict and Breen (1955)
Capsella bursa-pastoris	Shepherd's purse	USEPA (1973)
Helianthus annuus	Sunflower	Benedict and Breen (1955)
Malva parviflora	Cheeseweed	Benedict and Breen (1955)
Poa annua	Bluegrass, annual	Benedict and Breen (1955)
rou pratensis Portulaçã sp	Diveyrass, Kentucky	DENEUICI ANU BREEN (1955)
Spanting sp.	Saltarass	USEPA (1973)
spar-vena sp.	saltyrass	USEPA (1975)
	Resistant	
Chenopodium murale	Nettle-leaf goosefoot	Benedict and Breen (1955)
Dianthus sp.	Dianthus	USEPA (1973)
rnlox sp.	PNIOX	Linzon et al. (19/2)

Table C.1.  $SO_2$  Sensitivity Groupings for Herbaceous Native Plants/Weeds<sup>a</sup>

<sup>a</sup>The same genus may appear in more than one SO<sub>2</sub> category since the lists were compiled from the lists of numerous researchers.

Table C.2.  $SO_2$  Sensitivity Groupings for Woody Trees, Shrubs, and Ornamentals<sup>a</sup>

Common name	Scientific name	Reference				
·	Sensitive					
Alder, black	Alnus glutinosa	Davis and Wilhour (1976)				
Alder, thinleaf	Alnus tenuifolia	Davis and Wilhour (1976)				
Apple	Malus sp.	USDA (1973)				
Aspen, large-toothed	Populus grandidentata	Davis and Wilhour (1976)				
Aspen, trembling	Populus tremuloides	Davis and Wilhour (1976)				
Ash, red (green)	Fraxinus pennsylvanica	Skolly and lamo (1970)				
Ash, white Birch European	Retula pendula	Davis and Wilhour (1974)				
Birch, grav	Betula populifolia	Davis and Wilhour (1976)				
Birch, western paper	Betula papyrifera commutata	Davis and Wilhour (1976)				
Birch, white (paper)	Betula papyrifera	Davis and Wilhour (1976)				
Birch, yellow	Betula alleghanensis (lutea)	Davis and Wilhour (1976)				
Blackberry	Rubus sp.	Skelly and Lame (1974)				
Blueberry, lowbush	Vaccinium angustifolium	Davis and Wilhour (19/6)				
Catalpa	Catalpa sp.	USDA (1973) David and Wilhown (1076)				
Cherry, Ditter	Prunus emarginata	USEDA (1973)				
Cherry sour	Primie concere	Davis and Wilhour (1976)				
Cherry, sweet	Prunus avium	Davis and Wilhour (1976)				
Elm. Chinese	Ulmus parvifolia	Davis and Wilhour (1976)				
Fir, subalpine	Abies lasiocarpa	Davis and Wilhour (1976)				
Gooseberry	Ribes grossularia	USEPA (1973)				
Hazel, beaked	Corylus cornuta (rostrata)	Davis and Wilhour (1976)				
Hazel, California	Corylus cornuta californica	Davis and Wilhour (1976)				
Hazelnut	Corylus avellana	Davis and Wilhour (1976)				
Hemlock, mountain	Isuga mertensiana	USUA (1973) Davis and Wilhoum (1076)				
Horse chesthut	Larin cooidentalia	Davis and Wilhour (1976)				
Maple Manitoba	Acen negundo interius	Davis and Wilhour (1976)				
Maple, Manicoba Manle Jananese	Acer nalmatum	Davis and Wilhour (1976)				
Maple, Rocky Mountain	Acer alabrum	Davis and Wilhour (1976)				
Maple, sycamore	Acer pseudoplatanus	USEPA (1973)				
Mock-orange, Lewis	Philadelphus lewisi	Davis and Wilhour (1976)				
Mountain-ash, Sitka	Sorbus sitchensis	Davis and Wilhour (1976)				
Mulberry, Texas	Morus microphylla	Davis and Wilhour (1976)				
Ninebark, Pacific	Physcocarpus capitatus	Davis and Wilhour (1976)				
Ocean-spray	Holoaiscus arleafolius Drumus popoisa	USEDA (1973)				
Peach	Purue communie	USDA (1973)				
Pine eastern white	Pinus strobus	Davis and Wilhour (1976)				
Pine, jack	Pinus banksiana	Davis and Wilhour (1976)				
Pine, red	Pinus resinosa	Davis and Wilhour (1976)				
Pine, Virginia	Pinus virginiana	Skelly and Lame (1974)				
Plum, prune	Prunus domestia	USEPA (1973)				
Poplar, Lombardy	Populus nigra hybrid	Davis and Wilhour (1976)				
Red currant	Ribes rubrum	Davis and Wilhour (1976)				
Rockspirea, creambush	Holoalscus alscolor	Davis and Wilhour (1976)				
Serviceborry, low	Amelanchier spicala (scolonijera)	Davis and Wilhour (1976)				
Serviceberry litah	Amelanchier utahensis	Davis and Wilhour (1976)				
Sumac stachorn	Rhus tuphina	Davis and Wilhour (1976)				
Tulip tree	Liriodendron tulipifera	Skelly and Lame (1974)				
Willow, black	Salix nigra	Davis and Wilhour (1976)				
Walnut, English	Juglans regia	USDA (1973)				
Intermediate						
Alder, mountain	Alnus tenuifolia	Davis and Wilhour (1976)				
Apricot, Chinese	Prunus armeniaca var. Chinese	Davis and Wilhour (1976)				
Basswood	Tilia americana	Davis and Wilhour (1976)				
Birch, water	Betula occidentalis (fontinalis)	Davis and Wilhour (1976)				

### Alnus tenuifolia Prunus armeniaca var. Chinese Tilia americana Betula occidentalis (fontinalis)

# (continued)

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Common name	Scientific name	Reference
	Intermediate (cont.)	
Boxelder	Acer negundo	Davis and Wilhour (1976)
Cherry, bitter	Prunus emarginata	Davis and Wilhour (1976)
Chokecherry	Prunus virginiana	Davis and Wilhour (1976)
Cottonwood, black	Populus trichocarpa	Davis and Wilhour (1976)
Cottonwood, eastern	Populus deltoides	Davis and Wilhour (1976)
Cottonwood, narrowleaf	Populus angustifolia	Davis and Wilhour (1976)
Currant, sticky	Ribes viscosissimum	Davis and Wilhour (1976)
Dogwood, red osier	Cornus stolonifera	Davis and Wilhour (1976)
Douglas fir	Pseudotsuga menziesii	Davis and Wilhour (1976)
Elder, blueberry	Sambucus cerulea	Davis and Wilhour (1976)
Elm, American (White)	Ulmus americana	Davis and Wilhour (1976)
Fir, Dasalin	Abies palsamea	Davis and Wilhour (1976)
rir, yranu	Ables granals Vitio ringria	Davis and Wilhour (1976)
Hawthorn rod	Cratacone columbiana	Davis and Wilhour (1976)
Hazol witch	Hanamalia vinciniana	Davis and Wilhour (1976)
Hemlock western	Teyaa heteronhulla	Davis and Wilhour (1976)
Hibiscus	Hibisous SD.	USEPA (1973)
Honevsuckle, tatarian	Lonicera tatarica	Davis and Wilhour (1976)
Hydrangea	Hudranaea paniculata	Davis and Wilhour (1976)
Lilac, common	Surinaa vulaaris	Davis and Wilhour (1976)
Mahogany, mountain	Cercocarpus montanus	Davis and Wilhour (1976)
Maple. Douglas	Acer glabrum douglassi	Davis and Wilhour (1976)
Maple, red	Acer rubrum	Davis and Wilhour (1976)
Maple, Rocky Mountain	Acer glabrum	Davis and Wilhour (1976)
Mock-orange	Philadelphus sp.	USEPA (1973)
Mock-orange, coronarius	Philadelphus coronarius	Davis and Wilhour (1976)
Mock-orange, virginalis	Philadelphus virginalis	Davis and Wilhour (1976)
Mountain-ash, European	Sorbus aucuparia	Davis and Wilhour (1976)
Mountain-ash, western	Sorbus scopulina	Davis and Wilhour (1976)
Mountain-laurel	Ceanothus sanguineus	Davis and Wilhour (1976)
Oak, white	Quercus alba	Davis and Wilhour (1976)
Pine, Austrian	Pinus nigra	Davis and Wilhour (1976)
Pine, lodgepole	Pinus contorta	Davis and Wilhour (1976)
Pine, ponderosa	Pinus ponderosa	Davis and Wilnour (1976)
Pine, shortleaf	Pinus echinata	Tresnow (1970)
Pine, western white	Pinus monticola	Davis and Wilhour (1976)
Poplar, Dalsam	Populus palsamijera	IISEDA (1073)
KOSE Sagabauah big	Rosa sp.	Davis and Wilhour (1976)
Sagebrush, Dig	Hibumum sp	
Snowbarry mountain	Sumhani cannoe anconhilue	Davis and Wilhour (1976)
Snowberry, Columbia	Symphonicarpos cieupiccas	Davis and Wilhour (1976)
Snirea Van Houts	Spingea vanhouttei	Davis and Wilhour (1976)
Spirea, shinevleaf	Spiraea lucida	Davis and Wilhour (1976)
Sprice, Engleman	Picea engelmanni	Davis and Wilhour (1976)
Spruce, white	Picea glauca	Davis and Wilhour (1976)
Weigela	Weigela sp.	Davis and Wilhour (1976)
Wisteria	Wisteria sp.	USEPA (1973)
	Resistant	
Arborvitae (white cedar)	Thuja occidentalis	Davis and Wilhour (1976)

Arborvitae (white cedar) Beech, European Buck-brush Buffalo-berry Ceanothus, redstem Cedar, western red Citrus Cypress, Lawson

# (continued)

Fagus sylvatica

Thuja plicata

Citrus sp.

Ceanothus velutinus Shepherdia canadensis

Ceanothus sanguineus

Cupressus lawsoniana

Davis and Wilhour (1976) USDA (1973) Davis and Wilhour (1976) Davis and Wilhour (1976) Davis and Wilhour (1976) Davis and Wilhour (1976) USEPA (1973) USDA (1973)

Common name	Scientific name	Reference
	<u>Resistant</u> (cont.)	
Dogwood, white	Cornus florida	USDA (1973)
Fir, silver	Abies amabilis	Davis and Wilhour (1976)
Fir, white	Abies concolor	Davis and Wilhour (1976)
Forsythia	Forsythia viridissima	Davis and Wilhour (1976)
Gardenia	Gardenia sp.	USEPA (1973)
Ginkgo	Ginkgo biloba	Davis and Wilhour (1976)
Gum, black	Nyssa sylvatica	USDA (1973)
Hawthorn, black	Crataegus douglasii	Davis and Wilhour (1976)
Holly, English	Ilex aquifolium	USDA (1973)
Hornbeam, European	Carpinus betulus	USDA (1973)
Juniper, common	Juniperus communis	Davis and Wilhour (1976)
Juniper, Rocky Mountain	Juniperus scopulorum	Davis and Wilhour (1976)
Juniper, Utah	Juniperus osteosperma	Davis and Wilhour (1976)
Juniper, western	Juniperus occidentalis	Davis and Wilhour (1976)
Kinnikinnick	Arctostaphylos uva-ursi	Davis and Wilhour (1976)
Linden, littleleaf	Tilia cordata	Davis and Wilhour (1976)
Locust, black	Robinia pseudoacacia	USDA (1973)
Mahogany, curl-leaf mtn.	Cercocarpus ledifolius	Davis and Wilhour (1976)
Maple, hedge	Acer campestre	USDA (1973)
Maple, mountain	Acer spicatum	USDA (1973)
Maple, Norway	Acer platanoides	Davis and Wilhour (1976)
Maple, silver	Acer saccharinum	Davis and Wilnour (1976)
Maple, sugar	Acer saccharum	Davis and Wilnour (1976)
Oak, English	Quercus robur	USUA (1973)
Oak, Gambel	Quercus gambelii	Davis and Wilnour (19/6)
Uak, live	Quercus virginiana	USEPA (1973) David and Wilhows (1076)
Uak, northern red	quercus rubra	Davis and Wilhour (1976)
Uak, pin	quercus palustris	Davis and Wilhour (1976)
Uregon grape	Odostemon aquifolium	Davis and Wilhour (1976)
Pine, limber	Pinus flexilis	USDA (1072)
Pine, mugo	Pinus mugo	USDA (1973)
Pine, pinyon	Pinus edulis	Davis and Wilhour (1970)
Planetree, London	Platanus acerijolia	UAVIS ANU WITHOUR (1970) USDA (1973)
Planetree, Uriental	Platanus orientalis	USDA (1975)
(Sycamore)	Tomi andondrom radi cara mudharaii	Davis and Wilhour (1976)
Poison-ivy, western	Dowloadenaron radicuns ryaberger	Davis and Wilhour (1976)
Privot	Liquetrum SD	
Phododondnon	Phododondnon SD	USEPA (1973)
Sourwood	Orudendron anboneum	USDA (1973)
Spruce blue	Pigga nungens	Davis and Wilhour (1976)
Sallawbush	Rhus trilobata	Davis and Wilhour (1976)
Sumac. smooth	Rhus alabra	Davis and Wilhour (1976)
Svcamore American	Platanus occidentalis	USDA (1973)
(nlanetree)		/
Willow	Salix SD.	Skelly and Lame (1974)
Willow, shrubby	Salix tristis	Skelly and Lame (1974)
	- 1	Davie and Wilhoum (1076)

 $^{\rm a}{\rm The}$  same genus may appear in more than one  ${\rm SO}_2$  category since the lists were compiled from the lists of numerous researchers.

Common name	Scientific name	Reference	
	Sensitive		
Alfalfa	Medicago sativa	Carrier (1977)	
Barley	Hordeum vulgare	Carrier (1977)	
Bean, field	Phaseolus sp.	Carrier (1977)	
Bean, lima	Phaseolus lunatus	USEPA (1973)	
Clover	Trifolium sp.	Carrier (1977)	
Cotton	Gossypium hirsutum	USEPA (1973)	
Oats	Avena sativa	Carrier (1977)	
Pea	Pisum sativam	USEPA (1973)	
Potato, sweet Ipomoea batatas		USEPA (1973)	
Rubber tree Hevea brasiliensis		USEPA (1973)	
Rye	Secale cereale	Carrier (1977)	
Safflower	fflower Carthamus tinctoria		
Sovbean Glucine max		Carrier (1977)	
Sugar beet Beta vulgaris		Skelly and Lame (1974)	
Sweet clover Meliotus sp.		USEPA (1973)	
Tobacco	Nicotiana tabacum	USEPA (1973)	
Wheat Triticum aestivum		USEPA (1973)	
	Intermediate		
Clover	Trifolium sn	linzon et al. (1972)	
Pea	Pisum SD.	Linzon et al. $(1972)$	
Potato Irish	Solanum tuberosum	(1972)	
Sweet clover	veet clover Meliotus sp.		
	Resistant		
Corn	Tea mays	USEPA (1973)	
Sorghum	Sorghum sp.	Skelly and Lame (1974)	

# Table C.3. $SO_2$ Sensitivity Groupings for Crop Plants<sup>a</sup>

 $^{\rm a}{\rm The}$  same genus may appear in more than one  ${\rm SO}_2$  category since the lists were compiled from the lists of numerous researchers.

	[able	C.4.	S02	Sensitivity	Groupinas	for	Garden	Plantsa
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Common name	Scientific name	Reference					
Sensitive							
Bean	Phaseolus vulgaris	Carrier (1977)					
Bean, lima	Phaseolus lunatus	USEPA (1973)					
Beet	Carrier (1977)						
Broccoli	Brassica oleracea var. botrytis	Carrier (1977)					
Brussel sprouts	Brassica oleracea var. gemmifera	Carrier (1977)					
Cabbage	Brassica oleracea var. capitata	USEPA (1973)					
Carrot	Daucus carota	Carrier (1977)					
Celery	Apium graveolens	USEPA (1973)					
Cucumber	Cucumis sativa	USEPA (1973)					
Eggplant	Solanum melongena	USEPA (1973)					
Endive	Cichorium endivia	Carrier (1977)					
Kale	Brassica oleracea var. acephala	USEPA (1973)					
Leek	Allium porrum	USEPA (1973)					
Lettuce	Lactuca <sup>†</sup> sativa	Carrier (1977)					
Okra	Hibiscus esculentus	Carrier (1977)					
Onion	Allium cepa	USEPA (1973)					
Parsley	Petroselinum crispum	USEPA (1973)					
Parsnip	Pastinaca sp.	USEPA (1973)					
Pea	Pisum sativa	USEPA (1973)					
Pepper (bell, chili)	Capsicum frutescens	Carrier (1977)					
Potato, sweet	Ipomoea hatatas	Carrier (1977)					
Pumpkin	Cucurbita pepo	Carrier (1977)					
Radish	Raphanus sativus	Carrier (1977)					
Rhubarb	Rheum rhaponticum	Carrier (1977)					
Spinach	Spinacea oleracea	Carrier (1977)					
Squash	Cucurbita maxima	Carrier (1977)					
Swiss chard	Beta vulgaris var. cicla	Carrier (1977)					
Turnip	Brassica rapa	Carrier (1977)					
	Intermediate						
Castor bean	Ricinus communis	USEPA (1973)					
Horse-radish	Armoracia rusticana	USEPA (1973)					
	Resistant						
Cantaloupe	Cucumis melc	USEPA (1973)					
Corn	Zea mays	USEPA (1973)					

 $^{\rm a}{\rm The}$  same genus may appear in more than one  ${\rm SO}_2$  category since the lists were compiled from the lists of numerous researchers.

Common name	Scientific name	Reference	
	Sensitive		
Aster	Aster bigelovii	Carrier (1977)	
Bachelor's button	Centarea cyanus	Carrier (1977)	
Begonia	Begonia sp.	USEPA (1973)	
Coleus	Coleus blumei	USEPA (1973)	
Cosmos	Cosmos bipinnatus	Carrier (1977)	
Four-o'clock	Mirabilis jalapa	Carrier (1977)	
Gladiolus	Gladiolus sp.	USEPA (1973)	
Hollyhock	Althaea sp.	USEPA (1973)	
Iris	Iris sp.	USEPA (1973)	
Marigold	Tagetes sp.	USEPA (1973)	
Morning glory	Ipomoea purpurea	Carrier (1977)	
Nasturtium	Nasturtium sp.	USEPA (1973)	
Petunia	Petunia sp.	USEPA (1973)	
Sweet pea	Lathyrus odorata	Carrier (1977)	
Sweet william	Dianthus baratus	USEPA (1973)	
Verbena	Verbena canadensis	Carrier (1977)	
Violet	Viola	Carrier (1977)	
Zinnia	Zinnia elegans	Carrier (1977)	
	Intermediate		
Begonia	Begonia sp.	USEPA (1973)	
Canna lilv	Canna SD.	USEPA (1973)	
Castor bean	Ricinus communis	USEPA (1973)	
Chrysanthemum	Chrusanthemum Sp.	USEPA (1973)	
Gladiolus	Gladiolus Sp.	USEPA (1973)	
Hibiscus	Hibiscus SD.	USEPA (1973)	
Salvia	Salvia sp.	USEPA (1973)	
Snapdragon	Antirrhinum sp.	USEPA (1973)	
	Resistant		
Lilv	Lilium speciosum	USEPA (1973)	
Orchid	Cattleya Sp.	USEPA (1973)	
Orchid	Cumbidium sp.	USEPA (1973)	
Orchid	Odontoglossum sp.	USEPA (1973)	
Orchid	Oncidium sp.	USEPA (1973)	
Phlox	Phlox sp. Linzon et al. (1972		

Table C.5.  $SO_2$  Sensitivity Groupings for Herbaceous Flowers and Ornamentals<sup>a</sup>

 $^{\rm a}{\rm The}$  same genus may appear in more than one  ${\rm SO}_2$  category since the lists were compiled from the lists of numerous researchers.

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- Benedict, H. M., and W. H. Breen. 1955. The use of weeds as a means of evaluating vegetation damage caused by air pollution, pp. 177-189. In Proceedings of the Third National Air Pollution Symposium, Pasadena, California, April 18-20, 1955.
- Carrier, R. F. 1977. Plant interactions, pp. 8-1 to 8-118. <u>In</u> H. M. Braunstein, E. D. Copenhaver, and H. A. Pfuderer (eds.), Environmental, Health, and Control Aspects of Coal Conversion: An Information Overview, Vol. 2. ORNL/EIS-95. Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Davis, D. D., and R. G. Wilhour. 1976. Susceptibility of Woody Plants to Sulfur Dioxide and Photochemical Oxidants. EPA-600/3-76-102. Ecological Research Series, U.S. Environmental Protection Agency, Corvallis, Oregon. 71 pp.

Jones, H. C. 1975. Personal communication (Tennessee Valley Authority, Muscle Shoals, Alabama).

- Linzon, S. N., W. D. McIlveen, and P. J. Temple. 1972. Sulphur dioxide injury to vegetation in the vicinity of a sulphite pulp and paper mill. Water Air Soil Pollut. 2(1973):129-134.
- Skelly, J. M., and R. C. Lame. 1974. Diagnosis of Air Pollution Injury to Plants. Publ. 586. Virginia Polytechnic Institute and State University. 14 pp.
- Treshow, M. 1970. Environment and Plant Response. McGraw-Hill Book Company, New York. 422 pp.
- U.S. Department of Agriculture. 1973. Trees for polluted air. U.S. Forest Serv. Misc. Publ. No. 1230. 9 pp.
- U.S. Environmental Protection Agency. 1973. Effects of Sulfur Oxides in the Atmosphere on Vegetation. Revised Chapter 5 for Air Quality Criteria for Sulfur Oxides. EPA R3-73-030. National Environmental Research Center, Office of Research and Development, Research Triangle Park, N. C. 43 pp.

#### APPENDIX D. BEHAVIOR OF SELECTED TRACE ELEMENTS IN SOILS, PLANTS, AND ANIMALS

The following element-by-element description includes information on the availability, mobility, and toxicity of selected trace elements in soils, plants, and animals. In the reviewed literature, these elements were among those most often found in coal-fired power plant emissions. Although there are other elements emitted, the selection of elements also considered the relative toxicities of these elements to biota [as listed in Bowen (1966)] and the availability of information about the behavior and effects of each element. Additional data on toxicity are presented in Tables D.1 and D.2 at the end of this appendix.

#### ARSENIC

Arsenic usually exists in the soil solution as a divalent anion resembling phosphate. Like phosphate, it is fixed (converted from a readily available to a less available form) in the soil by iron, aluminum, and calcium and is more soluble under neutral or calcareous conditions (calcium forms are more soluble than iron or aluminum forms) (Berry and Wallace 1974; Wauchope 1975). Wauchope (1975) observed relatively higher levels of sorption of arsenate than phosphate in experiments utilizing alluvial soils. Although arsenic tends to be retained in the soil surface layers, it can be leached slowly to the lower soil horizons when it is in the soil solution (Berry and Wallace 1974; Lisk 1972; Vallee et al. 1960). Lime, organic matter, zinc compounds or chelates, and iron and aluminum compounds added to the soil may aid in maintaining the available arsenic (present in the soil in a form that can be readily absorbed and assimilated by growing plants) below toxic levels, whereas phosphate feritilization may enhance availability and thus toxicity (Lisk 1972).

Total endogenous soil concentrations of arsenic generally range from 0.1-40 ppm ( $\mu$ g/g) with an average of 6.0 ppm (Allaway 1968). However, total soil arsenic levels can reach several hundred ppm in areas where large amounts of arsenical pesticides have been used (Vallee et al. 1960).

Arsenic toxicity is dependent upon its oxidation state; the pentavalent state, which is most common in aerated soils, is much less toxic than the trivalent state (Allaway 1968; Berry and Wallace 1974; Lisk 1972). Organic arsenates such as cacodylic acid  $[(CH_3)_2HAsO_2]$  are toxic to plants but less toxic to animals, whereas the reverse is true for calcium and lead arsenates (Sullivan 1969a). Extremely toxic arsine gas (AsH<sub>3</sub>) may be produced by fungi in the soil (Berry and Wallace 1974). Elemental arsenic is considered to be relatively nontoxic (Berry and Wallace 1974; Sullivan 1969a).

According to Allaway (1968), plants grown on uncontaminated soils rarely contain greater than 1 ppm arsenic. In cases of arsenic toxicity the roots are usually severely affected, and plant growth is limited before much arsenic is translocated to the tops (Allaway 1968; Berry and Wallace 1974; Liebig 1966). Asparagus, tomato, carrot, tobacco, grape, and red raspberry appear to be among the most tolerant commercial plants whereas legumes, cucumber, sweet corn, and onions have little or no tolerance to arsenic (Vallee et al. 1960; Liebig 1966).

Arsenic compounds do not accumulate in mammals (Vallee et al. 1960; Frost 1967). Differences in the toxicity of various compounds have been correlated with animal excretion rates; compounds that are most slowly excreted tend to be the most toxic (Vallee et al. 1960; Frost 1967). The biological half-lives for excretion of arsenic compounds are reported to range from 30-60 hours (Sullivan 1969a; Frost 1967). The greatest danger to animals from arsenic emissions may be through the ingestion of arsenic-contaminated dust or soil on forage (Berry and Wallace 1974). Arsenic and its compounds do not appear to be carcinogenic, although there is some dispute about this in the literature (Allaway 1968; Sullivan 1969a; Frost 1967). Frost (1967), Buchanan (1962), and Vallee et al. (1960) have reviewed the toxicity and biological effects of arsenic in man and animals.

#### BARIUM

Very little barium is present in the soil in water-soluble form. Barium interacts with sulfates in the soil to form insoluble barium sulfate (Vanselow 1966a). Soils (notably acid

soils) may become infertile if the exchangeable barium exceeds the exchangeable calcium and magnesium. Liming will usually improve the calcium-to-barium ratio (Vanselow 1966a). Soluble barium compounds such as barium chloride, barium carbonate, barium sulfide, and barium oxide are highly toxic to animals when ingested (Miner 1969). Muscle tissue retains a moderate amount of barium when soluble salts of the element are ingested or injected in large doses; smaller amounts of barium are deposited and retained in bone (Browning 1961). Inhalation of most barium compounds can produce toxic effects in animals (Miner 1969); in general, however, the toxicity of inhaled barium is less than that of lead, cadmium, mercury, nickel, selenium, arsenic, or beryllium.

#### BERYLLIUM

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Beryllium is strongly fixed in soils and can readily displace other divalent cations (including barium, calcium, magnesium, and strontium) at sorption sites on the cation exchange complex (Lisk 1972; Romney and Childress 1965). Beryllium can also undergo isomorphic substitution in secondary clay minerals because of its chemical similarity to aluminum (Romney and Childress 1965). Like other cations, beryllium is more soluble and thus more available in acidic soils than in neutral or alkaline soils. Total endogenous concentrations of beryllium in uncontaminated soils generally range from 0.1-40 ppm ( $\mu$ g/g) with an average of 6 ppm (Allaway 1968).

Romney and Childress (1965) have demonstrated that beryllium can inhibit plant growth when it is present in the soil in a soluble form. In a series of experiments utilizing several crop plants and soil amended with beryllium to levels of 0, 10, and 20% of the cation exchange capacity, soluble  $Be(NO_3)_2$  and  $BeSO_4$  decreased yields, whereas insoluble  $BeCO_3$  and BeO had no effect on plant growth (Romney and Childress 1965). Because of beryllium's strong tendency to form complexes and colloidal aggregates when the soil pH is above 5.5, toxicity to plants is greatly reduced when soil pH is above this level (Lisk 1972; Romney and Childress 1965). Beryllium tends to accumulate in plant roots; relatively little is translocated to plant tops (Allaway 1968; Berry and Wallace 1974; Romney and Childress 1965; Romney et al. 1962). Of the aerial plant parts, leaves generally accumulate higher levels than stems, and fruits have the lowest concentrations (Romney and Childress 1965; Romney et al. 1962). The toxic effects of beryllium on plant growth appear to be centered in the root tissues (Romney and Childress 1965; Romney et al. (1962), where beryllium may affect certain enzyme systems (Hoagland 1952b; Klemperer 1950).

Beryllium and all of its known compounds (soluble or insoluble) are believed to be toxic to man depending on the quantity and duration of exposure (dose) (Durocher 1969). Very little information on the effects of beryllium on animals exists except for studies on laboratory animals. Beryllium sulfate was found to inhibit intestinal absorption of glucose in rats (Sols and Dierssen 1951); dogs given 1-3 g of beryllium carbonate daily in their diets showed a 25% decrease in the calcium content of their teeth (Cassarotto 1952). The major hazard to humans, and presumably to animals, is through inhalation (Berry and Wallace 1974; Durocher 1969). The result is berylliosis which has a mortality rate of 30% (Berry and Wallace 1974; Schubert 1958). The disease affects all regions of the respiratory tract and can involve all organs of the body except those in the pelvic area (Durocher 1969; Schubert 1958). Because beryllium has a long residence time in the body, it is a suspected carcinogen (Durocher 1969). Standards for the atmospheric concentration of beryllium in areas other than work places require that the average, short-term (24-hour) or monthly concentrations not exceed 0.01  $\mu$ g/m<sup>3</sup> (Berry and Wallace 1974; Durocher 1974; Durocher 1958).

#### BORON

Boron is essential for plant growth, but there is only a very narrow margin between deficiency and toxicity (Berry and Wallace 1974). Boron usually exists as undissociated boric acid at soil pH's less than 8.5; thus it is relatively leachable, although not as leachable as some chlorides, nitrates, or sulfates (Berry and Wallace 1974; Bingham et al. 1972). The addition of lime to soils may increase the sorption of boron by soils and may, therefore, be associated with boron deficiencies (Scott et al. 1975; Brady 1974). The interactions of boron with soil organic matter are not well known, and boron movement in soils high in organic matter may be quite different from movement in mineral soils (Berry and Wallace 1974). There are reports that soil sorption of boron generally increases with increasing organic matter content and increasing specific surface area  $(m^2/g)$  of the soil (John et al. 1977). Interactions of boron, calcium, and nitrogen occur in soils and plants, with results that are dependent on plant species, soil type, element concentrations, and environmental conditions (Gupta et al. 1976; John et al. 1977; Bradford 1966). The uptake of boron by plants is apparently reduced under conditions of low soil moisture availability, possibly due to a decreased mass flow of ions to root surfaces (Gupta et al. 1976).

According to Hewitt (1966), some plants have an optimum boron level in solution culture of 15 ppm ( $\mu$ g/mL) whereas other species exhibit toxic symptoms at 0.5 ppm in solution culture.

Generally, cereal grains require less boron than dicots. Bingham (1973) has identified boronsensitive, -semitolerant, and -tolerant crop species, with toxicities observed at 0.5-1.0, 1.0-5.0, and 5.0-10.0  $\mu$ g B/mL, respectively, in saturation extracts of soils. Sensitive species (in order of increasing susceptibility) include citrus, avocado, apricot, peach, cherry, persimmon, fig, grape, apple, pear, plum, navy bean, Jerusalem artichoke, and walnut. Semitolerant species include lima bean, sweet potato, bell pepper, oat, milo, corn, wheat, barley, olive, field pea, radish, tomato, cotton, and potato. Tolerant species include carrot, lettuce, cabbage, turnip, onion, broad bean, alfalfa, garden beet, mangel, sugar beet, palm, and asparagus.

### CADMIUM

Like other divalent cations, cadmium is usually more available in acid, sandy soils than in neutral or alkaline soils with large amounts of clay or organic matter (Lisk 1972; Hiatt and Huff 1975). An inverse relationship between soil pH and cadmium uptake by plants has been observed by several workers (Miller et al. 1976; John 1972; John et al. 1972; Lagerwerff 1971; Santillan-Medrano and Jurinak 1975). Also, as the cation exchange capacity of the soil is increased, cadmium uptake has been found to decrease (Miller et al. 1976; John et al. 1972; Haghiri 1974). Results of experiments by Haghiri (1974) indicate that soil organic matter fixes cadmium primarily through its cation exchange properties rather than its chelating ability. There is some evidence that the concentrations of certain elements in the soil (including Ca, Zn, P, K, and Al) may affect cadmium uptake (Miller et al. 1976; John et al. 1972; John 1976; Root et al. 1975). Cadmium levels in plant tissue may subsequently affect the balance of essential elements in the plant (John 1976; Root et al. 1975).

Cadmium occurs naturally in close association with zinc, usually in concentrations directly related to zinc levels (Athanassiadis 1969a). Cadmium to zinc ratios vary; for most soils and minerals, ratios of 1:1000 to 1:12,000 have been reported (Friberg et al. 1971). Since zinc is essential for most life forms, cadmium is probably present in all naturally occurring organic materials (Friberg et al. 1971). In most uncontaminated soils, cadmium concentrations range from 0.01 to 7.0 ppm ( $\mu$ g/g) with an average of 0.06 ppm (Allaway 1968).

Although plants normally contain < 0.5 ppm cadmium (Allaway 1968), many species may accumulate much higher concentrations (up to several hundred ppm) when they are grown on soils with elevated cadmium concentrations (Lisk 1972; Miller et al. 1976; John 1972; John et al. 1972; Lagerwerff 1971; Haghiri 1974; John 1973). Although some trace elements--such as beryllium, lead, and arsenic--are accumulated mainly in the roots, plants generally translocate relatively more cadmium to the above-ground plant parts (Hodgson 1970; Vaughan et al. 1975). However, each species varies in its ability to accumulate cadmium. The gross effects of cadmium toxicity in plants include wilting, chlorosis, necrosis, and a reduction of growth (Hiatt and Huff 1975; Root et al. 1975). Huang et al. (1974) found that cadmium generally inhibited soybean metabolism and adversely affected nitrogen fixation and photosynthesis.

Cadmium is an accumulative poison in animals (Berry and Wallace 1974; Hiatt and Huff 1975). Mammals seem to lack the ability to excrete cadmium, and they will continually absorb it, even though body levels are high (Berry and Wallace 1974). The biological half-life of cadmium is quite long compared to that of some other elements. Half-lives have been estimated as several hundred days for mice, greater than two years for squirrel monkeys, and from approximately 10 to 30 years for man (Hiatt and Huff 1975; Friberg et al. 1971; Lagerwerff 1972). It has been reported that cadmium can adversely affect the respiratory, cardiovascular, nervous, and reproductive systems; disrupt kidney and liver function; and cause gastric and intestinal disorders and anemia (Athanassiadis 1969a). Usually, 50-75% of the total cadmium body burden resides in the kidney and liver (Hiatt and Huff 1975). It has been demonstrated that cadmium and its compounds can be carcinogenic in laboratory animals (Athanassiadis 1969a; Friberg et al. 1971). As yet, there is no conclusive evidence that cadmium is carcinogenic in humans (Athanassiadis 1969a; Friberg et al. 1971). Friberg et al. (1971), Flick et al. (1971), and Athanassiadis (1969a) have reviewed the toxicity and biological effects of cadmium in man and animals.

Cadmium levels of 15 ppm in food may be injurious to man (Underwood 1962). The critical level of cadmium accumulation in man is believed to be 200 ppm in the renal cortex (Hiatt and Huff 1975). Yamagata and Shigematsu (1970) have shown that it is possible for cadmium to be incorporated into the food chain from contaminated soils and waters in quantities which are toxic to man. Carroll (1966) demonstrated a close correlation between atmospheric cadmium levels and death from hypertension and arteriosclerotic heart disease in 28 U.S. cities. Hiatt and Huff (1975) point out that cadmium concentrations in cigarettes and food could cause heavy smokers to come dangerously close to the "threshold of observable symptoms of cadmium poisoning" if exposed to additional sources of cadmium. All of this suggests that addition of cadmium to the environment from any source may have serious adverse effects to the food chain and man.

#### CHROMIUM

Chromium has oxidation states of 2+, 3+, and 6+. The divalent chromous compounds arereadily oxidized and, therefore, are rarely encountered in the natural environment (Sullivan 1969b). Chromium usually exists in soil as insoluble oxides (chromites), which are largely unavailable at pH's greater than 4.0 (Allaway 1968; Lisk 1972; Sullivan 1969b). Most of the more toxic hexavalent chromates are rare and unstable in soils (Lisk 1972). Soluble chromium added to soils will usually revert to the insoluble forms (Lisk 1972). The reduction of hexavalent chromium to insoluble trivalent chromium oxides is more rapid in acidic soils than in alkaline soils (Cary et al. 1977b). Working with soil suspensions, Bartlett and Kimble (1976a, 1976b) concluded that hexavalent chromium, if it remains in soils, behaves similarly to orthophosphate, but unlike phosphate it is quickly reduced by organic matter. Hexavalent chromium added to a soil apparently remains mobile only if its concentration exceeds both the adsorbing and reducing capacity of the soil. Conversely, oxidation of trivalent chromium to hexavalent chromium was not observed, even under conditions of high pH and maximum aeration. Trivalent chromium apparently behaves somewhat like aluminum in soils.

Toxic effects on plants may occur from serpentine soils which are often relatively high in chromium (Cannon 1970). Chromium is essential for animals, but it can be toxic at much higher concentrations (Berry and Wallace 1974). Plants do not seem to accumulate chromium, and animals apparently absorb little chromium from plant material in their digestive tract (Allaway 1968). In fact, Schroeder (1965) has concluded that food and feed crops currently produced contain insufficient chromium to meet the requirements of man and animals. Cary et al. (1977a) found that for the plant species studied in solution culture experiments, leafy vegetables that tend to accumulate iron (e.g., spinach and turnip leaves) were the most effective accumulators of chromium in edible plant parts. Head lettuce, cabbage, and other leafy vegetables, which do not accumulate relatively high iron concentrations, accumulated less chromium also. Little chromium appeared to be translocated to the seeds of beans, peas, corn and wheat.

In animals, trivalent chromium is less toxic than the hexavalent form, probably because the former permeates biological membranes less readily (Natl. Acad. Sci. 1974).

#### COBALT

Cobalt is an essential element for plants and animals. Cobalt ores are usually found in conjunction with iron and nickel (Ermolenko 1966). In alkaline soils, cobalt forms sparingly soluble hydrates, whereas in acid soils it is displaced from exchange sites by hydrogen, enters the soil solution, and is washed out of surface layers or may be taken up by plants (Ermolenko 1966). Oxidized compounds of cobalt are more mobile than sulfides (Ermolenko 1966). Vanselow (1966b) indicated that excesses of cobalt in nature are not likely for plants and animals. Fujimoto and Sherman (1950) added 225 kg/ha (200 lb/acre) cobalt to soils in pot experiments and found no toxicity to citrus or Sudan grass.

In nearly all mammalian tissues, cobalt concentrations are  $<0.1 \ \mu g/g$  wet weight (Williams 1977). Toxic doses depend upon the species and condition of the individual animal. Sheep can tolerate doses of 3 mg/kg body weight without adverse effects (Becker and Smith 1951). Toxic effects of cobalt include congestion, hemorrhages in the liver and adrenals, thickening of alveolar epithelium, and renal and pancreatic degeneration (Luckey and Venugopal 1977).

# COPPER

Copper, another essential element, is sorbed or bound more strongly to soil colloids than many other cations (Baker 1974). It forms complexes and chelate linkages with lignoproteins and other humate compounds (Reuther and Labanauskas 1966). Apparently, soluble complexing agents in the soil solution contribute significantly to the mobility of copper in soils (Nielsen 1976). Copper complexes in the soil are more stable than those of lead, iron, nickel, manganese, cobalt, zinc, and magnesium (Baker 1974), and are held most securely at a pH range of 7.0 to 8.0 (Reuther and Labanauskas 1966). The water-soluble sulfates are more mobile than the insoluble sulfides (Ermolenko 1966). The ratio of total copper in the soil to available copper ranges from 2:1 to 100:1 (Baker 1974). Copper toxicity on agricultural soils usually occurs after a period of many years in acid soil areas where copper residues from Bordeaux fungicides or copper sulfate fertilizers have accumulated (Baker 1974).

Chronic copper poisoning of animals can occur from contamination of feed or pastures. Sheep appear to be the most susceptible of all livestock to copper poisoning. Up to 2 g copper sulfate given daily to cows produced no adverse effects (Ferguson 1943).

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#### FLUORIDE

Fluoride is widely distributed in soils, usually increasing in concentration with depth. The normal range of fluoride in soils is 10-1000 ppm although certain soils, notably some in Idaho (3870 ppm) and Tennessee (8300 ppm), have much higher concentrations (Natl. Res. Counc. 1971; Pack 1971). Fluoride is usually insoluble or tightly bound to soil particles (except in very acid soils) (Allaway 1968; Groth 1975; Brewer 1966a; Treshow 1971). Over 90% of soil fluoride may be unavailable for plant uptake. Fluoride compounds are relatively persistent and not biodegradable (Groth 1975).

Airborne fluorides, including both gaseous and particulate forms, pose a greater potential hazard to vegetation than does fluoride uptake from soils (Natl. Res. Counc. 1971). Particulate fluorides are deposited on plant leaf surfaces whereas gaseous fluorides enter plants directly through the stomata. Upon absorption by the plant, the compounds are usually translocated to the leaves where they tend to accumulate in the leaf tips and margins (Treshow and Pack 1970; Treshow 1970; Hill 1969). The concentration of fluoride in these areas is usually several times higher than the concentration in the leaf as a whole (Treshow and Pack 1970).

Some sensitive plants, such as apricot, gladiolus, and grape, respond initially to fluoride by developing a dull, gray-green water-soaked discoloration of tissues along leaf margins and tips, usually within 24 hours after exposure to several parts per billion fluoride (Treshow and Pack 1970). After 48 hours, in hot weather, necrosis ensues and a characteristic reddish brown band between necrotic and healthy tissue develops. Cool temperatures can cause the delay of symptom expression by several days (Treshow and Pack 1970). In other species including citrus, poplar, and cherry, the characteristic symptom of fluoride accumulation is chlorosis (Treshow and Pack 1970; Treshow 1970). Flower and fruit production are usually not affected by fluoride pollution; however, peaches can develop "suture red spot" (a form of "soft suture" due to fluorides) rendering the fruit unmarketable (Treshow and Pack 1970; Treshow 1970; Weinstein and McCune 1971). Symptoms similar to "suture red spot" have been described for other fruits. including apricot, cherry, and pear (Treshow and Pack 1970; Treshow 1970). As a group, conifers are among the plants most sensitive to airborne fluorides (Natl. Res. Counc. 1971; Treshow 1970). Phytotoxic symptoms are primarily confined to the current year's growth and the method of injury and symptoms are similar to those described above (Treshow and Pack 1970; Treshow 1970). Some monocots such as gladiolus are extremely sensitive to airborne fluorides. Cereal grain crops are more resistant to fluoride pollution than are corn and sorghum. Symptoms of injury in monocots generally include chlorosis and necrosis (Treshow and Pack 1970; Treshow 1970).

Gaseous fluorides constitute a greater threat to vegetation than do particulate fluorides. Gaseous fluorides can enter the leaf directly through the stomata, whereas particulates deposited on the leaf surface enter the leaf only after being dissolved (Hill 1969). As with other gaseous pollutants, fluoride toxicity is influenced by concentration, duration of exposure, sequence and frequency of exposure, and is modified by environmental variables such as time of day (light intensity) and temperature (Treshow 1971; McCune and Hitchcock 1971). For example, high temperatures will speed up the development of phytotoxic symptoms. Suture red spot in peaches is influenced by calcium and boron nutrition (Treshow and Pack 1970). Damage to fruit trees is usually more severe in orchards that have been neglected and are in poor condition, than in nearby, well-managed, well-irrigated orchards (Treshow 1970; Hill 1969).

Species vary greatly in susceptibility to gaseous fluorides. The most susceptible species appear to be gladiolus and some other horticultural plants, some conifers, citrus, and some other fruit trees, notably apricot. Some varieties of corn and sorghum are quite susceptible to fluoride (Natl. Res. Counc. 1971). Wheat is generally considered fairly resistant (Natl. Res. Counc. 1971; Treshow 1970). Several researchers have reported that beans are moderately resistant to fluoride (Natl. Res. Counc. 1971; Pack 1971).

It is difficult to correlate observed vegetative damage with plant productivity and yield. However, MacLean et al. (1977) have observed a 20% reduction in the number and a 25% reduction in the fresh mass of marketable pods of beans continuously fumigated with 0.6  $\mu$ g F/m<sup>3</sup> (0.73 ppb) in field chambers from emergence to harvest (43 days). The leaves accumulated a mean of 71.1  $\mu$ g F/g dry weight (ppm) and whole pods accumulated a mean of 4.6  $\mu$ g F/g dry weight, but neither exhibited visual symptoms of HF phytotoxicity. Tomato plants exposed to similar conditions did not exhibit visual symptoms or a reduction in the number or fresh mass of tomato fruits. McCune (1969) has summarized the literature on fluoride toxicity in plants .

Toxic effects in animals due to ingestion of fluoride-contaminated vegetation and inhalation have been studied primarily in cattle, the most susceptible domestic animals (Natl. Res. Counc. 1971; Allaway 1968; Yamartino et al. 1976; Suttie et al. 1972). Controlled experiments indicate that long-term ingestion by dairy cattle of diets containing concentrations in excess of 40 ppm fluoride may have severe toxic effects (Natl. Acad. Sci. 1974). However, forage plants can tolerate several times this concentration (Phillips et al. 1955) and thus could be potentially toxic to grazing animals. Although the majority of research on animals to date has been conducted on herbivores, one report indicated that fluoride may accumulate throughout the food chain (Carlson 1973).

Animals exhibit three levels of symptoms due to the dose of fluoride ingested (Suttie 1976, <u>personal communication</u>). The most serious (acute toxicity) involves metabolic changes that result in severe toxic symptoms which include gastroenteritis, clonic convulsions, muscular weakness, pulmonary congestion, skeletal changes, and respiratory and cardiac failure (Natl. Res. Counc. 1971; Natl. Acad. Sci. 1974). A second level (chronic toxicity) is manifested by abnormal tooth development, especially in young animals. This condition can result in malnutrition, particularly in cattle. Changes in bone structure along with stiffness and lameness may also appear in cases of chronic fluoride toxicity (Natl. Res. Counc. 1971; Allaway 1968; Suttie 1976, <u>personal communication</u>). The third level, resulting from very low levels of fluoride ingestion, involves tooth discoloration. Usually, no other visible symptoms are observed (Suttie 1976, <u>personal communication</u>). Fluoride concentration in the bone is the most reliable indicator of toxicity as approximately 99% of the body burden is stored there (Natl. Acad. Sci. 1974).

Dietary fluoride is generally accepted as the major source of fluoride toxicity in animals. For cattle, the safe range for soluble fluorides is listed at 30-50 ppm, and for insoluble fluorides at 60-100 ppm (Phillips et al. 1960). Sheep and swine are less sensitive to soluble fluorides (70-100 ppm); horses are intermediate (Natl. Res. Counc. 1971). Poultry are the least sensitive of livestock, with safe fluoride levels as high as 150-300 ppm for chickens and 300-400 ppm for turkeys (Phillips et al. 1960).

The National Research Council (1971), Yamartino et al. (1976), and Treshow (1971) have provided a more complete review of the literature on fluoride.

#### LEAD

Most soil lead is relatively unavailable to plants (Zimdahl and Arvik 1973; Natl. Res. Counc. 1972) and is strongly fixed by the humic fraction of the soil (MacLean et al. 1969; Brewer 1966b). Hassett (1974) measured lead (as lead chloride) sorption in ten Illinois soils. Results of regression analysis indicated that of the soil properties analyzed, cation exchange capacity had a greater effect on lead sorption than soil pH, and soil pH had a greater effect than soluble phosphorus. According to Wilson and Cline (1966), only 0.003-0.005% of the total lead in soil is available for plant uptake. Absorbed lead is poorly translocated to plant tops (Berry and Wallace 1974). Ingestion of surface deposits of airborne lead on forage and inhalation of lead are significant additions to the total body burden of animals (Allaway 1968; Lisk 1972; Zimdahl and Arvik 1973). Lead poisoning of cattle and other grazing animals from ingestion of contaminated forage has been reported (Schmitt et al. 1971; Calif. Air Res. Board 1971; Hammond and Aronson 1964; Allcroft 1950, 1951). Lead concentrations are often highest near heavily traveled highways because of high lead levels in automobile engine exhaust (Lagerwerff 1972). Lead emissions from coal combustion will thus contribute to high lead levels in these areas.

#### MANGANESE

Manganese is an essential element and is relatively less toxic than a number of other trace elements. Excessive concentrations of manganese have been found in some soils in Kentucky, Connecticut, and Hawaii (Sherman 1957). Toxic concentrations, although rarely observed, usually occur in acidic or poorly aerated soils, which favor the formation of the available divalent form over the unavailable higher oxides (Leeper 1947; Piper 1931; Bradfield et al. 1934; Adams and Pearson 1967).

The normal manganese concentrations found in body tissues and fluids are characteristic of particular organs, with little variation among species or with age. Manganese tends to be higher in tissues rich in mitochondria and is associated with the presence of melanins. Manganese concentrations are usually greater within the mitochondria than in other cell components (Underwood 1971).

Manganese poisoning in animals has been noted for many years, but little is known about the long-term effects of exposure to relatively low-level environmental concentrations. Hens have tolerated up to 1000 ppm without adverse effects (Gallup and Norris 1938). Growing rats have had dietary intakes as high as 1000-2000 ppm with no apparent ill effects. However, lower feed intake and decreased body weight gains have been observed in calves on a basal ration supplemented with 2460 and 4920 ppm manganese sulfate (Cunningham et al. 1966).

#### MERCURY

Mercury in coal emissions exists as a vapor and in metallic form (perhaps some mercuric oxide also) adhering to fly ash particles (Huckabee 1973). Mercury in the soil is rapidly fixed by organic matter and clay fractions, although some escapes as the volatile elemental mercury (Berry and Wallace 1974; Lisk 1972). In general, organic mercury compounds are the most toxic (Stahl 1969a). Natural methylmercury formation is well documented for aquatic systems; however, Rogers (1976) and others have determined that methylation of divalent mercury does occur in agricultural soils. The results of Rogers (1976) indicate that a biological mechanism apparently exists which prevents the accumulation of methylmercury in soils. Lee (1974) reported that exchanges occur between organic and inorganic mercury compounds in the soil, and that levels of uptake for both are low. The results of a Hg-203 tagged fly ash microcosm experiment by Huckabee (1973) showed that mercury vapors are believed to be the primary source of phytotoxicity (Hitchcock and Zimmerman 1957).

Wildlife has occasionally been found with high levels of mercury in their tissues. In Sweden, Borg et al. (1969) determined that 28 out of 32 pheasants studied had ranges of 25-140 ppm mercury in their liver. The birds with the higher levels were either dead or dying when found, indicating that these levels were indeed toxic. These high tissue concentrations were attributed to the ingestion of seed dressed with a fungicide containing methylmercury. Elevated levels of mercury and its organoforms have been found in a number of fish-eating birds such as gulls, cranes, and white-tailed eagles (Borg et al. 1969). Mercury is more dangerous to man via inhalation than ingestion, and animals appear to be even more sensitive than man (Stahl 1969a).

#### MOLYBDENUM

Molybdenum is usually present in the soil as oxidized molybdates which are fairly mobile under alkaline conditions (Ermolenko 1966; Johnson 1966). Availability is low in acidic soils (Ermolenko 1966; Prince 1957). Molybdenum is an essential element for plants and toxicity is rarely observed in the field; most plants seem to tolerate high tissue concentrations (Allaway 1968; Johnson 1966). Molybdenum uptake and accumulation is generally higher in legumes than in grasses, and legumes grown on poorly drained soils usually have higher molybdenum tissue concentrations than those grown on well-drained soils (Kubota et al. 1967). Animals require very low amounts of molybdenum, usually less than 1 ppm of the dry diet (Allaway 1968). High levels of molybdenum in forage can cause molybdenosis (molybdenum-induced copper deficiency) in animals, especially ruminants (Allaway 1968; Johnson 1966). When dietary copper levels are low (< 4 ppm), 5 ppm molybdenum in the diet may have detrimental effects (Allaway 1968). It is often possible, however, to correct for high dietary levels of molybdenum by the use of copper injections or dietary supplements (Allaway 1968). Molybdenum emissions from coal-fired power plants may contribute to molybdenum toxicity in animals in some areas, but they may benefit molybdenum-deficient areas (acidic soils).

#### NICKEL

Nickel seems to be fixed and less available in soils with pH's above 7.0 or below 6.5 (Lisk 1972). Nickel interferes with the uptake of iron, and sufficient levels of iron appear to reduce the toxicity of nickel to plants (Lisk 1972). Naturally occurring nickel toxicity has been observed on some serpentine soils (Berry and Wallace 1974). Nickel is not highly toxic to animals when ingested (Natl. Res. Counc. 1975). Nickel carbonyl [Ni(CO)<sub>4</sub>] is considered extremely toxic to man when inhaled or absorbed through the skin (Lisk 1972; Sullivan 1969c).

## SELENIUM

Selenium fallout from coal combustion occurs both as elemental selenium, which is relatively insoluble and only slowly oxidized, and as  $SeO_2$ , which forms soluble selenite salts (Lakin 1973). In acidic soils, selenium is usually fixed as insoluble ferric selenite and is therefore largely unavailable to plants (Lisk 1972; Lakin 1973; Ganje 1966; Allaway et al. 1967). In arid, alkaline soils (pH > 8), selenium is generally available to plants as soluble calcium selenate and soluble organic selenium compounds (Allaway 1968; Lisk 1972; Lakin 1973; Ganje 1966).

In the United States, seleniferous soils (soils containing high levels of selenium; some reported as high as 80-90 ppm) are distributed patchily from North Dakota south to Texas and west to the Pacific (Ganje 1966; Rosenfeld and Beath 1964). These soils are generally alkaline in nature, contain  $CaCO_3$ , and are located in areas receiving less than 51 cm (20 inches) annual rainfall. However, most soils contain less than 1 ppm (µg/g) selenium (Lakin 1973).

Most of the research on the effects of selenium on plant species has been performed on selenium accumulator-indicator species. Certain plants, such as some *Astragalus* (milk vetch) species, are found growing only on soils containing selenium; these plants usually contain 1,000 to 10,000 ppm selenium (Berry and Wallace 1974; Rosenfeld and Beath 1964; Stahl 1969b). Secondary selenium accumulators [e.g., some species of *Atriplex* (saltbush) and *Aster* (aster)] are not restricted to seleniferous soils, but can accumulate 50 to 500 ppm when they grow on such soils (Rosenfeld and Beath 1964; Stahl 1969b). However, most crop plants, grains, and native grasses generally accumulate low levels (maximum, 30 ppm) of selenium (Rosenfeld and Beath 1964). In the Midwest, the normal concentration of selenium in crops is expected to be less than 0.5 ppm (Allaway 1968; Allaway et al. 1967).

Selenium appears to be biologically associated with sulfur, and may replace sulfur in some amino acids (Allaway 1968; Lakin 1973). Research has indicated that some crop plants accumulate selenium from selenate in direct proportion to their sulfur requirements (Hurd-Karrer 1937).

The primary indication of selenium injury in plants is growth inhibition. An additional symptom of selenate toxicity in grains is white chlorosis of some or all of the leaves. Leaves usually turn a darker green than normal in cases of selenite injury (Rosenfeld and Beath 1964). In a review article, Lisk (1972) reported that cereal grains and onions may accumulate 30 ppm selenium without toxic effects whereas grasses, clovers, and vegetables have a much lower tolerance (5 ppm). However, the literature contains many conflicting reports on the concentrations of selenium that can be tolerated by various non-accumulator crop plants and native grasses (up to a maximum of around 300 ppm). Variability is caused by different growth conditions such as soil type, chemical form of selenium in the soil, presence of other elements in the soil, and whether the selenium occurs naturally in the soil or was added to the soil for purposes of investigation.

The major cause of selenium poisoning in livestock is through the consumption of accumulatorindicator species. Most cases of poisoning have occurred west of the Mississippi River. In other areas, particularly in the northeastern states, available soil selenium levels are so low that selenium deficiencies occur in animals (Allaway 1968; Berry and Wallace 1974; Allaway et al. 1967; Rosenfeld and Beath 1964). No evidence was found of selenium poisoning of animals as a result of air pollution.

Upon consumption, selenium is transmitted via the circulatory system to all organs. Depending on the quantity and chemical form of the ingested selenium, high concentrations have been found in the liver, kidney, blood, spleen, brain, stomach, heart, lung, muscles, hair, skeleton, and hooves of animals (Rosenfeld and Beath 1964).

There are two levels of selenium poisoning in livestock: acute and chronic. Acute poisoning results in abnormal movement and posture, elevated temperature, rapid pulse, and finally death due to respiratory failure. Chronic selenium poisoning of livestock is manifested by two distinct types of symptoms, each dependent upon the chemical nature of the selenium compound ingested. "Blind staggers" results from the ingestion of moderate amounts of accumulatorindicator plants containing organically-bound selenium plus water-soluble selenates. "Alkali disease" results from the consumption of grains and grasses containing protein-bound selenium which is relatively insoluble in water (Rosenfeld and Beath 1964).

Selenium is required at low dietary levels (0.04-0.2 ppm depending on the kind of animal, type of diet, and chemical form of selenium) by animals and humans; however, it can be toxic in the diet when in the range of 4.0 to 5.0 ppm or greater (Allaway 1968; Lakin 1973). This presents a problem for animals feeding on vegetation which has accumulated even relatively low levels of selenium (Allaway 1968; Berry and Wallace 1974; Ganje 1966). Consumption of corn, grain, grasses, and hay containing 10-30 ppm selenium has caused alkali disease (Rosenfeld and Beath 1964). Hogs fed corn containing 5 ppm selenium did not develop alkali disease, whereas individuals fed corn containing 10 ppm developed symptoms of the disease including loss of hair, lesions on hooves and dewclaws, and sloughing of hoof keratin (Rosenfeld and Beath 1964).

For a more complete review of selenium toxicity, chemistry, sources, and biological effects, see Rosenfeld and Beath (1964), Stahl (1969b), and Muth et al. (1967).

#### VANADIUM

Allaway (1968) and Zoller et al. (1973) do not consider vanadium to be a serious hazard to plant or animal life at the present time. Plants (with the exception of a few accumulators) retain vanadium in their roots (tops seldom contain > 1 ppm) and therefore provide a fairly effective barrier to the food chain (Berry and Wallace 1974; Allaway 1968; Bhura and Tandon 1971). Animals tend to concentrate vanadium in their bones, which leaves their meat relatively free of vanadium, thus reducing the transport of vanadium to carnivores and man (Allaway 1968). The mechanism of vanadium toxicity is poorly understood. The element, especially its pentavalent compounds, inhibits the synthesis of many of the important amino acids and lipids.

Rabbits inhaling vanadium trioxide fumes intermittently over a period of 9 to 12 months developed chronic bronchitis, pulmonary emphysema, and fibrosis (Roschin 1967). Likewise, 5% vanadium pentoxide in the drinking water of laboratory animals caused marked anorexia and death within 10 weeks (Clarke and Clarke 1967).

Vanadium may have indirect effects on plants and animals. For example, vanadium may have a catalytic effect on the oxidation of atmospheric sulfur dioxide to sulfur trioxide (Zoller et al. 1973). Sulfur trioxide may then dissolve in water to form sulfuric acid or sulfates. This enhanced conversion of sulfur dioxide to sulfuric acid or sulfates may be undesirable in that sulfuric acid and sulfate aerosols may have greater adverse effects than sulfur dioxide (Anon. 1976).

### ZINC

Zinc, an essential element for all organisms, can be accumulated to toxic levels. This occurs most often in acid soils, soils developed from certain mineral ores, and soils in smelting regions (Berry and Wallace 1974; Little and Martin 1972). Zinc is readily accumulated in the leaves of many plants (Chapman 1966b); however, it is of low availability to animals, probably due to the formation of insoluble complexes of zinc with calcium and phytic acid in the plants (Oberleas et al. 1966). Zinc emissions from coal combustion may have adverse effects in smelting regions or in areas with acid soils already fairly high in zinc.

Mature animals appear to tolerate relatively large doses of zinc compared to young animals (Clarke and Clarke 1967); however, species differences in zinc tolerance may also be involved in the studies reporting the age differences (i.e., comparisons between young and mature animals were not always made with the same species).

Species	Element source	Source concentration	Plant part	Age	Tissue concentra- tion (ppm)	Effects and comments	References
ARSENIC							
Banana	Field		Leaves	Mature	0.25-2.00	Toxic	Fergus (1955)
Cotton	Pots-fine sandy loam	8 ppm H <sub>2</sub> O soluble	Tops	6 weeks	4.4	Toxic	Deuel and Swoboda (1972)
Cotton	Pots-clay	28 ppm H <sub>2</sub> O soluble	Tops	6 weeks	4.4	Toxic	Deuel and Swoboda (1972)
Soybean	Pots-fine sandy loam	3 ppm H <sub>2</sub> Ö soluble	Tops	6 weeks	1	Toxic	Deuel and Swoboda (1972)
Soybean	Pots-clay	12 ppm H <sub>2</sub> O soluble	Tops	6 weeks	1	Toxic	Deuel and Swoboda (1972)
Potato	v		Peel of tuber	Mature	24	Toxic	Sihlbom and Fredriksson (1960)
Potato			Peeled potato	Mature	· 1	Toxic	Sihlbom and Fredriksson (1960)
Tomato			Leaves		70	Toxic	Fergus (1955)
Lemon			Seedlings		11	Toxic	Liebig et al. (1959)
Cowpea		l ppm soluble	Tops, roots			Retarded growth	Albert and Arndt (1932)
BARIUM <sup>a</sup>							
Bears	Cuil in unto	AN	Topo vooto	25 davia		Sete ded much	Branch and Childrens (10CE)
Bearis	Soli in pots	>4% OT LEL	Tops, roots	35 days		Retarded growth	Romney and Childress (1965)
wheat	Soll in pots	>4% OT LEL	Tops, roots	75 days		Retarded growth	Romney and Childress (1965)
Lagino clover	Soll in pots	>4% OT LEL	lops, roots	105 days	403	Retarded growth	Romney and Unitoress (1965)
Bush bean	Nutrient solution	>I ppm	ROOTS	48 days	431	Stunting, de-	Romney et al. (1962)
Ruch boon	Nutrient colution	>1 nnm	Tops	AQ dave	24	Stunting do-	Pomney et al (1962)
Busin Dean	Nucl lenc solucion	>1 bhii	TOPS	40 Judys	- 24	crossed growth	Konney et als (1502)
Tomato	Nutrient colution	>2 nmm				If pH < 0 0 toxic	Hoadland (1952a)
	Nutrient colution	>2 ppm	Tong monte	54 days		Potarded growth	Pompey and Childress (1965)
Banlow	Nutrient colution	>2 ppm	Tops, roots	20 days		Retarded growth	Powney and Childress (1905)
bartey	Nutrient colution	>2 ppm	Tops, roots	20 days		Retarded growth	Bonney and Childress (1965)
Deag	Nutrient colution	>2 ppm	Tops, roots	20 days		Betanded anouth	Pompey and Childress (1965)
Peas	Nutrient solution	>2 ppin	Tops, roots	24 udys		Retarded growth	Konney and childress (1903)
BORON							
Wheat	Field-sandy loam	≤4.48 kg B/ha (+ N fertilizer)	Tops	Boot stage	>11	Decreased grain yield	Gupta et al. (1976)
Barley	Field-sandy loam	≤4.48 kg B/ha	Tops	Boot stage	>14	Light colored foli-	Gupta et al. (1976)
		(+ N fertilizer)				age, burned leaf tips during early growth	
Apricot	Field		Leaves	Oct.	82	Toxic	Eaton (1935)
Orange	Field		Leaves	3-7 months	>200	Toxic	Chapman and Vanselow (1955)
Wheat	Pots-sandy loam	≤l ppm applied B	Tops	Boot stage	>16	Burned leaf tips	Gupta et al. (1976)
		(+ N fertilizer)		5 A	-		· · · · ·
Barley	Pots-sandy loam	<pre>≤1 ppm applied B (+ N fertilizer)</pre>	Tops	Boot stage	>14	Severe browning of leaf edges	Gupta et al. (1976)

# Table D.1. Concentrations of Selected Trace Elements Which Have Been Found to Have Toxic Effects in Some Terrestrial Plants

(continued)

Table D.1. (Continued)

		na seconda de la companya de la comp Seconda de la companya	<u> </u>		Tissue	Efforts and	
Species	Element source	Source concentration	Plant part	Age	tion (ppm)	comments	References
BORON (cont.)		· · · · · · · · · · · · · · · · · · ·					· · · · · · · · · · · · · · · · · · ·
Corn	Pots-muck (organic soil)	50 ppm added B (37 ppm hot-H <sub>2</sub> 0 soluble)	Tops	4 weeks	1077	Significantly re- duced growth	John et al. (1977)
Corn	Pots-Monroe silt loam	50 ppm added B (23 ppm hot-H <sub>2</sub> O soluble)	Tops	4 weeks	2395	Significantly re- duced growth	John et al. (1977)
Corn. tu	Pots-Marble Hill silt loam	0.5 ppm added B (0.7 ppm hot-H <sub>2</sub> O soluble)	Tops	4 weeks	29	Significantly re-	John et al. (1977)
Spinach	Pots-muck (organic soil)	100 ppm added B (50 ppm hot-H <sub>2</sub> O soluble)	Tops	7 weeks	409	Growth reduction	John et al. (1977)
Spinach	Pots-Monroe silt loam	100 ppm added B (47 ppm hot-H <sub>2</sub> O soluble)	Tops	7 weeks	990	Growth reduction	John et al. (1977)
Spinach	Pots-Marble Hill silt loam	50 ppm added B (16 ppm hot-Ho0 soluble)	Tops	7 weeks	170	Growth reduction	John et al. (1977)
Alfalfa Asparagus Barley Bean Cabbage Cabbage Corn Tomato Cherry Corn Ky. bluegrass Reed fescue Perennial ryegrass	Sand Sand Sand Sand Sand Sand Sand Sand		Leaves Tops Plant Leaves Inner leaves Outer leaves Leaves Leaves Leaves Tops Leaf tips Leaf tips Leaf tips	April-Sep. May-Oct. July Aug. April April Oct. July-Aug. Oct. 25 days Burned stage Burned stage Burned stage	516-996 175-288 219-1111 151-1733 60-110 440-1152 179 253-1416 167 25 6820 7380 9540	Toxic Toxic Toxic Toxic Toxic Toxic Toxic Toxic Toxic Toxic Toxic Toxic Toxic Toxic Toxic Toxic	Eaton (1944) Eaton (1944) Eaton (1944) Eaton (1944) Eaton (1944) Eaton (1944) Eaton (1944) Eaton (1944) Woodbridge (1955) Marsh and Shive (1941) Oertlii and Kohl (1961) Oertlii and Kohl (1961)
CADMIUM Soybean Wheat Lettuce Spinach Peas Oats Radish Sunflower Sunflower Corn	Silty clay loam in pots Silty clay loam in pots Silty clay loam in pots Silt loam in pots Silt loam in pots Silt loam in pots 30 different soils in pots Nutrient solution Nutrient solution	2.5 ppm 2.5 ppm 2.5 ppm 40 ppm 40 ppm 100 ppm	Tops Tops Tops Leaves Seeds Grain Tops Excised leaves Tops Tops	5 weeks 5 weeks Maturity Maturity 3 weeks	7 3 11.5 207.5 10.1 20.8 528 (mean) 96 340 160	Decreased growth Decreased growth Toxic Toxic Toxic Decreased growth 50% decrease in photosynthesis 50% decrease in photosynthesis 50% decrease in photosynthesis	Haghiri (1973) Haghiri (1973) Haghiri (1973) John (1973) John (1973) John (1973) John et al: (1972) Bazzaz et al. (1974a) Carlson et al. (1975) Carlson et al. (1975)
Tomato	Nutrient solution	0.01 ppm CdCl <sub>2</sub>	Tops	6 weeks	1.4	50% decrease in yield	Turner (1973) estado (1920) &

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(continued)

# Table D.1. (Continued)

Species	Element source	Source concentration	Plant part	Age	Tissue concentra- tion (ppm)	Effects and comments	References
CHROMIUM		· · · · · · · · · · · · · · · · · · ·		•			
Corn			Leaves		4-8	Toxic	Soane and Saunder (1959)
Tobacco	Serpentine soil		Leaves		18-34	Toxic	Soane and Saunder (1959)
Tobacco	Serpentine soil		Roots		375-410	Toxic	Soane and Saunder (1959)
Vegetables, fruit	Soil with chromates	8.4-30 ppm at surface			1-9.8	Burning, necrosis	Desbaumes and Ramaciotti (1968
Ornamental trees	Soil with chromates	30-71 ppm at 30 cm			1-9.8	Burning, necrosis	Desbaumes and Ramaciotti (1968)
Oats	Nutrient solution	25 ppm	Leaves		252	Toxic	Hunter and Vergnano (1953)
CORALT							
Citrus			Leaves		11	Τοχίς	Vanselow (1966b)
Sudan grace	Soils	2000 lb/acre added	Leaves		19-32	Toxic	Fujimoto and Sherman (1950)
Dats	Nutrient solution	5 nm	leaves	40 days	116	Toxic	Hunter and Vergnano (1953)
0013	Hat Tene Sofation	o bbu	Leuves	10 4435			
COPPER							
Orange	Field		Leaves	4-7 months	23	Toxic	Reuther and Smith (1954)
Clover	Soi1	40 ppm easily extractable				Deleterious	Purves (1968)
Citrus	Very sandy soil	≥150 ppm total Cu				If soil pH ≤5, toxic	Reuther and Smith (1953)
Spinach, gladiolus	Soil	98-130 ppm exchangeable Cu				If soil pH 4.5-4.7,	Drouineau and Mazoyer (1953)
Millet	Sand		Leaves	Seedling stage	0.73-1.23	Toxic	Gopalakrishnan (1960)
Millet	Sand		Leaves	Vegetative stage	1.32-2.90	Toxic	Gopalakrishnan (1960)
Millet	Sand		Leaves	Flowering stage	1.04-1.27	Toxic	Gopalakrishnan (1960)
Tobacco	Nutrient solution	0.32 npm	Tons	5 weeks	17	Toxic	Struckmeyer et al. (1969)
Tobacco	Nutrient solution	0.32 ppm	Roots	5 weeks	>160	Toxic	Struckmeyer et al. (1969)
Barley	Nutrient solution	0.5 ppm	1100 03	•		Decreased growth	Piper (1942)
54. (2)						<b>3</b>	
FLUORINE	· · · ·					1	
Bean	NaF amended soil		Leaves		<310	lox1c	Daines et al. (1952)
Winter wheat	Amended soil	1000-1500 ppm F				40-65% decrease in	Groth (1975)
		· · ·				yield	a (1077)
Spiderwort	Amended soil	400 ppm F				28-34% decrease in	Groth (1975)
<b>T</b>	Fight front an time	$0.6 - 5(m^3/(0.72 mm^3))$	Loovor	Homeost 02 days	102 7	growin No vicual symptoms	Maclean et al (1977)
Iomato	Field Tunigation	0.6 µg F/m² (0.75 ppb)	Leaves	harvest-55 days	193.7	or effects on vield	MacLean ec un: (15/7)
Deen	Chambers Field fumigation	$0.6 \dots \sigma E(m^3 (0.73 \text{ ppb}))$	Loaves	Harvest-13 davs	71 7	No visual symptoms	Maclean et al (1977)
bean	riela Tumigation	continuourly	Stores	harvest-45 days	5.8	no decrease in	morean court (12/1)
	champers	continuousiy	libole pode		4.6	venetative growth	
			Dod bucks		3.5	and both a 20% de-	
			Soode		5 7	crease in number	
			Jeeus	-	5.7	and a 25% decrease	
						in fresh wt. of	
						marketable nods	
						marketable pous.	

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Table D.1.	(Continued)
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Species	Element source	Source concentration	Plant part	Age	Tissue concentra- tion (ppm)	Effects and comments	References
FLUORINE (cont.)	<u></u>						
Apple	Air	1.5 ppb F	Leaves		72-234	Toxic	Adams et al. (1957)
Blueberry	Air	1.5 ppb F	Leaves		34-53	Toxic	Adams et al. (1957)
English elm	Air	1.5 ppb F	Leaves		18-265	Toxic	Adams et al. (1957)
Larch	Air	1.5 ppb F	Needles		53-62	Toxic	Adams et al. (1957)
Apple	Air	5.0 ppb F	Leaves	1 - A - A	79-259	Toxic	Adams et al. (1957)
Blueberry	Air	5.0 ppb F	Leaves		72-103	Toxic	Adams et al. (1957)
English elm	Air	5.0 ppb F	Leaves		72	Toxic	Adams et al. (1957)
Larch	Air	5.0 ppb F	Needles		73-147	Toxic	Adams et al. (1957)
Apple	Air	10.0 ppb F	Leaves		142-194	Toxic	Adams et al. (1957)
Blueberry	Air	10.0 ppb F	Leaves		64	Toxic	Adams et al. (1957)
English elm	Air	10.0 ppb F	Leaves		160	Toxic	Adams et al. (1957)
Larch	Air	10.0 ppb F	Needles		106	Toxic	Adams et al. (1957)
Conifers	Air	0.5 µg F/m <sup>3</sup> , 10 days	Needles	At needle emergence	e	Toxic	Solberg et al. (1955)
Buckwheat	Exposed to HF gas		Leaves		594-1388	On acid soil, toxic	Griffin and Bayles (1952)
Sweet corn	HF in air	2-3 ppb F	Leaves (washed)	Mature	48-491	Toxic	Brewer (1960)
Susceptible species	Air, 1 day	3-4 µg F/m <sup>3</sup>				Threshold limit	Natl. Res. Counc. (1971)
Susceptible species	Air, ≥1 month	0.5 μg F/m <sup>3</sup>				Threshold limit	Natl. Res. Counc. (1971)
Intermediately sus-	Air, 1 day	≥10 µg F/m <sup>3</sup>				Threshold limit	Natl. Res. Counc. (1971)
Ceptible species	Ain . 1. month	1.2				Thuschold limit	Natl Dec Course (1071)
Intermediately sus-	ATr, ≥I montn	1-3 µg F/m <sup>3</sup>				Inreshold limit	Mati. Res. Counc. (1971)
ceptible species							
LEAD							
Lettuce	Silty clay loam	1000 ppm	Tops	44 days	126-140	Toxic	John and VanLaerhoven (1972)
Corn	Vermiculite solution	2000 ppm	Leaves	·	450	Decreased photosyn.	Bazzaz et al. (1974b)
	cultures					to 80% of control	
Corn	Vermiculite solution	4000 ppm	Leaves		350	Decreased photosyn.	Bazzaz et al. (1974b)
	cultures					to 48% of control	
Soybean	Vermiculite solution	2000 ppm	Leaves		∿75	Decreased photosyn.	Bazzaż et al. (1974b)
-	cultures					to 80% of control	
Soybean	Vermiculite solution	4000 ppm	Leaves		∿75	Decreased photosyn.	Bazzaz et al. (1974b)
	cultures					to 10% of control	
Sunflower	Nutrient solution		Excised leaves		193	50% decrease in	Bazzaz et al. (1974a)
						phótosyn.	
Oats, potato	Nutrient solution	50 ppm	Plant			Death in one week	Frear (no date)
Cress, mustard	Nutrient solution	345-1380 ppm				Germination delayed,	Dilling (1926)
						growth retarded	

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Species	Element source	Source concentration	Plant part	Age	Tissue concentra- tion (ppm)	Effects and comments	References
MANGANESE							· · · · · · · · · · · · · · · · · · ·
Oats Lespedeza Valencia orange	Field, pots Field Field Acid soil in pots	50 nom exchangeable Mo	Straw Tops Leaves	Harvest 4-7 months	3600 400-500 1000	Toxic Toxic Toxic Toxic	Coppenet (1959) Morris (1949) Reuther et al. (1949) Four (1964)
Barley Soybean	Nutrient solution	230 ppm exchangeable Pm	Tops Leaves	30 days	1000 173-999	Toxic Toxic Toxic	Loew and Sawa (1902-1903) Somers and Shive (1942)
Soybean Cotton Cotton	Nutrient solution Nutrient solution Nutrient solution	16 ppm 16 ppm	Roots Tops Roots	30 days	49-150 5150 2580	Decreased yield Decreased yield	Foy et al. (1969) Foy et al. (1969)
MERCURY							
Rose Velvet bentgrass	Vapor Soil	≤10 µg Hg/m <sup>3</sup> 455 ppm	Plants		1.68	Severe damage <u>No</u> toxicity	Stahl (1969a) Estes et al. (1973)
MOLYBDENUM Clover, lettuce Soybean, flax Oats Tomato	Nutrient solution Nutrient solution Nutrient solution Nutrient solution	5 ppm 10-20 ppm 200 ppm >10 ppm				Toxic Toxic Stunted growth Toxic	Warington (1950) Warington (1951) Hunter and Vergnano (1953) Arnon and Stout (1939)
NICKEL Oats Oats Sunflower	16-159 ppm amended soil Soil Nutrient solution	0.3-3.25 in soil solution 500 ppm	Tops Grain Excised leaves		88-308 60 79	Toxic Decreased yield 50% decrease in	Anderson et al. (1973) Halstead et al. (1969) Bazzaz et al. (1974a)
Sunflower, corn	Nutrient solution	$(1,1,2,\dots,n) \in \mathbb{R}^{n}$	Tops		290-350	50% decrease in	Carlson et al. (1975)
Oats Barley	Nutrient solution Nutrient solution	5 ppm 8 ppm	Leaves	40 days	196	Toxic Death	Hunter and Vergnano (1953) Wolff (1913)
SELENIUM Wheat	Soil in pots		Leaves, stems		450-1350	Toxic	Hurd-Karrer (1935)
Wheat Chrysanthemum Chrysanthemum Tomato	.Soil Soil flats Soil flats .Sand culture	30 ppm Na selenate	Lower leaves Upper leaves Leaves	Full bloom Full bloom 139 days	200-303 101-174 191	Severely damaged Toxic Tóxic Toxic	Hurd-Karrer (1934-1935) Kiplinger and Fuller (1946) Kiplinger and Fuller (1946) Neiswander and Morris (1940)
						·	

(continued)
# Table D.1. (Concluded)

Species	Element source	Source concentration	Plant part	Age	Tissue concentra- tion (ppm)	Effects and comments	References
VANADIUM Alfalfa Soybean, flax, peas	Sand Nutrient solution	500 ppm 2.5-5.0 ppm			:	Decreased growth Toxic	Jha (1969) Warington (1954)
ZINC Orange Oats Tomato	Field Sand Nutrient solution		Leaves Leaves Basal & median	4-7 months Mature Fruit setting	300 1700-7500 526-1489	Toxic Toxic Toxic	Reuther and Smith (1954) Hunter and Vergnano (1953) Lyon et al. (1943)
Cotton Many species	Nutrient solution	2 ppm	Leaves	31 days	200 200-2000	<pre>10% growth reduction Decreased yield,     toxicity symptoms</pre>	Ohki (1975) Boawn and Rasmussen (1971)

 $^{\rm a}{\rm No}$  data were found within the time constraints of this report.

Species	Concentration or dosage	Form or method of exposure	Effects and comments	Reference
ARSENIC				······································
Sheep	3.4 ppm		Toxic	Berry and Wallace (1974)
Rat	13 µg/g	Arsenic trioxide	LD <sub>50</sub>	Sullivan (1969a)
Bee	1 μg/bee		Death	Sullivan (1969a)
Man	0.0-0.5 g	Arsenic trioxide	LD <sub>50</sub>	Sullivan (1969a)
Man	70-180 mg	Arsenic trioxide	Fatal dose by ingestion	Hygienic Guide Series (1964)
Man	10-60 ppm	Arsine	Dangerous for 1/2-1 hr	Steel and Feltham (1950)
Man	250 ppm	Arsine	Lethal, 1/2 hr	Steel and Feltham (1950)
BARTIM				
Pigeon	500 ma/ka	Ba chloride oral	חו	Spector (1955)
Horse	800-1200 mg/kg	Ba chloride, oral		Spector $(1955)$
Dog	90 mg/kg	Ba chlorida, oral		Spector (1955)
Dog Dabbit	170 mg/kg	Ba chlorido, oral		Spector $(1955)$
Rabbit Pat		Pa cambonato oral	1D in 19 days	Spector (1955)
Rai Dot	255 522 mg/kg	Ba chlonida, oral	LD <sub>50</sub> In I-O days	Spector (1955)
Kal	555-555 mg/kg	Ba chioride, oral		Speciol (1955)
BERYLLIUM <sup>a</sup>				
BORON	• · · · · ·			
Dog	>1 a/ka	Boric acid oral		Adams (1964)
Монсе	2-3 a/ka	Borax (Na borate) oral		Adams (1964)
Rabbit		Boric acid oral		Adams (1964)
Rat	$\frac{7}{5} \frac{9}{14} \frac{89}{14}$	Boric acid oral		Adams (1964)
Man (infants)	25.14 9/ Kg	Boric acid ingestion	LD50 Death	Durocher (1969)
Man (adulte)	<5 g	Boric acid, ingestion	Death	Durocher (1969)
Man (adurts)	5-20 g	Borne della, ingestion	Death	Durochen (1969)
Man (chituren)	5-10 g	borax (Na borace), ingestion	Death	burbener (1909)
CADMIUM				
Man, animals	15 ppm	In food	Injurious	Underwood (1962)
Japanese quail	75 mg/kg of diet	Cadmium chloride	Testicular hypoplasia	Richardson et al. (1974)
Japanese quail	5 mg Cd/kg body wt.	Cadmium chloride in diet	Depressed hemoglobin	Jacobs et al. (1974)
Rabbit	160 ppm	Cadmium chloride in commercial chow	Retarded growth, anemia	Stowe et al. (1972)
Dog	27 ma/ka	CdSO,	LD	Athanassiadis (1969a)
Rat	0.1-10 ppm	Cd metal for 1 year	Increased conc. in liver & kidney	Natl. Air Samp. Netwk. (1966)
Rat	5-75 ppm	Cd metal, single dose	lethal	Natl. Air Samp, Netwk (1966)
Rat	5 nnm	In $H_{2}O$	Decreased life span	Schroeder et al. (1965)
Man	67 nnm	Cd metal in drink, single dose	Sickness in children	Garrity (1948)
Man	2500 mg/m <sup>3</sup>	CdO inhalation	Fatal in 1 min	Athanassiadis (1969a)

Table D.2. Concentrations of Selected Trace Elements Which Have Been Found to Have Toxic Effects in Some Terrestrial Animals and Man

(continued)

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	Table	D.2. (	(Continued)	
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Species	Concentration or dosage	Form or method of exposure	Effects and comments	Reference
CHROMIUM	· · · · · · · · · · · · · · · · · · ·		na a na an an an an an an Anna	
Dog	1-2 g Cr	As K dichromate, oral, daily	Fatal in 3 months	Brard (1935)
Rat	500 ppm Cr	As K chromate in H <sub>2</sub> O daily	Max. nontoxic conc.	Gross and Heller (1946)
Rat, mouse	1% Cr	As Zn chromate in feed daily	Max. nontoxic conc.	Gross and Heller (1946)
CORAL T				
Cattle	>0.9 ma/ka		Toxic	Elv at al (1049)
Sheep	$\sim 3 \text{ mg/kg}$	CoCl. in dict	Depressed appetite	$\begin{array}{c} \text{Ely et al. (1940)} \\ \text{Booken and Smith (1051)} \end{array}$
Dog	20 mg/kg	coch2 in diet	Lettel	becker and Smith (1951)
bog	SU liig/ kg		Lethal	tion Commission (1950)
Rat	200 mg/kg		Toxic	Elv et al. (1948)
Rat	500 mg/kg		Lethal in 3-5 weeks	Ely et al. (1948)
COPPER				
Sheep	>20-30 ppm	In feed or forage	Toxic	Baker (1974)
0xen	5 g daily	Copper sulfate in diet	Fatal	Kidder (1949)
FLUORINE				
Deer	1500 ppm found in bono	Enom vogotation and aim in	Eluonocic	$C_{\text{moth}}$ (1075)
Deci		F-contaminated area	FIGURUSIS	Groch (1975)
Livestock	≤50 ppm	In forage	Toxic	Phillips et al. (1955)
Cattle	>40 mg/kg	In diet or H <sub>o</sub> O	Decreased milk production, lameness	Natl. Res. Counc. (1971)
Silkworm larvae	15 mg F	NaF or KF in <sup>2</sup> foliage consumed	Lethal	Fuiii and Honda (1972)
Frogs	900 ppm	Immersion for 1 week in F-	Lethal (ICco)	Groth (1975)
		contaminated water		
Frogs	5-300 ppm	Kent in E-contaminated water for	Decrease in red and white	Groth (1975)
- 3-	• • • • • • • • • • • • •	prolonged periods	blood cell counts	
Frog tadpoles	0.5 and 4.5 npm	In E-contaminated water	Metamorphosis delayed abnormal	Groth (1975)
trog dauportes		In r-containnated water	thyroid	
Man	2500-5000 mg/day	Single dose	Lethal	Natl. Res. Counc. (1971)
Man	20-80 mg/day		In 10-20 yrs., crippling fluorosis	Natl. Res. Counc. (1971)
LEAD				
Japanese quail	10 ppm	lead acetate in diet	Age of egg production increased	Edens (1976)
Japanese quail	1000 ppm	Lead acetate in diet	Eag production prevented	Edens (1976)
lananese quail	1-1000 ppm	lead acetate in feed	Delayed testicular development	Edens $(1576)$
Bobwhite quail	3000 ppm	lead acetate in diet	Increased montality weight loss	Dampon and Wilcon $(1075)$
Toads	816 ppm	Given in canthworms	Affected lowels of doltaaminolao	Incland (1977)
10005	oro ppili	diven in ear chworms	vulic acid hydrogenase	
Horses	80 ppm (dry wt.)	In grass	Toxic	Mueller and Stanley (1970)
Horses, cattle	120-150 ppm	In diet	Toxic	Hammond and Aronson (1964)
Cows	6-7 mg/kg/day	Lead in feed	Minimum cumulative fatal dose	Hammond and Aronson (1964)

(continued)

Concentration or dosage Species Form or method of exposure Effects and comments Reference MANGANESE MERCURY Pheasant 3-13 ppm found in pheas-Mercury from environment Produced eggs containing 0.5-Peakall and Lovett (1972) ant liver tissue 1.5 ppm mercury 1.3-2 ppm in eggs Decreased hatchability Pheasant eggs Mercury from environment Fimreite (1974) Red-tailed hawk 10 ppm in livers of Hawks fed chicks contaminated Lethal after one month Fimreite and Karstad (1971) chicks eaten with methylmercury Japanese quail 50 ppm Mergamma DB in diet Female survival decreased, reduced Dwernychuck et al. (1974) egg production Japanese quail 12.5 ppm Mergamma DB and phenylmercuric Reduced fertility, embryo viability Dwernychuck et al. (1974) acetate in diet and hatchability Mallards Reduced reproduction, altered 3 ppm Methylmercury dicyandiamide in Heinz (1976) avoidance behavior in offspring diet Partridge Organomercury in diet 12-34 mg/kg LD50 Peakall and Lovett (1972) Cockere1 Methylmercury dicvandiamide in Increased mortality 18 ppm Peakall and Lovett (1972) diet Rat 30-150 mg/kg Organic mercurials LD50 Peakall and Lovett (1972) Inorganic Hg compounds Rat 20-50 mg/kg LD<sub>50</sub> Peakall and Lovett (1972) MOLYBDENUM Ruminants 10-20 ppm In diet Disturbs Cu metabolism Allaway (1968) Ruminants 5 ppm In diet Detrimental if <4 ppm Cu in diet Allaway (1968) NICKEL  $240 \text{ mg/m}^3$ Rat Inhaled Ni carbonyl  $LC_{50}$ Christensen (1973a) Calves 1000 ppm Ni carbonate in diet for 8 weeks Decreased growth 0'Dell et al. (1970) Chicks 700 ppm Ni acetate & sulfate in diet Decreased growth of 4-week old Weber and Reid (1968) chicks SELENIUM Livestock Alkali disease 24 mg/kgConsumed in vegetation Rothstein (1953) Livestock 100-1000 mg/kg Consumed in vegetation Death Rothstein (1953) Cattle 2 mg/animal pound Lethal Miller and Byers (1935) Cattle 1-4 mg/kgChronic poisoning In fodder Russell (1944) Sodium selenite in feed Hog 1.2 g Fatal in 3 days Dudley (1936) Sheep 465 g In selenite-bearing plants Fatal in 20 hours Dudley (1936) Tyler (1949) Poultry Toxic threshold 5 mg/kg Drv ration Sodium selenite in drinking water Duck 20 ppm Fatal Twomey and Twomey (1936)

Table D.2. (Continued)

(continued)

Table D.2. (Concluded)

Species	Concentration or dosage	Form or method of exposure	Effects and comments	Reference
VANADIUM				
Chicks	20 mg V/kg	Ca vanadate in diet	Inhibits growth	Romoser et al. (1960)
Rat	10-20 ppm	Na vanadate	LD50	Faulkner-Hudson (1964)
Rat	540 ppm	V dichloride, oral	LD50	Christensen (1973b)
Rat	140 ppm	Vanadyl chloride, oral		Christensen (1973b)
Man	60-120 mg V	Inhaled	LD <sub>50</sub>	Stokinger (1963)
ZINC				
Calf. lamb.	500-1000 mg/kg	Zn in diet	Depressed weight	Ott et al. (1966a, 1966b)
oxen				
Rat		Zn carbonate in feed	Anemia and osteoporosis	Waltner et al. (1929)
Rat	1.1% Zn	In diet	Tolerable	Sutton et al. (1937)
Rat	≥0.5% Zn	In diet	Decreased reproductive capacity	Sutton et al. (1937)
Rat	1% Zn	In diet	Inhibited growth, caused severe	Sutton et al. (1937)
रूप ह			anemia and death	
Rat	2.2 g/kg	Zn sulfate, oral	LD	Vallee (1962)
Rabbit	1.9-2.2 g/kg	Zn sulfate, oral	LD	Vallee (1962)

<sup>a</sup>Specific studies on the toxic effects of beryllium are too complicated to be presented in this table. Atmospheric beryllium concentration standards are discussed in the text of this appendix. See Durocher (1969) for a review of toxicity data. <sup>b</sup>No data were found within the time constraints of this report.

- Adams, D. F., J. W. Hendrix, and H. G. Applegate. 1957. Relationship among exposure periods, foliar burn, and fluorine content of plants exposed to hydrogen fluoride. J. Agric. Food Chem. 5:108-116. [As cited in Chapman (1966a).]
- Adams, F., and R. W. Pearson. 1967. Crop response to lime in the Southern United States and Puerto Rico, pp. 161-206. <u>In</u> R. W. Pearson and F. Adams (eds.), Soil Acidity and Liming. No. 12 in the series, Agronomy. American Society of Agronomy, Madison, Wisconsin. [As cited in National Research Council (1973).]
- Adams, R. W. (ed.). 1964. Boron, Metallo-Boron Compounds and Boranes. Wiley, New York. [As cited in Durocher (1969).]
- Albert, W. B., and C. H. Arndt. 1932. The Concentration of Soluble Arsenic as an Index of Arsenic Toxicity to Plants. S. C. Agric. Exp. Stn. Annu. Rep. No. 44. [As cited in Deuel and Swoboda (1972).]
- Allaway, W. H. 1968. Agronomic controls over the environmental cycling of trace elements. Adv. Agron. 20:235-274.
- Allaway, W. H., E. E. Cary, and C. F. Ehlig. 1967. The cycling of low levels of selenium in soils, plants, and animals, pp. 273-296. <u>In</u> O. H. Muth, J. E. Oldfield, and P. H. Weswig (eds.), Symposium: Selenium in Biomedicine. The Avi Publishing Co., Inc., Westport, Conn.
- Allcroft, R. 1950. Lead as a nutritional hazard to farm livestock. IV, Distribution of lead in the tissues of bovines after ingestion of various lead compounds. J. Comp. Pathol. Exp. Ther. 60:190.
- Allcroft, R. 1951. Lead poisoning in cattle and sheep. Vet. Rec. 63:583-590.
- Anderson, A. J., D. R. Meyer, and F. K. Mayer. 1973. Heavy metal toxicities: levels of nickel, cobalt, and chromium in the soil and plants associated with visual symptoms and variation in growth of an oat crop. Aust. J. Agric. Res. 24:557-571.

Anonymous. 1976. California Air Resources Board. ARB Bull., pp. 2-3.

- Arnon, D. I., and P. R. Stout. 1939. Molybdenum as an essential element for higher plants. Plant Physiol. 14:599-602.
- Athanassiadis, Y. C. 1969a. Air Pollution Aspects of Cadmium and Its Compounds. Litton Systems, Inc., Bethesda, Md. 82 pp.
- Athanassiadis, Y. C. 1969b. Air Pollution Aspects of Vanadium and Its Compounds. Litton Systems, Inc., Bethesda, Md. 93 pp.
- Athanassiadis, Y. C. 1969c. Air Pollution Aspects of Zinc and Its Compounds. Litton Systems, Inc., Bethesda, Md. 79 pp.
- Baker, D. E. 1974. Copper: soil, water, plant relationships. Fed. Proc. 33:1188-1193.
- Bartlett, R. J., and J. M. Kimble. 1976a. Behavior of chromium in soils: I. Trivalent forms. J. Environ. Qual. 5:379-382.
- Bartlett, R. J., and J. M. Kimble. 1976b. Behavior of chromium in soils: II. Hexavalent forms. J. Environ. Qual. 5:383-386.
- Bazzaz, F. A., R. W. Carlson, and G. L. Rolfe. 1974a. The effect of heavy metals on plants. Part 1, Inhibition of gas exchange in sunflower by Pb, Cd, Ni, and Tl. Environ. Pollut. 7:241-246.
- Bazzaz, F. A., G. L. Rolfe, and P. W. Windle. 1974b. Differing sensitivity of corn and soybean photosynthesis and transpiration to lead contamination. J. Environ. Qual. 3:156-157.
- Beavington, F. 1975. Some aspects of contamination of herbage with copper, zinc, and iron. Environ. Pollut. 8:65-71.
- Becker, D. E., and S. E. Smith. 1951. The level of cobalt tolerance in yearling sheep. J. Anim. Sci. 10:266-271.

- Berry, W. L., and A. Wallace. 1974. Trace Elements in the Environment--Their Role and Potential Toxicity as Related to Fossil Fuels--A Preliminary Study. University of California, Laboratory of Nuclear Medicine and Radiation Biology. 66 pp.
- Bhura, D. C., and S. G. Tandon. 1971. Unsaturated N-arylhydroxamic acids as colorimetric reagents for vanadium (V). Spectrophotometric determination with N-phenyl-3-styrylacrylhydroxamic acid. Anal. Chim. Acta 53:379-386. [As cited in National Research Council (1974b).]
- Bingham, F. T. 1973. Boron in cultivated soils and irrigation waters, pp. 130-138. In E. L. Kothny (ed.), Trace Elements in the Environment. Adv. Chem. Series 123. American Chemical Society, Washington, D.C.
- Bingham, F. T., A. W. Marsh, R. Branson, R. Mahler, and G. Ferry. 1972. Reclamation of saltaffected high boron soils in western Kern County. Hilgardia 41(8):195-211. [As cited in Bingham (1973).]
- Boawn, L. C., and P. E. Rasmussen. 1971. Crop response to excessive zinc fertilization of alkaline soils. Agron. J. 63:874-976. [As cited in Little and Martin (1972).]
- Borg, K., et al. 1969. Alkyl mercury poisoning in Swedish wildlife. Viltrevy (Stockholm) 6(4):301-379. [As cited in Kreitzer (1974).]
- Bowen, H. J. M. 1966. Trace Elements in Biochemistry. Academic Press, Inc., London. 241 pp.
- Boyd, H. W. 1971. Manganese toxicity to peanuts in autoclaved soil. Plant Soil 34:133-144.
- Bradfield, R., L. P. Batjer, and J. Oskamp. 1934. Soils in relation to fruit growing in New York. Part IV, The significance of the oxidation-reduction potential for evaluating soils for orchard purposes. N.Y. (Cornell) Agric. Exp. Stn. Bull. 592. [As cited in Labanauskas (1966).]
- Bradford, G. R. 1966. Boron, pp. 33-61. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Brady, N. C. 1974. The Nature and Property of Soils, 8th ed. Macmillan Publishing Co., Inc., New York. 639 pp.
- Brard, D. 1935. Toxicologie du Chrome. Herman and Co., Paris. [As cited in National Research Council (1974a).]
- Brewer, R. F. 1960. Unpublished data on file at the Department of Soils and Plant Nutrition, University of California, Riverside. [As cited in Chapman (1966a).]
- Brewer, R. F. 1966a. Fluorine, pp. 180-196. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Brewer, R. F. 1966b. Lead, pp. 213-217. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Browning, E. 1961. Toxicity of Industrial Metals. Butterworth's, London. pp. 53-56.
- Buchanan, W. D. 1962. Toxicity of Arsenic Compounds. Van Nostrand Publishing Co., New York.
- California Air Resources Board. 1971. A Joint Study of Pb Contamination Relative to Horse Deaths in the Area of Southern Solano County. Report, December 1971. [As cited in Wesolowski et al. (1973).]
- Cannon, H. L. 1970. Trace element excesses and deficiencies in some geochemical provinces of the U. S., pp. 21-43. <u>In</u> D. D. Hemphill (ed.), Proceedings of the University of Missouri Third Annual (1969) Conference on Trace Substances in Environmental Health, Vol. III. University of Missouri Press, Columbia.

Carlson, C. E. 1973. Fluoride pollution in Montana. Fluoride 6:127-137.

- Carlson, R. W., F. A. Bazzaz, and G. L. Rolfe. 1975. The effects of heavy metals on plants. Part II, Net photosynthesis and transpiration of whole corn and sunflower plants treated with Pb, Cd, Ni, and Tl. Environ. Res. 10:113-120.
- Carroll, R. E. 1966. The relationship of cadmium in the air to cardiovascular disease death rate. J. Am. Med. Assoc. 198:267-269. [As cited in Berry and Wallace (1974).]

- Cary, E. E., W. H. Allaway, and O. E. Olson. 1977a. Control of chromium concentrations in food plants. 1. Absorption and translocation of chromium by plants. J. Agric. Food Chem. 25:300-304.
- Cary, E. E., W. H. Allaway, and O. E. Olson. 1977b. Control of chromium concentrations in food plants. 2. Chemistry of chromium in soils and its availability to plants. J. Agric. Food Chem. 25:305-309.
- Cassarotto, G. 1952. L'Azione del carbonato del berrilio sui denti. Clin. Odontoiat 7:113. [As cited in Reeves (1965).]
- Chapman, H. D. (ed.). 1966a. Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley. 793 pp.
- Chapman, H. D. 1966b. Zinc, pp. 484-499. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Chapman, H. D., and A. P. Vanselow. 1955. Boron deficiency and excess. Calif. Citrogr. 40:455-460. [As cited in Chapman (1966a).]
- Christensen, H. E. (ed.). 1973. The Toxic Substances List, 1973 ed. U.S. Government Printing Office, Washington, D.C. [1973a: As cited in National Research Council (1975); 1973b: As cited in USEPA (1975).]
- Clarke, E. C., and M. L. Clarke. 1967. Garner's Veterinary Toxicology, 3rd ed. Williams and Wilkins Co., New York. 477 pp. (p. 93.)
- Coppenet, M. 1959. Manganese in the soils of Brittany and its relationship to plant growth. Ann. Agron. (Paris) 10:155-218. [As cited in Chapman (1966a).]
- Cunningham, G. N., et al. 1966. Effect of high dietary levels of manganese on the performance and blood constituents in calves. J. Anim. Sci. 25:532-538.
- Daines, R. H., I. A. Leone, and E. G. Brennan. 1952. The effect of fluorine on plants, as determined by soil nutrition and fumigation studies, pp. 97-105. <u>In</u> U.S. Technical Conference on Air Pollution Proceedings. McGraw Hill Book Co., New York. [As cited in Chapman (1966a).]
- Damron, B. L., and H. R. Wilson. 1975. Lead toxicity of bobwhite quail. Bull. Environ. Contam. Toxicol. 14(4):489-496.
- Desbaumes, P., and D. Ramaciotti. 1968. Etude chimique de l'action sur la végétation d'un effluent gazeux industriel dontenant du chrome hexavalent. Pollut. Atmos. 10:224-226. [As cited in National Research Council (1974a).]
- Deuel, L. E., and A. R. Swoboda. 1972. Arsenic toxicity to cotton and soybeans. J. Environ. Qual. 1:317-320.
- Dilling, W. J. 1926. Influence of lead and the metallic ions of copper, zinc, thorium, beryllium, and thallium on the germination of seeds. Ann. Appl. Biol. 13:160. [As cited in McKee and Wolf (1963).]
- Drouineau, G., and R. Mazoyer. 1953. Copper toxicity and soil evaluation under the influence of fungicides. C. R. Acad. Agric. France 39:390-392. [As cited in Chapman (1966a).]
- Dudley, H. C. 1936. Toxicology of selenium. I, A study of the distribution of selenium in acute and chronic cases of selenium poisoning. Am. J. Hygiene 23:169-179.
- Durocher, N. L. 1969. Air Pollution Aspects of Beryllium and Its Compounds. Litton Systems, Inc., Bethesda, Md. 47 pp.
- Dwernychuk, L. W., D. H. Sheppard, and L. E. Haley. 1974. Mergamma DB and phenylmercuric acetate: their effect on the reproduction of Japanese quail (*Coturnix coturnix japonica* Temminck and Schlegel). Can. J. Zool. 52:291-300.
- Eaton, F. M. 1935. Boron in Soils and Irrigation Waters and Its Effect on Plants, with Particular Reference to the San Joaquin Valley of California. U.S. Dep. Agric. Tech. Bull. 448. [As cited in Chapman (1966a).]
- Eaton, F. M. 1944. Deficiency, toxicity, and accumulation of boron in plants. J. Agric. Res. 69:237-277. [As cited in Chapman (1966a).]

- Edens, F. W. 1976. Effects of dietary lead on reproductive performance in Japanese quail. Toxicol. Appl. Pharmacol. 38:307-314.
- Edens, F. W., E. Benton, S. W. Burisian, and G. W. Morgan. 1976. Effect of dietary lead on reproductive performance in Japanese quail, *Coturnix coturnix japonica*. Toxicol. Appl. Pharmacol. 28:307-314.
- Ely, R. E., K. M. Dunn, and C. F. Huffman. 1948. Cobalt toxicity in calves resulting from high oral administration. J. Anim. Sci. 1:239. [As cited in McKee and Wolf (1963).]
- Ermolenko, N. F. 1966. Trace Elements and Colloids in Soils, 2nd ed. Nauka i Tekhnika Minsk. Translated from the Russian, 1972. Published for the U.S. Department of Agriculture and the National Science Foundation, Washington, D.C., by Israel Program for Scientific Translations, Jerusalem. 259 pp.
- Estes, G. O., W. E. Knoop, and F. D. Houghton. 1973. Soil-plant response to surface-applied mercury. J. Environ. Qual. 2:451-452.
- Faulkner-Hudson, T. G. 1964. Vanadium, Toxicology and Biological Significance. Elsevier Publishing Co., New York. [As cited in National Research Council (1974b).]
- Fergus, I. F. 1955. A note on arsenic toxicity in some Queensland soils. Queensl. J. Agric. Sci. 12:95-100. [As cited in Chapman (1966a).]
- Ferguson, W. S., et al. 1943. The teart pastures of Somerset. IV, The effect of continuous administration of copper sulfate to dairy cows. J. Agric. Sci. 33:116-118.
- Fimreite, N. 1974. Mercury contamination of aquatic birds in northwestern Ontario. J. Wildl. Manage. 38(1):120-131.
- Fimreite, N., and L. Karstad. 1971. Effects of dietary methyl mercury on red-tailed hawks. J. Wildl. Manage. 35(2):293-300.
- Flick, D. F., H. F. Kraybill, and J. M. Dimitroff. 1971. Toxic effects of cadmium: a review. Environ. Res. 4:71-85.
- Foy, C. D. 1964. Toxic Factors in Acid Soils of the Southwestern United States as Related to the Response of Alfalfa to Lime. U.S. Dep. Agric. Prod. Res. Rep. 80. [As cited in National Research Council (1973).]
- Foy, C. D., A. L. Fleming, and W. H. Arminger. 1969. Differential tolerance of cotton varieties to excess manganese. Agron. J. 61:690-694. [As cited in National Research Council (1973).]
- Frear, D. E. H. Pesticide Index. College Science Publ., State College, Pa. [As cited in McKee and Wolf (1963).]
- Friberg, L., M. Piscator, and G. Nordberg. 1971. Cadmium in the Environment. CRC Press, Cleveland, Ohio. 166 pp.
- Frost, D. V. 1967. Arsenicals in biology retrospect and prospect. Fed. Proc. 26:194-208.
- Fujii, M., and S. Honda. 1972. The relative oral toxicity of some fluorine compounds for silkworm larvae. J. Seric. Sci. Japan 41:104-110. [As cited in Groth (1975).]
- Fujimoto, G., and G. D. Sherman. 1950. Cobalt content of typical soils and plants of the Hawaiian Islands. Agron. J. 42:477-581. [As cited in Vanselow (1966b.)]
- Gallup, W. D., and L. C. Norris. 1938. The amount of manganese required to prevent perosis in the chick. Science 87(2245):18-19.
- Ganje, T. J. 1966. Selenium, pp. 394-404. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Garrity, L. V. 1948. Possible hazards due to cadmium-coated pipe and fittings. J. Am. Water Works Assoc. 40:1194. [As cited in Athanassiadis (1969a.]
- Gopalakrishnan, S. 1960. Copper nutrition of millets, part II. Madras Agric. J. 47:95-108. [As cited in Chapman (1966a).]

Griffin, S. W., and B. B. Bayles. 1952. Some effects of fluorine plumes on vegetation, pp. 106-115. In U.S. Technical Conference on Air Pollution Proceedings. McGraw Hill Book Co., New York. [As cited in Chapman (1966a).]

- Gross, W. G., and V. G. Heller. 1946. Chromates in animal nutrition. J. Ind. Hyg. Toxicol. 28:52-56. [As cited in National Research Council (1974a).]
- Groth, E., III. 1975. An evaluation of the potential for ecological damage by chronic, low level environmental pollution by fluoride. Fluoride 8:224-240.
- Gupta, U. C., J. A. MacLeod, and J. D. E. Sterling. 1976. Effects of boron and nitrogen on grain yield and boron and nitrogen concentrations of barley and wheat. Soil Sci. Soc. Am. J. 40:723-726.
- Haghiri, F. 1973. Absorption and uptake of cadmium by plants. Ohio Rep. Res. Dev. 58:72-74.
- Haghiri, F. 1974. Plant uptake of cadmium as influenced by cation exchange capacity, organic matter, zinc, and soil temperature. J. Environ. Qual. 3:180-183.
- Halstead, R. L., B. J. Finn, and A. J. MacLean. `1969. Extractability of nickel added to soils and its concentration in plants. Can. J. Soil Sci. 49:335-342. [As cited in National Research Council (1975).]
- Hammond, P. B., and A. L. Aronson. 1964. Lead poisoning in cattle and horses in the vicinity of a smelter. Ann. N. Y. Acad. Sci. 111:595-611.
- Hassett, J. J. 1974. Capacity of selected Illinois soils to remove lead from aqueous solution. Commun. Soil Sci. Plant Anal. 5:499-505.
- Heinz, G. H. 1976. Methylmercury: second-year feeding effects on mallard reproduction and duckling behavior. J. Wildl. Manage. 40(1):82-90.
- Hewitt, E. J. 1966. Sand and Water Culture Methods Used in the Study of Plant Nutrition, 2nd ed. Tech. Bull. No. 22. Commonwealth Bureau of Horticulture and Plantation Crops. [As cited in Berry and Wallace (1974).]
- Hiatt, V., and J. E. Huff. 1975. The environmental impact of cadmium: an overview. Int. J. Environ. Stud. 7:277-285.
- Hill, A. C. 1969. Air quality standards for fluoride vegetation effects. J. Air Pollut. Control. Assoc. 21:410-413.
- Hitchcock, A. E., and P. W. Zimmerman. 1957. Toxic effects of vapors of mercury and of compounds of mercury on plants. Ann. N. Y. Acad. Sci. 65:474. [As cited in Stahl (1969a).]
- Hoagland, M. B. 1952a. Beryllium and growth. II, The effect of beryllium on plant growth. Arch. Biochem. Biophys. 35:249-258. [As cited in Romney and Childress (1965).]
- Hoagland, M. B. 1952b. Beryllium and growth. III, The effect of beryllium on plant phosphatase. Arch. Biochem. Biophys. 35:259-267. [As cited in Romney and Childress (1965).]
- Hodgson, J. F. 1970. Chemistry of trace elements in soils with reference to trace element concentration in plants, pp. 45-58. <u>In</u> D. D. Hemphill (ed.), Proceedings of the University of Missouri's 3rd Annual (1969) Conference on Trace Substances in Environmental Health, Vol. III. University of Missouri Press, Columbia.
- Huang, C. Y., F. A. Bazzaz, and L. N. Vanderhoef. 1974. The inhibition of soybean metabolism by cadmium and lead. Plant Physiol. 54:122-124.
- Huckabee, J. W. 1973. Mosses: sensitive indicators of airborne mercury pollution. Atmos. Environ. 7:749-754.
- Hunter, J. G., and O. Vergnano. 1953. Trace element toxicities in oat plants. Ann. Appl. Biol. 40:761-777. [As cited in Anderson et al. (1973) and McKee and Wolf (1963).]
- Hurd-Karrer, A. M. 1934-1935. Selenium absorption by plants and their resulting toxicity to animals. Smithson. Inst. Annu. Rep. 1934-35:289. [As cited in McKee and Wolf (1963).]
- Hurd-Karrer, A. M. 1935. Factors affecting the absorption of selenium from soil by plants. J. Agric. Res. 50:413-427. [As cited in Chapman (1966a).]

- Hurd-Karrer, A. M. 1937. Selenium adsorption by crop plants as related to their sulfur requirement. J. Agric. Res. 54:601-608. [As cited in Rosenfeld and Beath (1964).]
- Hygienic Guide Series. 1964. Arsenic and its compounds. Am. Ind. Hyg. Assoc. J. 25:610. [As cited in Sullivan (1969a).]
- Ireland, M. P. 1977. Lead retention in toads, *Xenopus Laeuis*, fed increasing levels of leadcontaining earthworms. Environ. Pollut. 12:85-91.
- Jacobs, R. M., M. R. S. Fox, B. E. Fry, Jr., and B. F. Harland. 1974. The effect of a two-day exposure to dietary Cd on the concentration of elements in duodenal tissue of Japanese quail. <u>In</u> Trace Element Metabolism in Animals-2. Proceedings of the 2nd International Symposium of Trace Element Metabolism in Animals, Madison, Wis., 1973. University Park Press, Baltimore.
- Jha, K. K. 1969. Effect of vanadium and tungsten on nitrogen fixation and the growth of *Medicago sativa*. J. Indian Soc. Soil Sci. 17:11-13. [As cited in USEPA (1975).]
- John, M. K. 1972. Uptake of soil-applied cadmium and its distribution in radishes. Can. J. Plant Sci. 52:715-719.
- John, M. K. 1973. Cadmium uptake by eight food crops as influenced by various soil levels of cadmium. Environ. Pollut. 4:7-15.
- John, M. K. 1976. Interrelationships between plant cadmium and uptake of some other elements from culture solutions by oats and lettuce. Environ. Pollut. 11:85-95.
- John, M. K., and C. J. VanLaerhoven. 1972. Lead uptake by lettuce and oats as affected by lime, nitrogen, and sources of lead. J. Environ. Qual. 1:169-171.
- John, M. K., C. J. VanLaerhoven, and H. H. Chuah. 1972. Factors affecting plant uptake and phytotoxicity of cadmium added to soils. Environ. Sci. Technol. 6:1005-1009.
- John, M. K., H. H. Chuah, and C. J. VanLaerhoven. 1977. Boron response and toxicity as affected by soil properties and rates of boron. Soil Sci. 124:34-39.
- Johnson, C. M. 1966. Molybdenum, pp. 286-301. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Kidder, R. W. 1949. Symptoms of induced copper toxicity in a steer. J. Anim. Sci. 8:623-624 (abstract).
- Kiplinger, D. C., and G. Fuller. 1946. Selenium studies with some flowering greenhouse plants. Proc. Am. Soc. Hortic. Sci. 47:451-462. [As cited in Chapman (1966a).]
- Klemperer, F. W. 1950. The effect of beryllium on certain enzymes. J. Biol. Chem. 187:189-196. [As cited in Romney and Childress (1965).]
- Kreitzer, J. F. 1974. Residues of organochlorine pesticides, mercury, and PCB's in mourning doves from eastern U.S., 1970-71. Pestic. Monit. J. 7(3/4):195-200.
- Kubota, J., V. A. Lazar, G. H. Simonson, and W. W. Hill. 1967. The relationship of soils to molybdenum toxicity in grazing animals in Oregon. Soil Sci. Soc. Am. Proc. 31:667-671.
- Labanauskas, C. K. 1966. Manganese, pp. 264-285. In H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Lagerwerff, J. V. 1971. Uptake of cadmium, lead, and zinc by radish from soil and air. Soil Sci. 111:129-133.
- Lagerwerff, J. V. 1972. Lead, mercury, and cadmium as environmental contaminants, pp. 593-637. In J. J. Mortvedt, P. M. Giordano, and W. L. Lindsay (eds.), Micronutrients in Agriculture. Soil Science Society of America, Inc., Madison, Wis.
- Lakin, H. W. 1973. Selenium in our environment, pp. 96-111. <u>In</u> E. L. Kothny (ed.), Trace Elements in the Environment. Adv. Chem. Series 123. American Chemical Society, Washington, D.C.
- Lee, C. C. 1974. <sup>203</sup>Hg tracer studies on mercury uptake from soil by wheat and barley. Bull. Environ. Contam. Toxicol. 11:551-553.

Leeper, G. W. 1947. The forms and reactions of manganese in the soil. Soil Sci. 63:79. [As cited in Boyd (1971).]

- Liebig, G. F., Jr. 1966. Arsenic, pp. 13-23. In H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Liebig, G. F., G. R. Bradford, and A. P. Vanselow. 1959. Effects of arsenic compounds on citrus plants in solution culture. Soil Sci. 88:342-348.

Lisk, D. J. 1972. Trace metals in soils, plants, and animals. Adv. Agron. 24:267-325.

- Little, P., and M. H. Martin. 1972. A survey of zinc, lead, and cadmium in soil and natural vegetation around a smelting complex. Environ. Pollut. 3:241-254.
- Loew, O., and S. Sawa. 1902-1903. The action of manganese compounds on plants. Imp. Univ. (Tokyo) Coll. Agric. Bull. 5:161-172. [As cited in Chapman (1966a).]
- Luckey, T. G., and B. Venugopal. 1977. Metal Toxicity in Mammals: Physiologic and Chemical Basis for Metal Toxicity, Vol. 1. Plenum Press, New York. 238 pp.
- Lyon, C. B., K. C. Beeson, and G. H. Ellis. 1943. Effects of micronutrient deficiencies on growth and vitamin content of the tomato. Bot. Gaz. (Chicago) 104:495-514. [As cited in Chapman (1966a).]
- MacLean, A. J., R. L. Halstead, and B. J. Finn. 1969. Extractability of added lead in soils and its concentration in plants. Can. J. Soil Sci. 49:327-334. [As cited in National Research Council (1972).]
- MacLean, D. C., R. E. Schneider, and D. C. McCune. 1977. Effects of chronic exposure to gaseous fluoride on yield of field-grown bean and tomato plants. J. Am. Soc. Hortic. Sci. 102:297-299.
- Marsh, R. P., and J. W. Shive. 1941. Boron as a Factor in the Calcium Metabolism of the Corn Plant. Soil Sci. 51:141-151. [As cited in Chapman (1966a).]
- McCune, D. C. 1969. On the establishment of air quality criteria with reference to the effects of atmospheric fluorine on vegetation. Air Qual. Monogr. 69-3. American Petroleum Institute, New York. 33 pp.
- McCune, D. C., and A. E. Hitchcock. 1971. Fluoride in forage: factors determining its accumulation from the atmosphere and concentration in the plant, pp. 289-292. <u>In</u> H. M. Englund and W. T. Beery (eds.), Proceedings of the Second International Clean Air Congress. Academic Press, New York.
- McKee, J. E., and H. W. Wolf. 1963. Water Quality Criteria, 2nd ed. Publ. 3A. The Resources Agency of California, State Water Quality Control Board, Sacramento. 548 pp. (Reprint, June 1, 1974).
- Miller, J. E., J. J. Hassett, and D. E. Koeppe. 1976. Uptake of cadmium by soybeans as influenced by soil cation exchange capacity, pH, and available phosphorus. J. Environ. Qual. 5:157-160.
- Miller, J. T., and H. G. Byers. 1935. A selenium spring. Ind. Eng. Chem. News Ed. 13:456 and J. Am. Water Works Assoc. 28:1159 (1936). [As cited in McKee and Wolf (1963).]
- Miner, S. 1969. Air Pollution Aspects of Barium and Its Compounds. Litton Systems, Inc., Bethesda, Md. 60 pp.
- Morris, H. D. 1949. The soluble manganese content of acid soils and its relation to the growth and manganese content of sweet clover and lespedeza. Soil Sci. Soc. Am. Proc. 13:362-371. [As cited in Chapman (1966a),]
- Mueller, P. K., and R. L. Stanley. 1970. Origin of lead in surface vegetation. AIHL Report 87. California Department of Public Health, Air and Industrial Hygiene Laboratory, Berkeley. 15 pp. [As cited in National Research Council (1972).]
- Muth, O. H., J. E. Oldfield, and P. H. Weswig (eds.). 1967. Symposium: Selenium in Biomedicine. The Avi Publishing Co., Westport, Conn.
- National Academy of Sciences. 1974. Effects of Fluorides in Animals. Washington, D.C. 70 pp.

- National Air Sampling Network. 1966. Air Quality Data, 1964-1965. U.S. Department of Health, Education and Welfare, Public Health Service, Division of Air Pollution. Cincinnati, Ohio. [As cited in Athanassiadis (1969a).]
- National Research Council, Committee on Biologic Effects of Atmospheric Pollutants. 1971. Fluorides. National Academy of Sciences, Washington, D.C. 295 pp.
- National Research Council, Committee on Biologic Effects of Atmospheric Pollutants. 1972. Lead: Airborne Lead in Perspective. National Academy of Sciences, Washington, D.C. 330 pp.
- National Research Council, Committee on Biologic Effects of Atmospheric Pollutants. 1973. Manganese. National Academy of Sciences, Washington, D.C. 191 pp.
- National Research Council, Committee on Biologic Effects of Atmospheric Pollutants. 1974a. Chromium. National Academy of Sciences, Washington, D.C. 155 pp.
- National Research Council, Committee on Biologic Effects of Atmospheric Pollutants. 1974b. Vanadium. National Academy of Sciences, Washington, D.C. 117 pp.
- National Research Council, Committee on Biologic Effects of Atmospheric Pollutants. 1975. Nickel. National Academy of Sciences, Washington, D.C. 275 pp.
- Neiswander, C. R., and V. H. Morris. 1940. Introduction of selenium into plant tissues as a toxicant for insects and mites. J. Econ. Entomol. 33:517-525. [As cited in Chapman (1966).]
- Nielsen, N. E. 1976. The effect of plants on the copper concentration in the soil solution. Plant Soil 45:679-687.
- Oberleas, D., M. E. Muhrer, and B. L. Odell. 1966. The availability of zinc from foodstuffs, pp. 225-238. In A. S. Prasad (ed.), Zinc Metabolism. C. C. Thomas, Springfield, Illinois. [As cited in Allaway (1968).]
- O'Dell, G. D., W. J. Miller, W. A. King, S. L. Moore, and D. M. Blackmon. 1970. Nickel toxicity in the young bovine. J. Nutr. 100:1447-1453. [As cited in National Research Council (1975).]
- Oertlii, J. J., and H. C. Kohl. 1961. Some considerations about the tolerance of various plant species to excessive supplies of boron. Soil Sci. 92:243-247. [As cited in Chapman (1966a).]
- Ohio River Valley Water Sanitation Commission, Subcommittee on Toxicities, Metal Finishing Industries Action Committee. 1950. Report No. 3. [As cited in McKee and Wolf (1963).]
- Ohki, K. 1975. Lower and upper critical zinc levels in relation to cotton growth and development. Physiol. Plant. 35:96-100.
- Ott, E. A., W. H. Smith, R. B. Harrington, and W. Beeson. 1966a. Zinc toxicity in ruminants. I, Effects of high levels of dietary zinc on gains, feed consumption and feed efficiency of lambs. J. Anim. Sci. 25:414-418.
- Ott, E. A., W. H. Smith, and R. B. Harrington. 1966b. Zinc toxicity in ruminants. II, Effects of high levels of dietary zinc on gains, feed consumption and feed efficiency of beef cattle. J. Anim. Sci. 25:419-423.
- Pack, M. R. 1971. Effects of hydrogen fluoride on production and organic reserves of bean seed. Environ. Sci. Technol. 5:1128-1132.
- Peakall, D. B., and D. J. Lovett. 1972. Mercury: its occurrence and effects in the ecosystem. BioScience 22:20-25.
- Phillips, P. H., D. A. Greenwood, C. S. Hobbs, and C. F. Huffman. 1955. The Fluorosis Problem in Livestock Production. NAS-NRC Publ. 381. National Academy of Sciences, Washington, D.C. [As cited in Brewer (1966a).]
- Phillips, P. H., et al. 1960. The fluorosis problem in livestock production, a report of the Committee on Animal Nutrition. NAS-NRC Publ. 824. [As cited in National Research Council (1971).]
- Piper, C. S. 1931. The availability of manganese in the soil. J. Agric. Sci. 21:762-779. [As cited in Boyd (1971).]

- Piper, C. S. 1942. Investigation on copper deficiency in plants. J. Agric. Sci. 32:143-178. [As cited in Struckmeyer et al. (1969) except date incorrectly cited as 1939.]
- Prince, A. L. 1957. Trace element delivering capacity of 10 New Jersey soil types as measured by spectrographic analysis of soils and mature corn leaves. Soil Sci. 84:413-418.
- Purves, D. 1968. Trace element contamination of soils in urban areas. Trans. Int. Congr. Soil Sci. Adelaide, 9th, 2:351-355. [As cited in Beavington (1975).]
- Reeves, A. L. 1965. The absorption of beryllium from the gastrointestinal tract. Arch. Environ. Health 11:209-214.
- Reuther, W., and C. K. Labanauskas. 1966. Copper, pp. 157-179. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Reuther, W., and P. F. Smith. 1953. Effects of high copper content of sandy soil on growth of citrus seedlings. Soil Sci. 75:219-224. [As cited in Chapman (1966a).]
- Reuther, W., and P. F. Smith. 1954. Leaf analysis of citrus, pp. 257-294. In N. F. Childers (ed.), Mineral Nutrition of Fruit Crops. [As cited in Chapman (1966a).]
- Reuther, W., P. F. Smith, and A. W. Specht. 1949. A comparison of the mineral composition of Valencia orange leaves from the major producing areas of the U. S. Proc. Fla. State Hortic. Soc. 62:38-45. [As cited in Chapman (1966a).]
- Richardson, M. E., M. R. Spivey-Fox, and B. E. Fry, Jr. 1974. Pathological changes produced in Japanese quail by ingestion of cadmium. J. Nutr. 104:323-338.
- Rogers, R. D. 1976. Methylation of mercury in agricultural soils. J. Environ. Qual. 5:454-458.
- Romney, E. M., and J. D. Childress. 1965. Effects of beryllium in plants and soil. Soil Sci. 100:210-217.
- Romney, E. M., J. D. Childress, and G. V. Alexander. 1962. Beryllium and the growth of bush beans. Science 135:786-787.
- Romoser, G. L., L. Loveless, L. J. Machlin, and R. S. Gordon. 1960. Toxicity of vanadium and chromium for the growing of chicken. Poult. Sci. 39:1288. [As cited in McKee and Wolf (1963).]
- Root, R. A., R. J. Miller, and D. E. Koeppe. 1975. Uptake of cadmium--its toxicity, and effect on the iron ratio in hydroponically grown corn. J. Environ. Qual. 4:473-476.
- Rosenfeld, I., and O. A. Beath. 1964. Selenium: Geobotany, Biochemistry, Toxicity, and Nutrition. Academic Press, New York. 411 pp.
- Roshchin, I. V. 1967. Toxicity of vanadium compounds used in modern industry. Gig. Sanit. 32:4-6. [As cited in Underwood (1971).]
- Rothstein, A. 1953. Toxicology of the Minor Metals. AEC Project UR-262. University of Rochester. [As cited in McKee and Wolf (1963).]
- Russell, F. C. 1944. Minerals in Pasture, Deficiencies, and Excesses in Relation to Animal Health. Tech. Commun. No. 15. Imperial Bureau of Animal Nutrition, Aberdeen, Scotland. [As cited in McKee and Wolf (1963).]
- Santillan-Medrano, J., and J. J. Jurinak. 1975. The chemistry of lead and cadmium in soil: solid phase formation. Soil Sci. Soc. Am. Proc. 39:851-856.
- Schmitt, N., G. Brown, E. L. Devlin, A. A. Larsen, E. D. McCausland, and J. M. Saville. 1971. Lead poisoning in horses, an environmental health hazard. Arch. Environ. Health 23:185-195.
- Schoening, H. W. 1936. Production of so-called alkali disease in hogs by feeding corn grown in affected areas. North Am. Vet. 17:22-28. [As cited in Rosenfeld and Beath (1964).]
- Schroeder, H. A. 1965. Diabetic-like serum glucose levels in chromium deficient rats. Life Sci. 4:2057-2062. [As cited in Allaway (1968).]

- Schroeder, H. A., J. J. Balassa, and W. H. Vinton, Jr. 1965. Chromium, cadmium, and lead in rats: effects on life span, tumors, and tissue levels. J. Nutr. 86:51. [As cited in John (1973).]
- Schubert, J. 1958. Beryllium and berylliosis. Sci. Am. 199:27-33.
- Scott, H. D., S. D. Beasley, and L. F. Thompson. 1975. Effect of lime on boron transport to and uptake by cotton. Soil Sci. Soc. Am. Proc. 39:1116-1121.
- Sherman, G. D. 1957. Manganese and soil fertility, pp. 135-139. <u>In</u> Soil, USDA Yearbook, 1957. [As cited in Labanauskas (1966).]
- Sihlbom, E., and L. Fredriksson. 1960. Yield and arsenic content in potatoes grown in arsenitecontaining soil. Sver. Utsädesforën Tidskr. 70:312-317. [As cited in Chapman (1966a).]
- Soane, B. D., and D. H. Saunder. 1959. Nickel and chromium toxicity of serpentine soils in southern Rhodesia. Soil Sci. 88:322-330. [As cited in Chapman (1966).]
- Solberg, R. A., D. F. Adams, and H. A. Ferchau. 1955. Some effects of hydrogen fluoride on the internal structure of *Pinus ponderosa* needles, pp. 164-196. <u>In</u> Proceedings of the 3rd National Air Pollution Symposium, Pasadena, California. [As cited in Treshow (1971).]
- Sols, A., and W. Dierssen. 1951. Beryllium and intestinal absorption. Rev. Esp. Fisiol. 7:179.
- Somers, I. I., and J. W. Shive. 1942. The iron-manganese relation in plant metabolism. Plant Physiol. 17:582-602. [As cited in Chapman (1966a).]
- Spector, W. S. 1955. Handbook of Toxicology, Vol. 1. Division of Biology and Medicine, National Academy of Sciences, National Research Council, Washington, D.C. [As cited in Miner (1969).]
- Stahl, Q. R. 1969a. Air Pollution Aspects of Mercury and Its Compounds. Litton Systems, Inc., Bethesda, Md. 99 pp.
- Stahl, Q. R. 1969b. Air Pollution Aspects of Selenium and Its Compounds. Litton Systems, Inc., Bethesda, Md. 78 pp.
- Steel, M., and D. V. G. Feltham. 1950. Arsine poisoning in industry: report of a case. Lancet 1:108-110. [As cited in Vallee et al. (1960).]
- Stokinger, H. E. 1963. Vanadium. In F. A. Patty (ed.), Industrial Hygiene and Toxicology. Interscience Publishers, New York. [As cited in Athanassiadis (1969b).]
- Stowe, H., et al. 1972. Clinical morphological effects of oral cadmium toxicity in rabbits. Arch. Pathol. 94.
- Struckmeyer, B. E., L. A. Peterson, and F. Hsi-mei Tai. 1969. Effects of copper on the composition and anatomy of tobacco. Agron. J. 61:932-936.
- Sullivan, R. J. 1969a. Air Pollution Aspects of Arsenic and Its Compounds. Litton Systems, Inc., Bethesda, Md. 63 pp.
- Sullivan, R. J. 1969b. Air Pollution Aspects of Chromium and Its Compounds. Litton Systems, Inc., Bethesda, Md. 76 pp.
- Sullivan, R. J. 1969c. Air Pollution Aspects of Nickel and Its Compounds. Litton Systems, Inc., Bethesda, Maryland. 69 pp.
- Suttie, J. W. 1976. Personal communication (Dept. of Biochemistry, University of Wisconsin--Madison).
- Suttie, J. W., J. R. Carlson, and C. C. Faltin. 1972. Effects of alternating periods of highand low-fluoride ingestion in dairy cattle. J. Dairy Sci. 55:790-804.
- Sutton, W. R., et al. 1937. Studies on zinc. Proc. Soc. Exp. Biol. Med. 36:211. [As cited in Athanassiadis (1969c).]
- Treshow, M. 1970. Environment and Plant Response. McGraw-Hill Book Co., New York. pp. 267-301.

- Treshow, M. 1971. Fluorides as air pollutants affecting plants. Ann. Rev. Phytopathol. 9:21-44.
- Treshow, M., and M. R. Pack. 1970. Fluoride, pp. D1-D17. In J. S. Jacobson and A. C. Hill (eds.), Recognition of Air Pollution Injury to Vegetation: A Pictorial Atlas. Informative Report 1. TR-7 Agricultural Committee, Air Pollution Control Association, Pittsburgh. [As cited in National Research Council (1971).]
- Turner, M. A. 1973. Effects of cadmium treatment on cadmium and zinc uptake by selected vegetable species. J. Environ. Qual. 2:118-119.
- Twomey, A. C., and S. J. Twomey. 1936. Selenium and duck sickness. Science 83:470-471.
- Tyler, C. 1949. The mineral requirements and metabolism of poultry. III, Elements other than calcium and phosphorus. Nutr. Abst. Rev. 19:263. [As cited in McKee and Wolf (1963).]
- Underwood, E. J. 1962. Trace Elements in Human and Animal Nutrition, 2nd ed. Academic Press, New York. 429 pp. [As cited in Berry and Wallace (1974).]
- Underwood, E. J. 1971. Trace Elements in Human and Animal Nutrition, 3rd ed. Academic Press, New York. 543 pp.
- U.S. Environmental Protection Agency, Office of Toxic Substances. 1975. Preliminary Investigation of Effects on the Environment of Boron, Indium, Nickel, Selenium, Tin, Vanadium, and Their Compounds. Vol. VI, Vanadium. EPA-560/2-75-005F. 84 pp.
- Vallee, B. L. 1962. Zinc. In C. L. Comar and F. Bronner (eds.), Mineral Metabolism, Vol. II, Part B. Academic Press, New York. [As cited in Athanassiadis (1969c).]
- Vallee, B. L., D. D. Ulmer, and W. E. C. Wacker. 1960. Arsenic toxicology and biochemistry. Arch. Ind. Health 21:132-151.
- Vanselow, A. P. 1966a. Barium, pp. 24-32. In H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. Unversity of California, Division of Agricultural Science, Berkeley.
- Vanselow, A. P. 1966b. Cobalt, pp. 142-156. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Vanselow, A. P. 1966c. Nickel, pp. 302-309. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Vaughan, B. E., K. H. Abel, D. A. Cataldo, J. M. Hales, C. E. Hane, L. A. Rancitelli, R. C. Routson, R. E. Wildung, and E. G. Wolf. 1975. Review of Potential Impact on Health and Environmental Quality from Metals Entering the Environment as a Result of Coal Utilization. Battelle Energy Progress Report, Pacific Northwest Laboratories-Battelle Memorial Institute, Richland, Washington. 75 pp.
- Waltner, K., et al. 1929. Uber die wirkung einiger Metalle. Arch. Exp. Pathol. Pharmakol. 141:123. [As cited in Athanassiadis (1969c).]
- Warington, K. 1950. The effect of variations in calcium supply, pH value and nitrogen content of nutrient solutions on the response of lettuce and red clover to molybdenum. Ann. Appl. Biol. 37:607. [As cited in McKee and Wolf (1963).]
- Warington, K. 1951. Some interrelationships between manganese, molybdenum, and vanadium in the nutrition of soybeans, flax, and oats. Ann. Appl. Biol. 38:624. [As cited in McKee and Wolf (1963).]
- Warington, K. 1954. The influence of iron supply on toxic effects of manganese, molybdenum, and vanadium on soybeans, peas, and flax. Ann. Appl. Biol. 41:1-22. [As cited in USEPA (1975).]
- Weber, C. W., and B. L. Reid. 1968. Nickel toxicity in growing chicks. J. Nutr. 95:612. [As cited in Sullivan (1969c).]
- Weinstein, L. H., and D. C. McCune. 1971. Effects of fluoride on agriculture. J. Air Pollut. Control Assoc. 21:410-413.
- Wesolowski, J. J., W. John, and R. Kaifer. 1973. Lead source identification by multi-element analysis of diurnal samples of ambient air, pp. 1-16. <u>In</u> E. L. Kothny (ed.), Trace Elements in the Environment. Adv. Chem. Ser. 123. American Chemical Society, Washington, D.C.

Williams, R. B. 1977. Trace elements in animals. Comp. Anim. Nutr. 2:87-143.

- Wilson, D. O., and J. F. Cline. 1966. Removal of plutonium-239, tungsten-185, and lead-210 from soils. Nature 209:941-942. [As cited in National Research Council (1972).]
- Wolff, J. 1913. The influence of iron on the development of barley, and the nature of its action. C. R. Acad. Sci. (Paris) 157:1022-1024. [As cited in Vanselow (1966c).]
- Woodbridge, C. G. 1955. The boron requirement of stone-fruit trees. Can. J. Agric. Sci. 35:282-286. [As cited in Chapman (1966a).]
- Yamagata, N., and I. Shigematsu. 1970. Cadmium pollution in perspective. Inst. Public Health Tokyo Bull. 19:1-27. [As cited in Berry and Wallace (1974).]
- Yamartino, R. J., Jr., et al. 1976. Environmental Implications of Ground-Base and Airborne Hydrogen Fluoride Laser Operations. Argonne National Laboratory, Argonne, Ill. 106 pp. (Draft report).
- Zimdahl, R. L., and J. H. Arvik. 1973. Lead in soils and plants: a literature review. CRC Crit. Rev. Environ. Control 3:213-224.
- Zoller, W. H., G. E. Gordon, E. S. Gladney, and A. G. Jones. 1973. The sources and distribution of vanadium in the atmosphere, pp. 31-47. In E. L. Kothny (ed.), Trace Elements in the Environment. Adv. Chem. Ser. 123. American Chemical Society, Washington, D.C.

# APPENDIX E. SOURCES AND REGIONAL DISTRIBUTIONS OF TRACE ELEMENTS IN U.S. SOILS

## NATURAL AND INDUSTRIAL SOURCES

Naturally occurring sources of trace elements depend largely on the geological history of the soil parent material. Rock type is one important parameter. The average concentrations of selected trace elements in igneous and sedimentary rocks are given in Table E.1. The weathering of rocks can release and mobilize trace elements, and soils formed from various rock types usually reflect the elemental nature of the rock parent material. For example, Ermolenko (1966) stated that the weathering of granites leaves the soil with alkaline elements (potassium. rubidium, cesium, and lithium), barium, and others. The weathering of basic and neutral rocks (basalts, andesites, diorites) can result in iron, titanium, copper, and vanadium in the soil, whereas ultrabasic rocks (pyroxenites, serpentinites, dunites, etc.) leave behind chromium, nickel, cobalt, and magnesium. Soils may be formed in place over rock parent materials, or more likely, soils are formed from transported and deposited parent materials such as loess, alluvium, glacial drift, and coastal plain sands. The movement of such materials also causes movement and redistribution of trace elements. Parent material and other soil-forming factors (climate, living organisms, topography, and time) determine the elemental forms and, thus, the mobility of the trace elements present in the soil.

Element	Igneous rocks <sup>a</sup>	Shales <sup>b</sup>	Sandstones <sup>b</sup>	Limestones <sup>b</sup>
Arsenic	1.8	13	]	1
Barium	425	580	50	120
Beryllium	2.8	3	<1	<1
Boron	10	100	35	20
Cadmium	0.2	0.3	0.05	0.035
Chromium	100	90	35	11
Cobalt	25	19	0.3	0.1
Copper	55	45	5	4
Fluorine	625	740	270	330
Lead	12.5	20	7	9
Manganese	950	850	50	1100
Mercury	0.08	0.4	0.03	0.04
Molybdenum	1.5	2.6	0.2	0.4
Nickel	75	68	2	20
Selenium	0.05	0.6	0.05	0.08
Vanadium	135	130	20	20
Zinc	70	95	16	20

Table E.l.	Average Trace-Element Concentrations (	ppm)	in
	Igneous and Sedimentary Rocks		

<sup>a</sup>Data from Taylor (1964) as compiled by Bowen (1966). <sup>b</sup>Data from Turekian and Wedepohl (1961) as compiled by Bowen (1966).

Another source of trace elements in soil is the upward movement of groundwater. Trace elements solubilized in the underlying strata, particularly metal ores, can rise to the surface layers with groundwater and be retained by soil colloids when the water evaporates (Ermolenko 1966). This phenomenon is probably most important in areas of low precipitation and high evaporative demand, and in areas with rich ore deposits.

Trace elements can reach the soil through naturally occurring atmospheric transport. Sea spray, wind-eroded soil particles, pollen, and meteoritic and volcanic material may reach a soil by either dry or wet atmospheric deposition (Lisk 1972).

Human activities cause increased trace-element concentrations in soils, which can be locally heavy and in some cases toxic. Generally, many industrial activities release trace elements either as aerial emissions or waste effluents. Several papers document the increased trace-element levels in urbanized and industrialized areas (e.g., Purves 1972). The smelting of metal ores is one of the most notorious sources of trace-element emissions. Hutchinson and Whitby (1974), Whitby and Hutchinson (1974), Little and Martin (1972), Wood and Nash (1976), Ragaini et al. (1977), and John et al. (1976) have all observed extremely high and toxic levels of many trace elements in the soils and vegetation surrounding smelters. Many of the highest reported soil concentrations of certain trace elements come from soils close to smelters. With the advent of the application of digested sewage sludge to soils for fertilizing and recycling purposes, trace elements discharged into wastewater by industrial sources are being added to soils. Many studies are currently under way to determine the long-term effects of sewage sludge application to soils (e.g., Andersson 1977; Sidle et al. 1977; Kirkham 1975; Sidle and Sopper 1976; Hinesly et al. 1977).

Trace elements are added to the soil by the use of agricultural chemicals such as pesticides and herbicides although this practice is decreasing with the increasing use of organics for this purpose. Certain trace elements--including Cd, Cr, Cu, Ni, Pb, and Zn--have been found as impurities in fertilizers, particularly phosphate fertilizers (Mortvedt and Giordano 1977). However, based on a series of pot experiments, Mortvedt and Giordano (1977) concluded that uptake of the trace-element contaminants, other than zinc, is probably not significant, at least for corn, at the rates that phosphate fertilizer is normally applied under field conditions.

Other areas which can be high in trace elements include metal and coal mine spoils and floodplains. Rivers polluted by industrial effluents or other sources will inundate the soils of their floodplains with new trace-element loadings during each flood.

Table E.2 is a compilation of information on some of the natural and industrial sources of 17 selected trace elements. Although not a complete listing, it does list most of the major sources for each of the elements. Coal combustion is not listed but is a source of each element in the table. The listing of these trace-element sources does not necessarily imply that significant quantities of the element will reach terrestrial systems from each source. Rather, the purpose of the table is to point out sources of each element which can be considered in an evaluation of impacts if a proposed coal-fired power plant is to operate close to one or more of these potential trace-element sources.

#### REGIONAL TRACE-ELEMENT DISTRIBUTIONS IN THE UNITED STATES

Maps and summaries of regional trends in trace-element distribution are difficult to produce because the scale of any practical map or summary forces generalization unless only a very small area is considered. However, since the importance of micronutrient trace elements to agricultural production has been recognized, some maps and summaries of the trace-element concentrations in plants have been produced and have proven useful to agronomists, horticulturists, growers, and fertilizer manufacturers (Kubota and Allaway 1972). Most maps and summaries are concerned with delineating areas of micronutrient deficiency rather than areas of toxicity or unessential elements because (1) they were developed for agricultural use, and (2) areas where toxic concentrations occur are usually somewhat localized (e.g., see Fig. E.5 for selenium). Caution must also be exercised in the use of these maps and summaries because they may not be valid on the local level. For instance in Illinois, Peck et al. (1977, personal communication) have determined that micronutrient concentrations in agricultural soils and crops vary from farm to farm, due to the types of fertilizers used over a period of years, and that this fact prohibits anything but a very general characterization of micronutrient deficiencies or excesses based on soil type or geographic area alone. Additionally, most national maps and summaries reflect data on agricultural species which may or may not apply to vegetation utilized by wildlife.

With the above limitations in mind, the following section contains a brief survey of the regional distributions of seven essential trace elements in the United States as discussed by Kubota and Allaway (1972) and Hodgson et al. (1971), except where noted.

Element	Source	References
Arsenic	Man	
	Pb, Cu, Au smelting plants; some Ni and Cd smelters	Sullivan (1969a)
	Cotton gins and their trash burning areas (As is used as a dessicant for cotton	Sullivan (1969a)
	plants prior to picking)	
	Arsenical pesticides, herbicides, defoliants, soil sterilants, and silvicides	Sullivan (1969a); Vallee et al. (1960);
	(Pb and Ca arsenates and organic As compounds) <sup>a</sup>	Allaway (1968); Walsh et al. (1976a)
<b>.</b> .		
Barium	Man	$N_{\rm eff} = 1 (1074)$
	Mordants for printing fabrics and acid dyes	Yopp et al. (1974)
	An agent in rubber vulcanization and lubricants b	Yopp et al. (1974)
	An agent in electroplating and bleaching processes	Yopp et al. (1974)
Bervllium	Man	
bergrinam	Tomponent of special metal allovs <sup>b</sup>	Everest (1964)
	Moderator in atomic reactors (stable and radioactive Be has been found in	Everest (1964)
	effluent streams) <sup>b</sup>	
Popon	Na + 1 ma ]	
DUTUI	Naturai	Bundfond (1066)
	Aria solis	Drautoru (1900)
	solis derived from marine sediments	Bradford (1966)
	Young deposits and parent materials rich in B minerals (e.g., borax)	Bradford (1966)
	Man	
	Irrigation water (B in irrigation water tends to accumulate in soil and can	Walsh et al. (1976a)
	depress vields)	
	Sewage sludge applications	Bradford (1966)
	Acidification of neutral or alkaline soils	Bradford (1966)
	Misuse of B-based fortilizers	Bradford (1966)
	High K for this ation of D_wigh soils	Bradford (1966)
	Fly sh incomparing into coils	Mulford and Mantons (1971)
	Frigaine from the Te industry	Dunachan (1960)
	Emissions from the Fe industry	Durocher (1969)
	Plants engaged in B use or production	Durocher (1969)
	Areas near high-energy borane fuel sites	Durocher (1969)
Cadmium	Man	
	$\overline{Zn}$ , Pb, and Cu smelters (Cd occurs naturally in close association with Zn)	Hiatt and Huff (1975); Lagerwerff (1972)
	Galvanizing processes	Hiatt and Huff (1975): Lagerwerff (1972):
		Friberg et al. (1971)
	Steel production	Hiatt and Huff (1975): Lagerwerff (1972):
		=  Erihora et al (1971)
	Manufacture of plactics battories pigments and allows	Histt and Hiff $(1075)$ , Lacomics ff $(1072)$ .
	manuracture or prastics, batteries, proments, dnu alloys	$\frac{1}{1000} = \frac{1}{1000} = 1$
		rriberg et al. (1971)

Table E.2. Potential Natural and Man-Caused Sources, Other Than Coal Combustion, of Trace Elements in Soils

(continued)

Table E.2. (Continued)

Element	Source	References
Cadmium (contd.)	Automobile tire wear	Hiatt and Huff (1975); Lagerwerff (1972); Friberg et al. (1971)
(0011001)	Sewage sludge applications	Hiatt and Huff (1975); Lagerwerff (1972); Friberg et al. (1971)
	Agricultural chemicals with Cd impurities (notably superphosphates)	Hiatt and Huff (1975); Lagerwerff (1972); Friberg et al. (1971)
	Burning of wood, paper, and urban trash	Lagerwerff and Specht (1970)
Chromium	<u>Natural</u>	
	Ultrabasic rocks and soils formed from them (pyroxenitic and serpentine soils in particular)	Walsh et al. (1976a); Yopp et al. (1974); Ermolenko (1966)
	Man	
	industries utilizing chromate compounds	Sullivan (1969b)
	May be present in cement and asbestos Sewage sludge application	Sullivan (1969b) Walsh et al. (1976a) Walsh et al. (1976a)
	Snow meiting saits	Waish et al. (1976a)
Cobalt	Natural Weathering of ultrabasic rocks (pyroxenites, serpentinites, dunites, etc.)	Ermolenko (1966)
Copper	Natural Basic or neutral rock weathering (basalts, andesites, diorites)	Ermolenko (1966)
	Man Accumulation of Cu residues from prolonged use of Bordeaux fungicides (containing	Baker (1974)
	$CuSO_4$ ) and $CuSO_4$ fertilizers	
	Use of $U_{4}$ as an algoride in water and to remove aquatic weeds Industrial wastes, e.g., from the electroplating industry Mine offluents	Yopp et al. (1974) Walsh et al. (1976a); Yopp et al. (1974) Yopp ot al. (1974)
	Sewage sludge application	Yopp et al. (1974)
Fluorine	Natural Volcanic eruptions	Yopp et al. (1974)
	Man	
	Manufacturing processes of aluminum and steel	Yopp et al. (1974)
and the second	Processing of phosphates in Florida and lennessee for fertilizers	Yopp et al. (1974) Yopp et al. (1974)
	Use of fluorspar ( $CaF_2$ ) as a metallurgical fluxing material or as a source of etching acid for glassware	Yopp et al. (1974)

(continued)

# Table E.2. (Continued)

Element	Source	References
Lead	Natural Soil parent material including the principally mined forms: sulfides (galena), carbonates (cerussite), and oxides (anglesite) Volcanic emissions of Pb halides and silicates Forest-fire aerosol ash, and sea-salt aerosols	Edwards et al. (1971); Vinogradov (1959); Goldschmidt (1937) Natl. Res. Counc. (1972) Natl. Res. Counc. (1972)
	Man Automobile (internal combustion engine) exhaust	Walsh et al. (1976a); Natl. Res. Counc. (1972); Zimdahl and Arvik (1973)
	Metal smelting	Natl. Res. Counc. (1972); Little and
	Pb impurities in fertilizers	Walsh et al. (1976a); Natl. Res. Counc. (1972); Brewer (1966b)
	Pb-arsenate use as a pesticide (discontinued) Sewage sludge application	Walsh et al. (1976a); Brewer (1966b) Walsh et al. (1976a)
Manganese	<u>Natural</u> Soils with Mn-containing minerals (manganite and pyrolusite, principally)	Yopp et al. (1974)
	<u>Man</u> Mine seepage Application of fly ash to soils Impurities in phosphate fertilizers Sewage sludge application	Natl. Res. Counc. (1973) Natl. Res. Counc. (1973) Natl. Res. Counc. (1973) Walsh et al. (1976a)
Mercury	<u>Natural</u> Weathering and sublimation of Hg ores (cinnabar, a red sulfide of Hg found in western and southwestern United States)	Walsh et al. (1976a); Yopp et al. (1974)
	<u>Man</u> Hg-catalysts used in the plastic industry <sup>b</sup> Phenylmercurials used in the paper pulp industry <sup>b</sup> Hg electrodes used in chlorine-alkali industrial plants <sup>b</sup> Mercurial pesticides and fungicides Sewage sludge application	Yopp et al. (1974) Yopp et al. (1974) Yopp et al. (1974) Walsh et al. (1976a); Yopp et al. (1974) Walsh et al. (1976a)
Molybdenum	<u>Natural</u> Soils containing weathered Mo sulfide ore (molybdenite)	Yopp et al. (1974)
	<u>Man</u> Production of special steel alloys (e.g., high-speed steel for cutting tools) may release Mo to the environment	Yopp et al. (1974)
	(continued)	

Table E.2. (Concluded)

Element	Source	References
Nickel	<u>Natural</u> Soils formed from ultrabasic rocks (serpentinites)	Walsh et al. (1976a); Yopp et al. (1974); Ermolenko (1966)
	Man Leaching of mine tailings Ni impurities in superphosphate fertilizers Automobile exhausts Metal smelting Sewage sludge application	Yopp et al. (1974) Lagerwerff (1967) Lagerwerff and Specht (1970) Walsh et al. (1976a) Cunningham et al. (1975)
Selenium	<u>Natural</u> Soils formed from volcanic rock Soils formed from marine sediments Soils formed from Cretaceous outcroppings (especially shales)	Ganje (1966) Ganje (1966) Ganje (1966); Rosenfeld and Beath (1964)
	<u>Man</u> Sewage sludge application Impurities in superphosphate fertilizers Se extraction and processing plants Pigment manufacturing <sup>b</sup> Rubber manufacturing (Se is a vulcanizing agent) <sup>b</sup> Manufacturing of rectifiers and photoelectric cells <sup>b</sup>	Walsh et al. (1976a) Walsh et al. (1976a) Rosenfeld and Beath (1964) Rosenfeld and Beath (1964) Rosenfeld and Beath (1964) Rosenfeld and Beath (1964)
Vanadium	<u>Natural</u> Soils containing vanadates of Cu, Zn, Pb, U, Fe, Mn, Ca, and K ( <u>may</u> be phytotoxic in certain soils containing carnoitite or tyuyamunite minerals in N.M., Colo., and Utah)	Cannon (1963)
	<u>Man</u> Combustion of residual fuel oil (particularly in the northeastern United States)	Zoller et al. (1973)
Zinc	<u>Natural</u> Soils containing weathered Zn ore (sphalerite, a mixed sulfide of Zn and Fe)	Yopp et al. (1974)
	Man Galvanizing processes Alloy production (especially brass) Zn-based pesticides Mine wastes Sewage sludge application Impurities in superphosphate fertilizers Effluents from metal plating works	Yopp et al. (1974) Yopp et al. (1974) Yopp et al. (1974) Walsh et al. (1976a) Walsh et al. (1976a) Walsh et al. (1976a) Heit (1977)

<sup>a</sup>The use of inorganic arsenicals was banned in 1967, thus reducing the application of arsenic to soils (Walsh et al. 1976b). <sup>D</sup>Denotes element is used in this process and may therefore be present in emissions or effluents which could contaminate soils.

## Boron

Boron deficiencies have been identified in at least 41 states in the United States, occurring mostly in humid zones (Berger 1962). Boron deficiency or toxicity is more dependent upon individual plant species' needs or tolerances than on actual available soil concentrations. Boron toxicity has been reported in the western states, mostly associated with the use of highboron irrigation water.

#### Cobalt

Cobalt is required by legumes to maintain symbiotic nitrogen-fixation. Ruminant animals also require cobalt. Figure E.1 shows the geographic distribution of cobalt-deficient areas in the eastern United States. Areas where legumes usually contain < 0.07 ppm cobalt (approximately), on a dry weight basis, are considered deficient areas for ruminants. Forage grasses and cereal grains grown on the same soils frequently contain even lower concentrations of cobalt. Legumes containing 0.1-0.2 ppm cobalt, on a dry weight basis, are usually considered to have adequate cobalt levels for ruminants. The western United States generally has adequate cobalt concentrations.

# COBALT

Areas where legumes usually contain less than 0.07 ppm of cobalt.

from 0.05 to 0.1 ppm of cobalt.

Grasses generally contain less than 0.10 ppm of cobait throughout most of the U.S.



Figure E.l. Geographic Distribution of Cobalt-Deficient Areas in the Eastern United States. From Kubota and Allaway (1972) (with permission, see credits).

#### Copper

Copper deficiencies are apparently less common than deficiencies of other micronutrients in the United States. Deficiency is usually localized; however, there are some reports of copper deficiency in the eastern half of the country (especially the Florida citrus area) and the Pacific Coast states. Copper is often deficient in organic soils (Histosols) and very sandy soils. There are few reports of "naturally occurring" copper toxicity in the United States. Figure E.2 gives a regional distribution of copper in alfalfa in the eastern and central United States.

#### Manganese

Manganese deficiencies appear to be more widespread in humid regions of the eastern United States than in the western states, and often occur in naturally wet soils that have been drained for crop production. Acid soils may have toxic levels of available manganese. Excessive concentrations of manganese have been observed in some soils in Kentucky and Connecticut (Sherman 1957). Figure E.2 shows the regional distribution of manganese in alfalfa in the eastern and central states.



Figure E.2. Regional Distribution of Copper, Iron, and Manganese in Alfalfa in the Eastern and Central United States. From Hodgson et al. (1971) (with permission, see credits).

# Molybdenum

Molybdenum deficiencies have been reported in 21 states (Berger 1962), mostly on acid soils. No broad regions appear uniformly deficient in molybdenum, but most reports of deficiencies come from the Eastern Seaboard, the Great Lakes states, and the Pacific Coast states. Molybdenum toxicity in plants is rarely observed in the field; most plants seem to tolerate fairly high tissue concentrations (Allaway 1968; Johnson 1966). However, animals require only very low amounts of molybdenum, usually < 1 ppm of the dry diet (Johnson 1966). High levels of molybdenum in forage can cause molybdenosis (molybdenum-induced copper deficiency) in animals, especially ruminants. When dietary copper levels are low (< 4 ppm), 5 ppm molybdenum in the diet may have detrimental effects (Allaway 1968). The condition is most often associated with dietary molybdenum levels of 10-20 ppm or more and normal (4-10 ppm) copper concentrations.

A generalized pattern for the United States of molybdenum concentrations in legumes (when grown on the same soils, legumes generally accumulate more molybdenum than grasses) is presented in Figure E.3; the general locations of both naturally occurring molybdenum-toxic areas and areas of industrially caused molybdenosis are also illustrated. Figure E.4 shows general areas of the western United States where molybdenum concentrations in forages have induced molybdenosis in ruminants and areas where molybdenum concentrations in forages are potentially toxic to ruminants. Although Figures E.3 and E.4 present generalized areas of molybdenum toxicity, the problem areas are actually localized within these areas. The problem soils are characteristically "poorly drained neutral or alkaline soils formed in granitic alluvium of wet, narrow floodplains and alluvial fans of small streams. Soil textures may range from loamy sand to clay loam. They typically have either a thick A1 horizon or an A1 horizon capped by a thin layer of peat or muck" (Kubota and Allaway 1972).



- AREAS WITH BACKGROUND LEVELS OF 6 to 8 ppm OF Mo
- AREAS WITH BACKGROUND LEVELS OF 2 to 4 ppm OF Mo
- AREAS WITH BACKGROUND LEVELS OF 1ppm or LESS OF Mo
- Ø GENERAL LOCATION OF NATURALLY OCCURRING MOLYBDENUM-TOXIC AREAS
- x GENERAL LOCATION OF INDUSTRIAL MOLYBDENOSIS
- Figure E.3. Generalized Regional Pattern of Molybdenum Concentrations in Legumes (Courtesy of Dr. J. Kubota, see credits).



# MOLYBDENUM

Areas where molybdenum toxicity has
been observed in ruminants and where forages are high (>10 to 400 ppm).

Areas where forages contain from 10 to x 60 ppm but where molybdenum toxicity in ruminants has not been confirmed.

Figure E.4. Distribution of General Areas of Molybdenum Toxicity in the Western United States. From Kubota and Allaway (1972) (with permission, see credits).

#### Selenium

Selenium probably exhibits the most striking geographic pattern of distribution of all the essential trace elements (Fig. E.5). The reason for the strong geographic trends is apparently due to the selenium concentrations in the soil parent materials of each region. As with molybdenum, plants can accumulate selenium to concentrations which are toxic to grazing animals. However, these concentrations are not toxic to the plants. Generally, selenium toxicity occurs in localized areas in the Great Plains and Rocky Mountain states on alkaline soils formed from seleniferous parent material (Figs. E.5 and E.6).



Low - approximately 80% of all forage and grain contain <0.05 ppm of selenium.

Variable - approximately 50% contains >0.1 ppm.

- Adequate 80% of all forages and grain contain >0.1 ppm of selenium.
- Local areas where selenium accumulator plants contain >50 ppm.

Figure E.5. Geographic Distribution of Low-, Variable-, and Adequate-Selenium Areas in the United States. From Kubota and Allaway (1972) (with permission, see credits).

### Zinc

Zinc deficiencies are found throughout the country, especially in soils which are cropped extensively. In the West (to the 100th parallel), areas devoted to wheat, native grassland, and range are less likely to exhibit zinc deficiency than areas producing high-value crops (i.e., vegetables and fruits). The Southeast (east of the 100th parallel and south of the Ohio and Potomac rivers) also has many areas which are zinc deficient, particularly on sandy, well drained, acid soils and on soils formed from phosphatic rocks in Kentucky and Tennessee. The citrus-producing region of Florida may be the largest single area of general zinc deficiency.



Figure E.6. Distribution of Seleniferous Vegetation in the Western United States and Canada. Each open dot represents the place of collection of a plant specimen containing 50-500 ppm selenium; each solid dot, specimens containing more than 500 ppm. From Rosenfeld and Beath (1964) (with permission, see credits).

The remaining states (the northeastern quarter of the country) probably have the lowest occurrence of zinc-deficient areas. Zinc deficiency is probably least prevalent in the slightly to moderately acid Mollisols of the central Corn Belt. Figure E.7 shows the regional distribution of zinc concentrations in corn and alfalfa. According to Kubota and Allaway (1972), the only reported cases of naturally occurring zinc toxicity in plants (in the United States) came from organic soils (Histosols) in New York.

# Trace Elements in Specific Geochemical Environments

Cannon (1970) discussed the possible excesses and deficiencies of trace elements in soils and vegetation that are characteristic of specific geochemical environments. Table E.3 summarizes data presented in Cannon (1970).



Figure E.7. Regional Distribution of Zinc in Corn and Alfalfa in the Eastern and Central United States. From Hodgson et al. (1971) (with permission, see credits).

		Maximum measured	concentrations in	n geochemical en	vironment
Unique geologic environments	Possible deficiencies in geologic unit	Possible excess in geologic unit	In soils (ppm, dry wt.)	In plants (ppm, dry wt.)	In water (ppm)
Limestones	Molybdenum, s`trontium, calcium	Phosphorus Potassium Lead Zinc		· · · · · · ·	•
Glaciated areas: Drift	Strontium, molybdenum, cobalt, boron, manganese, phosphorus, iodine	Titanium Iron Chromium Nickel Zipo			
		Lead Strontium			
Peat bogs	Copper (unavailable)	Zinc Copper	161; 800	10,000	8.3
		Lead Cadmium	250 190	58 0.96	
Coastal plain sands	Iron, manganese, copper, selenium, cobalt, boron, chromium	· · ·			
Serpentine	Nitrogen, phosphorus, calcium, molybdenum, manganese	Nickel Chromium Magnesium Iron	6,000	630	
Shales of North Central Plains	Phosphorus	Selenium Molybdenum	130	8,000	
Evaporative basins: Nevada and California		Strontium Chlorine Magnesium Sodium Boron Potassium Lithium Fluorine	1,500	83,000 400	12
Arizona, Gila River basin	Chromium, barium	Molybdenum Magnesium Lithium Chlorine Boron Strontium		2.25 >3,000	0.025 66 0.380 1,080 0.430 3.8
Phosphate rock: Idaho and Wyoming		Vanadium Uranium Nickel Chromium Zinc Manganese Phosphorus		55 0.34	
Complex ores		Copper Lead Zinc Gold Arsenic Cadmium		1,370 140 25	
Uranium deposits: Colorado Plateau		Uranium Vanadium Selenium Molybdenum	1,500	38 319 6,000 109	

# Table E.3. Excesses and Deficiencies to be Expected in Areas of Marked Geochemical Differentiation<sup>a</sup>

<sup>a</sup>Adapted from Cannon (1970) (with permission, see credits).

REFERENCES

- Allaway, W. H. 1968. Agronomic controls over the environmental cycling of trace elements. Adv. Agron. 20:235-274.
- Andersson, A. 1977. Some aspects on the significance of heavy metals in sewage sludge and related products used as fertilizers. Swed. J. Agric. Res. 7:1-5.

Baker, D. E. 1974. Copper: soil, water, plant relationships. Fed. Proc. 33:1188-1193.

- Berger, K. C. 1962. Micronutrient deficiencies in the United States. J. Agric. Food Chem. 10:178-181. [As cited in Bingham (1973).]
- Bingham, F. T. 1973. Boron in cultivated soils and irrigation waters, pp. 130-138. In E. L. Kothny (ed.), Trace Elements in the Environment. Adv. Chem. Ser. 123. American Chemical Society, Washington, D. C.
- Bowen, H. J. M. 1966. Trace Elements in Biochemistry. Academic Press, London. 241 pp.
- Bradford, G. R. 1966. Boron, pp. 33-61. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Brewer, R. F. 1966. Lead, pp. 213-217. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Cannon, H. L. 1963. The biogeochemistry of vanadium. Soil Sci. 96:196. [As cited in Yopp et al. (1974).]
- Cannon, H. L. 1970. Trace element excesses and deficiencies in some geochemical provinces of the U. S., pp. 21-43. <u>In</u> D. D. Hemphill (ed.), Proceedings of the University of Missouri Third Annual (1969) Conference on Trace Substances in Environmental Health, Vol. III. University of Missouri Press, Columbia.
- Cunningham, J. D., D. R. Keeney, and J. A. Ryan. 1975. Yield and metal composition of corn and rye grown on sewage sludge-amended soil. J. Environ. Qual. 4:448-454.
- Durocher, N. L. 1969. Air Pollution Aspects of Beryllium and Its Compounds. Litton Systems, Inc., Bethesda, Md. 82 pp.
- Edwards, H. W., M. L. Corrin, L. O. Grant, L. M. Hartman, E. R. Reiter, R. K. Skogerboe, C. G. Wilber, and R. L. Zimdahl. 1971. Impact on Man of Environmental Contamination Caused by Lead. Interim Report. Colorado State University, Fort Collins. [As cited in Yopp et al. (1974).]
- Ermolenko, N. F. 1966. Trace Elements and Colloids in Soils, 2nd ed. Nauka i Tekhnika Minsk. Translated from the Russian, 1972. Published for the U.S. Department of Agriculture and the National Science Foundation, Washington, D.C., by Israel Program for Scientific Translations, Jerusalem. 259 pp.
- Everest, D. A. 1964. The Chemistry of Beryllium. Elsevier Publishing Co. [As cited in Yopp et al. (1974).]
- Friberg, L., M. Piscator, and G. Nordberg. 1971. Cadmium in the Environment. CRC Press, Cleveland, Ohio. 166 pp.
- Ganje, T. J. 1966. Selenium, pp. 394-404. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Science, Berkeley.
- Goldschmidt, V. M. 1937. The principles of distribution of chemical elements in minerals and rocks. Chem. Soc. 655. [As cited in Yopp et al. (1974).]
- Heit, M. 1977. A Reivew of Current Information on Some Ecological and Health Related Aspects of the Release of Trace Metals into the Environment Associated with the Combustion of Coal. HASL-320, Health and Safety Laboratory, Energy Research and Development Administration, New York. Technical Information Center, Energy Research and Development Administration.
- Hiatt, V., and J. E. Huff. 1975. The environmental impact of cadmium: an overview. Int. J. Environ. Stud. 7:277-285.
- Hinesly, T. D., R. L. Jones, E. J. Ziegler, and J. J. Tyler. 1977. Effects of annual and accumulation applications of sewage sludge on assimiliation of zinc and cadmium by corn (*Zea mays* L.). Environ. Sci. Technol. 11:182-188.

- Hodgson, J. F., W. H. Allaway, and R. B. Lockman. 1971. Regional plant chemistry as a reflection of environment, pp. 57-72. <u>In</u> H. L. Cannon and H. C. Hopps (eds.), Environmental Geochemistry in Health and Disease. Geol. Soc. Am. Mem. 123.
- Hutchinson, T. C., and L. M. Whitby. 1974. Heavy-metal pollution in the Sudbury mining and smelting region of Canada. I, Soil and vegetation contamination by nickel, copper, and other metals. Environ. Conserv. 1:123-132.
- John, M. K., C. J. Van Laerhoven, and J. H. Bjerring. 1976. Effect of a smelter complex on the regional distribution of cadmium, lead, and zinc in litters and soil horizons. Arch. Environ. Contam. Toxicol. 4:456-468.
- Johnson, C. M. 1966. Molybdenum, pp. 286-301. In H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils, pp. 286-301. University of California, Division of Agricultural Science, Berkeley.
- Kirkham, M. B. 1975. Trace elements in corn grown on long-term sludge disposal site. Environ. Sci. Technol. 9:765-768.
- Kubota, J., and W. H. Allaway. 1972. Geographic distribution of trace element problems, pp. 525-554. In J. J. Mortvedt, P. M. Giordano, and W. L. Lindsay (eds.), Micronutrients in Agriculture. Soil Science Society of America, Inc., Madison, Wis.
- Labanauskas, C. K. 1966. Manganese, pp. 264-285. <u>In</u> H. D. Chapman (ed.), Diagnostic Criteria for Plants and Soils. University of California, Division of Agriculture, Berkeley.
- Lagerwerff, J. V. 1967. Heavy metal contamination of soils. <u>In</u> N. C. Brady (ed.), Agriculture and the Quality of Our Environment. American Association for the Advancement of Science, Washington, D. C. [As cited in Walsh et al. (1976a).]
- Lagerwerff, J. V. 1972. Lead, mercury, and cadmium as environmental contaminants, pp. 593-637. In J. J. Mortvedt, P. M. Giordano, and W. L. Lindsay (eds.), Micronutrients in Agriculture. Soil Science Society of America, Inc., Madison, Wis.
- Lagerwerff, J. V., and A. W. Specht. 1970. Contamination of roadside soil and vegetation with cadmium, nickel, lead, and zinc. Environ. Sci. Technol. 4:583-585.
- Lisk, D. J. 1972. Trace metals in soils, plants, and animals. Adv. Agron. 24:267-325.
- Little, P., and M. H. Martin. 1972. A survey of zinc, lead and cadmium in soil and natural vegetation around a smelting complex. Environ. Pollut. 3:241-254.
- Mortvedt, J. J., and P. M. Giordano. 1977. Crop uptake of heavy-metal contaminants in fertilizers, pp. 402-416. <u>In</u> H. Drucker and R. E. Wildung (chairmen), Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium, Richland, Washington, September 29-October 1, 1975. CONF-750929. ERDA Symposium Series 42. Technical Information Center, Energy Research and Development Administration.
- Mulford, F. R., and D. C. Martens. 1971. Response of alfalfa to boron in flyash. Soil Sci. Soc. Am. Proc. 35:296-300.
- National Research Council, Committee on Biologic Effects of Atmospheric Pollutants. 1972. Lead: Airborne Lead in Perspective. National Academy of Sciences, Washington, D. C. 330 pp.
- National Research Council, Committee on Biologic Effects of Atmospheric Pollutants. 1973. Manganese. National Academy of Sciences, Washington, D. C. 191 pp.
- Peck, T. R., et al. 1977. Personal communication (Argonomy Dept., University of Illinois, Urbana).
- Purves, D. 1972. Consequences of trace-element contamination of soils. Environ. Pollut. 3:17-24.
- Ragaini, R. C., H. R. Ralston, and H. Roberts. 1977. Environmental trace metal contamination in Kellogg, Idaho, near a lead smelting complex. Environ. Sci. Technol. 11:773-781.
- Rosenfeld, I., and O. A. Beath. 1964. Selenium: Geobotany, Biochemistry, Toxicity, and Nutrition. Academic Press, New York. 411 pp.
- Sherman, G. D. 1957. Manganese and soil fertility, pp. 135-139. <u>In</u> Soil, USDA Yearbook, 1957. [As cited in Labanauskas (1966).]

- Sidle, R. C., and W. E. Sopper. 1976. Cadmium distribution in forest ecosystems irrigated with treated municipal waste water and sludge. J. Environ. Qual. 5:419-422.
- Sidle, R. C., J. E. Hook, and L. T. Kardos. 1977. Accumulation of heavy metals in soils from extended wastewater irrigation. J. Water Pollut. Control Fed. 49:311-318.
- Sullivan, R. J. 1969a. Air Pollution Aspects of Arsenic and Its Compounds. Litton Systems, Inc., Bethesda, Md. 63 pp.
- Sullivan, R. J. 1969b. Air Pollution Aspects of Chromium and Its Compounds. Litton Systems, Inc., Bethesda, Md. 76 pp.
- Taylor, S. R. 1964. Abundance of chemical elements in the continental crust, a new table. Geochim. Cosmochim. Acta 28:1273. [As cited in Bowen (1966).]
- Turekian, K. K., and K. H. Wedepohl. 1961. Bull. Geol. Soc. Am. 72:175. [As cited in Bowen (1966).]
- Vallee, B. L., D. D. Ulmer, and W. E. C. Wacker. 1960. Arsenic toxicology and biochemistry. Arch. Ind. Health 21:132-151.
- Vinogradov, A. P. 1959. The Geochemistry of Rare and Dispersed Elements in Soils. Consultant Bureau, Inc., New York. [As cited in Yopp et al. (1974).]
- Walsh, L. M., M. E. Sumner, and R. B. Corey. 1976a. Consideration of soils for accepting plant nutrients and potentially toxic nonessential elements, pp. 22-47. In Land Application of Waste Materials. Soil Conservation Society of America, Ankeny, Iowa.
- Walsh, L. M., et al. 1976b. Application of Sewage Sludge to Cropland: Appraisal of Potential Hazards of the Heavy Metals to Plants and Animals. Report No. 64, Council for Agricultural Science and Technology, Iowa State University, Ames. Prepared for the U.S. Environmental Protection Agency, Office of Water Program Operations, Municipal Construction Division, Washington, D. C. MCD-33; EPA-430/9-76-013.
- Whitby, L. M., and T. C. Hutchinson. 1974. Heavy-metal pollution in the Sudbury mining and smelting region of Canada. II, Soil toxicity tests. Environ. Conserv. 1:191-200.
- Wood, C. W., Jr., and T. N. Nash III. 1976. Copper smelter effluent effects on Sonoran Desert vegetation. Ecology 57:1311-1316.
- Yopp, J. H., W. E. Schmid, and R. W. Holst. 1974. Determination of Maximum Permissible Levels of Selected Chemicals That Exert Toxic Effects on Plants of Economic Importance in Illinois. Document No. 74-33. Illinois Institute for Environmental Quality, Chicago.

Zimdahl, R. L., and J. H. Arvik. 1973. Lead in soils and plants: a literature review. CRC Crit. Rev. Environ. Control 3:213-224.

Zoller, W. H., G. E. Gordon, E. S. Gladney, and A. G. Jones. 1973. The sources and distribution of vanadium in the atmosphere, pp. 31-47. <u>In</u> E. L. Kothny (ed.), Trace Elements in the Environment. Adv. Chem. Ser. 123. American Chemical Society, Washington, D. C.

#### APPENDIX F. BEHAVIOR AND TOXICITY OF SELECTED TRACE ELEMENTS TO ADUATIC BIOTA

The following is a generic discussion of the behavior of selected trace elements in aquatic systems. The degree of toxicity of these elements is often dependent on the elemental valence. A toxicity table based on bioassay determinations for the selected elements is also included. Additional information on trace-element behavior and toxicity relative to power plant operation is available in Becker and Thatcher (1973).

# ARSENIC

Arsenic may be biologically concentrated through aquatic food chains; benthic algae, molluscs, crustacea, and fish can concentrate arsenic to levels 200, 650, 400, and 700 times as great as those in the environment, respectively (Braunstein et al. 1977). Freshwater organisms generally contain lower concentrations of arsenic than their marine counterparts; concentration ratios reported for saltwater fish range from 10 to 100 times higher than those reported for freshwater fish (Woolson 1975). In general, arsenic is toxic to aquatic organisms within the range of 1.0 to 45 mg/L arsenite (McKee and Wolf 1963). The arsenite ion is generally considered more toxic than arsenate (Ferguson and Gavis 1972; Braunstein et al. 1977).

#### CADMIUM

In a study by Mathis and Cummings (1973), benthic organisms appear to concentrate cadmium in higher concentrations than other aquatic organisms. Also, anadromous fish species appear to be quite sensitive to cadmium (Jones 1939). Model projections by Dvorak et al. (1977) indicate that cadmium enrichment potential in some basins appears to be considerable, particularly in the Northwest Region where large spawning runs of salmon and trout occur.

#### CHROMIUM

Chromium toxicity to aquatic organisms is dependent on several factors, particularly the ionic state, pH, and water hardness. Trivalent chromium often appears to be the ionic form most poisonous to fish. Fish may tolerate various chromium salts, but invertebrates are more sensitive to chromium salts (Becker and Thatcher 1973).

# COPPER

Toxicity of copper and copper sulfate to aquatic organisms varies considerably and is dependent on such factors as temperature, turbidity, water hardness, and the carbon dioxide content of the water. Cupric ions introduced to natural waters of pH 7 or above will quickly precipitate as copper hydroxide or as basic copper carbonate (Braunstein et al. 1977).

#### LEAD

Lead may be taken up by fish and aquatic invertebrates through the body surface (including the gills) or through ingestion of other organisms (Adams 1975). In aquatic systems, lead is readily complexed and poorly soluble (Lake Mich. Enforcement Conf. 1972). As most lead is found in bottom sediments (Warnick and Bell 1969), benthic communities may be adversely affected. Toxicity of lead to aquatic organisms generally occurs at concentrations greater than 0.01 mg/L.

#### MANGANESE

Freshwater invertebrates accumulate manganese (valence state unknown) in greater concentrations than their marine counterparts; however, marine fish accumulate manganese in greater concentrations than freshwater fish.

#### MERCURY

Methylmercury is very soluble in water and thus is readily accumulated by aquatic organisms and concentrated in tissues (Schmidt-Nielsen 1974). Organic mercurial compounds are more toxic to aquatic organisms than are inorganic mercurials, partly because of a more rapid uptake of organic mercurials (Braunstein et al. 1977). Mercury is poorly scavenged by current stack-gas cleaning equipment.

## NICKEL

Nickel compounds are only moderately toxic to aquatic organisms, and adverse impacts to aquatic systems resulting from coal combustion are probably small.

#### SELENIUM

Selenium has been shown to be carcinogenic and teratogenic, but it is antagonistic to the carcinogenic and teratogenic effects of cadmium and arsenic (Braunstein et al. 1977). Selenium compounds also have a protective effect against the toxic action of mercury compounds (Koeman et al. 1975). Selenium generally becomes tied-up in sediments of aquatic systems, and invertebrates tend to concentrate higher levels of selenium than fish.

# ZINC

Zinc is relatively toxic to fish and other aquatic organisms, and it may combine with copper or nickel to produce a synergistic toxic effect (Brown and Dalton 1970). Zinc sulfate is highly soluble in water and its degree of toxicity to aquatic organisms is dependent on the species involved as well as various chemical conditions of the water body. In addition, the toxicity of zinc in aquatic systems is strongly influenced by water hardness. Zinc emissions from coal-fired power plants may reach concentrations injurious to aquatic systems.

Organism	Element (mg/L)	Remarks <sup>b</sup>	Reference
	<u> </u>	Arsenic	
Aquatic organisms (general)	1.1-45.	Lethal, arsenite	Ferguson and Gavis (1972)
Daphnia magna	2.85	LC <sub>50</sub> , 3 weeks	Biesinger and Christensen (1972)
Daphnia magna	0.52	16% reproductive impairment	Biesinger and Christensen (1972)
Oncorhynchus gorbuscha	5.0	Lethal, 10 days	McKee and Wolf (1963)
Oncorhynchus keta	8.4	$LC_{50}$ , 48 hours	McKee and Wolf (1963)
Trout	7.6	Tolerated, 30 days	McKee and Wolf (1963)
Trout	5.0	Tolerated, 24 hours	McKee and Wolf (1963)
Alburnus alburnus	2.2	Lethal, 72 hours	McKee and Wolf (1963)
Alburnus alburnus	1.1-1.6	Tolerated, 11 days	McKee and Wolf (1963)
Cyprinus carpio	3.1	Lethal, 4-6 days	McKee and Wolf (1963)
Cyprinus carpio	2.2	Tolerated, 13 days	McKee and Wolf (1963)
Minnows	11.6	Lethal, 36 hours	McKee and Wolf (1963)
Minnows	60	Lethal, 16 hours	McKee and Wolf (1963)
Minnows	29	LC <sub>50</sub> , 48 hours	McKee and Wolf (1963)
Minnows	15	Tolerated, 96 hours	McKee and Wolf (1963)
Lucioperca sp.	1.1-2.2	Lethal, 48 hours	McKee and Wolf (1963)
Lucioperca sp.	0.7-1.1	Tolerated, 11 days	McKee and Wolf (1963)
		<u>Cadmium</u>	
Ephemerella subvaria (mayfly)	2.0	$LC_{50}$ , 96 hours	Warnick and Bell (1969)
Daphnia magna	0.005	LC <sub>50</sub> , 3 weeks	Biesinger and Christensen (1972)
Daphnia magna	0.0017	LC <sub>50</sub> , 3 weeks 16% reproductive impairment	Biesinger and Christensen (1972)
Eurypanopeus depressus (mud crab)	4.9	$LC_{50}$ , 72 hours	Collier et al. (1973)
Eurypanopeus depressus	11.0	LC <sub>100</sub>	Collier et al. (1973)
Pimephales promelas (fathead minnow)	0.029	LC <sub>50</sub> , 30 days	Pickering and Gast (1972)
Fish (general)	0.029-73.5	LC <sub>50</sub> , 96 hours	Eisler (1971)
Lepomis macrochirus	80	LC <sub>50</sub> , 11 months (adults)	Eaton (1974)
Lepomis macrochirus	1.94	LC <sub>50</sub> , 96 hours (fry)	Pickering and Gast (1972)
Lepomis cyanellus	2.84	LC <sub>50</sub> , 96 hours (fry)	Pickering and Henderson (1964)
Carassius auratus	2.34	LC <sub>50</sub> , 96 hours (fry)	Pickering and Henderson (1964)
Poecilia reticulata	1.27	LC <sub>50</sub> , 96 hours (fry)	Pickering and Henderson (1964)
Lepomis gibbosus	1.5	LC <sub>50</sub> , 96 hours (fry)	Rehwolt et al. (1972)
Cyprinus carpio	0.24	LC <sub>50</sub> , 96 hours (fry)	Rehwolt et al. (1972)

(continued)
Organism	Element (mg/L)	Remarks <sup>b</sup>	Reference
		<u>Cadmium</u> (contd.)	······································
Anguilla rostrata	0.82	$LC_{50}$ , 96 hours (fry)	Rehwolt et al. (1972)
Roccus americanus	8.4	LC <sub>50</sub> , 96 hours (fry)	Rehwolt et al. (1972)
Roccus saxatilis	1.1	LC <sub>50</sub> , 96 hours (fry)	Rehwolt et al. (1972)
Fundulus diaphanus	0.11	$LC_{50}$ , 96 hours (fry)	Rehwolt et al. (1972)
		Chromium	
Daphnia magna	<1.2	Threshold immobilization, 64 hours	Anderson (1950)
Daphnia magna	0.33	<pre>16% reproductive impairment,     3 weeks</pre>	Biesinger and Christensen (1972)
Daphnia magna	0.60	50% reproductive impairment, 3 weeks	Biesinger and Christensen (1972)
Acroneuria lycorias	32	LC <sub>50</sub> , 7 days	Warnick and Bell (1969)
Ephemerella subvaria	16	LC <sub>50</sub> , 96 hours	Warnick and Bell (1969)
Hydropsyche betteri	32	LC <sub>50</sub> , 7 days	Warnick and Bell (1969)
Hexagenia (nymphs)	8.6	Mortality, 96 hours	Winona State College (1970)
Lepomis macrochirus	71.9	$LC_{50}$ , 96 hours $Cr^{3+}$	Pickering and Henderson (1964)
Fathead minnow	64.7	LC <sub>50</sub> , 96 hours Cr <sup>3+</sup>	Pickering and Henderson (1964)
Fathead minnow	2.0	Reproductive impairment, 10 months	Pickering and Henderson (1964)
Carassius auratus	37.5	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Lebistes reticulatus	30.0	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Brook trout	0.40	Reproductive impairment, 2 years	Lake Mich. Enforcement Conf. (1972)
Brook trout	50.0	TL <sub>m</sub> , 96 hours	Lake Mich. Enforcement Conf. (1972)
Rainbow trout	0.40	Reproductive impairment, 2 years	Lake Mich. Enforcement Conf. (1972)
Rainbow trout	69.0	TL <sub>m</sub> , 96 hours	Lake Mich. Enforcement Conf. (1972)
Largemouth bass	195	TL <sub>m</sub> , 48 hours	Fromm and Schiffman (1958)
Largemouth bass	94	TL <sub>m</sub> , 80 hours	Fromm and Schiffman (1958)
		Copper	
Daphnia magna	0.022	LC <sub>50</sub> , 16% reproductive impairment, 3 weeks	Biesinger and Christensen (1972)

(1972)		
Biesinger an (1972)	nd Chi	ristensen
Warnick and	Bell	(1969)
		1

Warnick and Bell (1969)

(continued)

LC<sub>50</sub>, 96 hours

 $LC_{50}$ , 48 hours

0.035

8.3

0.32

Daphnia magna

Acroneuria lycomas

Ephemerella subvaria

 $LC_{50}$ , 50% reproductive impairment, 3 weeks

Organism	Element (mg/L)	Remarks <sup>b</sup>	Reference
		<u>Copper</u> (contd.)	
Hydropsyche betteri	32 <sup>-</sup>	LC <sub>50</sub> , 14 days	Warnick and Bell (1969)
Orconectes resticus	3	LC <sub>50</sub> , 96 hours	Hubschman (1967)
Campeloma decisum	1.7	LC <sub>50</sub> , 96 hours	Arthur and Leonard (1970)
Physa integra	0.039	LC <sub>50</sub> , 96 hours	Arthur and Leonard (1970)
Gammarus pseudolimnaeus	0.020	LC <sub>50</sub> , 96 hours	Arthur and Leonard (1970)
Pimephales promelas	0.023	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Pimephales promelas	0.018	Reproductive impairment, 10 months	Mount and Stephan (1969)
Pimephales promelas	0.075	LC <sub>50</sub> , 96 hours	Mount and Stephan (1969)
Lepomis macrochirus	0.66	$LC_{50}$ , 96 hours	Pickering and Henderson (1964)
Carassius auratus	0.036	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Lebistes reticulatus	0.036	$LC_{50}$ , 96 hours	Pickering and Henderson _(1964)
Salvelinus fontinalis	0.10	$LC_{50}$ , 96 hours	McKim and Benoit (1971)
Salvelinus fontinalis	0.03	43% survivial of adults, 8 months	McKim and Benoit (1971)
Ictalurus nebulosus	0.18	$LC_{50}$ , 96 hours	Brungs et al. (1973)
Sockeye and pink salmon	0.025	Mortality, retarded development	Martens et al. (1970)
Rainbow trout	0.037	Reduced egg and fry survival	McKim and Eaton (1972)
Steelhead	0.03	Fry mortality, 96 hours	Chapman (1972)
Lake trout	0.111	Reduced egg and fry survival	McKim and Eaton (1972)
Brown trout	0.037	Reduced egg and fry survival	McKim and Eaton (1972)
		Lead	
Daphnia magna	0.45	$LC_{50}$ , 48 hours	Biesinger and Christensen (1972)
Daphnia magna	1-0.3	LC <sub>50</sub> , 3 weeks	Biesinger and Christensen (1972)
Acroneuria lycorias	64.0	LC <sub>50</sub> , 14 days	Warnick and Bell (1969)
Ephemerella subvaria	16.0	LC <sub>50</sub> , 7 days	Warnick and Bell (1969)
Hydropsyche betteri	32.0	LC <sub>50</sub> , 7 days	Warnick and Bell (1969)
Pimephales promelas	5.6	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Lepomis macrochirus	23.8	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Carassius auratus	31.4	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Lebistes reticulatus	20.6	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Coho salmon	0.3	Fry mortality, 96 hours	Chapman (1972)
Chinook salmon	1.0	Fry mortality, 96 hours	Chapman (1972)

(continued)

Organism	Element (mg/L)	Remarks <sup>b</sup>	Reference
	· · · · · · · · · · · · · · · · · · ·	Lead (contd.)	
Steelhead	0.6	Fry mortality, 96 hours	Chapman (1972)
Brook trout	0.5	Fry mortality, 3 weeks	McKim and Eaton (1972)
Fathead minnow	5.58	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
		Manganese	
Daphnia magna	5.20	Reproductive impairment, 3 weeks	Lake Mich. Enforcement Conf. (1972)
Daphnia magna	5.7	LC <sub>50</sub> , 3 weeks	Lake Mich. Enforcement Conf. (1972)
Daphnia magna	4.1	<pre>16% reproductive impairment,     3 weeks</pre>	Lake Mich. Enforcement Conf. (1972)
Anguilla japonica	4.1	Lethal	Doudoroff and Katz (1953)
	•	Mercury	· · · · · · · · · · · · · · · · · · ·
Macrocystis pyrifera	50	50% reduction in photo- synthesis, 4 days	Nuzzi (1972)
Phytoplankton	100	Complete inactivation, 4 days	Nuzzi (1972)
Nitzschia delicatissima	0.1	Reduced growth and photo- synthesis	Nuzzi (1972)
Daphnia magna	0.13	LC <sub>50</sub> , 3 weeks	Biesinger and Christensen (1972)
Daphnia magna	6.7	50% reproductive impairment, 3 weeks	Biesinger and Christensen (1972)
Daphnia magna	3.4	10% reproductive impairment, 3 weeks	Biesinger and Christensen (1972)
Daphnia magna	5.0	$LC_{50}$ , 48 hours	Biesinger and Christensen (1972)
	¢	Nickel	
Daphnia magna	0.51	LC <sub>50</sub> , 48 hours	Biesinger and Christensen (1972)
Daphnia magna	0.13	50% reproductive impairment, 3 weeks	Biesinger and Christensen (1972)
Daphnia magna	0.03	<pre>16% reproductive impairment,     3 weeks</pre>	Biesinger and Christensen (1972)
Acroneuria lycorias	33.5	LC <sub>50</sub> , 96 hours	Warnick and Bell (1969)
Ephemerella subvaria	4.0	LC <sub>50</sub> , 96 hours	Warnick and Bell (1969)
Hydropsyche betteri	64.0	LC <sub>50</sub> , >14 days	Warnick and Bell (1969)
Pimephales promelas	4.58	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Lepomis macrochirus	5.18	LC <sub>50</sub> , 96 hours	Pickering and Henderson

(1964)

Table	F.1.	(Concluded)

Organism	Element (mg/L)	Remarks <sup>b</sup>	Reference
		Nickel (contd.)	
Carassius auratus	9.82	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Lebistes reticulatus	4.45	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Rainbow trout	32	$LC_{50}$ , 48 hours	Brown and Dalton (1970)
		Selenium	
Fathead minnows (fry)	2.9	LC <sub>50</sub> , 96 hours	Cardwell et al. (1976)
Bluegill juveniles	40.0	$LC_{50}$ , 96 hours	Cardwell et al. (1976)
		Zinc	
Selenastrum capricornutum	0.5	Not tolerated	Bartlett et al. (1974)
Daphnia magna	0.10	$LC_{50}$ , 48 hours	Biesinger and Christensen (1972)
Daphnia magna	0.158	LC <sub>50</sub> , 3 weeks	Biesinger and Christensen (1972)
Daphnia magna	0.07	<pre>16% reproductive impairment,     3 weeks</pre>	Biesinger and Christensen (1972)
Daphnia magna	0.102	50% reproductive impairment, 3 weeks	Biesinger and Christensen (1972)
Acroneuria lycorias	32	LC <sub>50</sub> , 14 days	Warnick and Bell (1969)
Ephemerella subvaria	16	LC <sub>50</sub> , 10 days	Warnick and Bell (1969)
Hydropsyche betteri	32	LC <sub>50</sub> , 11 days	Warnick and Bell (1969)
Pimephales promelas	0.96	$LC_{50}$ , 96 hours	Pickering and Henderson (1964)
Salmo gairdneri	0.5	LC <sub>50</sub> , 48 hours	Lloyd (1960)
Lepomis macrochirus	6.44	$LC_{50}$ , 96 hours	Pickering and Henderson (1964)
Carassius reticulatus	1.27	LC <sub>50</sub> , 96 hours	Pickering and Henderson (1964)
Coho salmon	0.14	Fry mortality, 96 hours	Chapman (1972)
Chinook salmon	0.30	Fry mortality, 96 hours	Chapman (1972)
Steelhead	0.30	Fry mortality, 96 hours	Chapman (1972)
Rainbow trout	4.6	LC <sub>50</sub> , 5 days	Ball (1967)

<sup>a</sup>Adapted from Dvorak et al. (1977). Common names and scientific names for the organisms are used exactly as they were given in the original references.  $^{\rm b}{
m LC}_{50}$  is the lethal concentration to 50% of a population.  ${
m LC}_{100}$  is the lethal concentration to 100% of a population. TL<sub>50</sub> is the tolerance limit for 50% of a population. TL<sub>m</sub> is the median tolerance limit.

- Adams, E. S. 1975. Effects of lead and hydrocarbons from snowmobile exhaust on brook trout (*Salvelinus fontinalis*). Trans. Am. Fish. Soc. 104(2):363-373.
- Anderson, B. G. 1950. The apparent thresholds of toxicity of Daphnia magna for chlorides of various metals when added to Lake Erie water. Trans. Am. Fish. Soc. 78:98-113.
- Arthur, J. W., and E. N. Leonard. 1970. Effects of copper on Gammarus pseudolimnaeus, Physa integra, and Campeloma decisum in soft water. J. Fish. Res. Board Can. 27:1277-1283.
- Ball, I. R. 1967. The relative susceptibilities of some species of freshwater fish to poisons. II, Zinc. Water Res. 1:777-783.
- Bartlett, L., F. W. Rabe, and W. H. Funk. 1974. Effects of copper, zinc, and cadmium on Selanastrum capricornutum. Water Res. 8:179-185.
- Becker, C. D., and T. O. Thatcher (eds.). 1973. Toxicity of Power Plant Chemicals to Aquatic Life. WASH-1249. Prepared by Battelle Pacific Northwest Laboratories, Richland, Wash., for the U.S. Atomic Energy Commission. 1 v. (various pagings).
- Biesinger, K. E., and G. M. Christensen. 1972. Effects of various metals on survival, growth, reproduction, and metabolism of *Daphnia magna*. J. Fish. Res. Board Can. 29:1691-1700.
- Braunstein, H. M., E. D. Copenhaver, and H. A. Pfuderer (eds.). 1977. Environmental, Health, and Control Aspects of Coal Conversion: An Information Overview. ORNL/EIS-95. Oak Ridge National Laboratory, Oak Ridge, Tennessee. v. 2.
- Brown, V. M., and R. A. Dalton. 1970. The acute lethal toxicity to rainbow trout of mixtures of copper, phenol, zinc and nickel. J. Fish. Biol. 2:211-216.
- Brungs, W. A., E. N. Leonard, and J. M. McKim. 1973. Acute and long-term accumulation of copper by the brown bullhead, *Ictalurus nebulosus*. J. Fish. Res. Board Can. 30:583-586.
- Cardwell, R. D., D. G. Foreman, T. R. Payne, and D. J. Wilbur. 1976. Acute toxicity of selenium dioxide to freshwater species. Arch. Environ. Contam. Toxicol. 4:129-144.
- Chapman, G. 1972. Unpublished data. [As cited in Lake Michigan Enforcement Conference (1972).]
- Collier, R. S., J. E. Miller, M. A. Dawson, and F. P. Thurberg. 1973. Physiological response of the mudcrab, *Eurypaneopeus depressus*, to cadium. Bull. Environ. Contam. Toxicol. 10:378-382.
- Doudoroff, P., and M. Katz. 1953. Critical review of literature on the toxicity of industrial wastes and their components to fish. II, The metals as salts. Sewage Ind. Wastes 25:802-839.
- Dvorak, A. J., et al. 1977. The Environmental Effects of Using Coal for Generating Electricity. NUREG-0252. Prepared for the U.S. Nuclear Regulatory Commission by Argonne National Laboratory, Argonne, Ill. 221 pp.
- Eaton, J. G. 1974. Chronic cadmium toxicity to the bluegill (Lepomis macrochirus Rafinesque). Trans. Am. Fish. Soc. 103:729-735.
- Eisler, R. 1971 Cadmium poisoning in *Fundulus heteroclitus* (Pisces: Cyprinodontidae) and other marine organisms. J. Fish. Res. Board Can. 28:1225-1234.
- Ferguson, J. F., and J. Gavis. 1972. A review of the arsenic cycle in natural waters. Water Res. 6:1259-1274.
- Fromm, P. O., and R. H. Schiffman. 1958. Toxic action of hexavalent chromium on largemouth bass. J. Wildl. Manage. 22(1):40.
- Hubschman, J. H. 1967. Effects of copper on the crayfish Orconectes rusticus (Girard). I, Acute toxicity. Crustaceana 12(L):33-42.
- Jones, J. R. E. 1939. The relation between the electrolytic solution pressures of the metals and other toxicity to the stickleback (*Gasterosteus aculeatus* L.). J. Exp. Biol. 16:425-437.
- Koeman, J. H., W. S. M. Van de Van, J. J. M. de Goeij, P. S. Tljoe, and J. L. Van Haaften. 1975. Mercury and selenium in marine mammals. Sci. Total Environ. 3:279-287.

- Lake Michigan Enforcement Conference, Interstate Pesticides Committee. 1972. Report of the Pesticide Technical Committee to the Lake Michigan Enforcement Conference on Selected Trace Metals. 87 pp.
- Lloyd, R. 1960. The toxicity of zinc sulphate to rainbow trout. Ann. Appl. Biol. 48:84-94.
- Martens, D. W., R. W. Gordon, and J. A. Servizi. 1970. Toxicity of Copper to Sockeye and Pink Salmon during Their Early Freshwater Life. Manuscript report. N. Westminster, B. C., Canada.
- Mathis, B. J., and T. F. Cummings. 1973. Selected metals in sediments, water, and biota in the Illinois River. J. Water Pollut. Control Fed. 45:1573-1583.
- McKee, J. E. and H. W. Wolf (eds.). 1963. Water Quality Criteria, 2nd ed. Publ. 3A. The Resources Agency of California, State Water Quality Control Board, Sacramento. 548 pp. (Reprint December 1971).
- McKim, J. M., and D. A. Benoit. 1971. Effect of long-term exposure to copper on survival, growth and reproduction of brook trout (*Salvelinus fontinalis*). J. Fish. Res. Board Can. 28:655-662.
- McKim, J. M., and J. G. Eaton. 1972. Unpublished data. [As cited in Lake Michigan Enforcement Conference (1972).]
- Mount, D. I., and C. E. Stephan. 1969. Chronic toxicity of copper to the fathead minnow (*Pimephales promelas*) in soft water. J. Fish. Res. Board Can. 26:2449-2457.
- Nuzzi, R. 1972. Toxicity of mercury to phytoplankton. Nature 237:38-40.
- Pickering, Q. H., and M. H. Gast. 1972. Acute and chronic toxicity of cadium to the fathead minnow (*Pimephales promelas*). J. Fish. Res. Board Can. 29:1099-1106.
- Pickering, Q. H., and C. Henderson. 1964. The acute toxicity of some heavy metals to different species of warm water fishes. Int. J. Air Water Pollut. 10:453-463.
- Rehwolt, T., L. W. Menapace, B. Nerrie, and D. Alessandrello. 1972. The effect of increased temperature upon the acute toxicity of some heavy metal ions. Bull. Environ. Contam. Toxicol. 8:91-96.
- Schmidt-Nielsen, B. 1974. Osmoregulation: effect of salinity and heavy metals. Fed. Proc. 33(5):2137-2146.
- Warnick, S. L., and H. L. Bell. 1969. The acute toxicity of some heavy metals to different species of aquatic insects. J. Water Pollut. Control Fed. 41(2):280-284.
- Winona State College. 1970. Mayfly Distribution as a Water Quality Index. Water Pollut. Control. Res. Series, USEPA 1630 DQH 11/70. 46 pp.
- Woolson, E. A. 1975. Bioaccumulation of arsenicals, pp. 97-107. <u>In</u> Arsenical Pesticides. Symposium sponsored by the Division of Pesticide Chemical Society, Atlantic City, N. J., 9 September 1974. ACS (Am. Chem. Soc.) Symp. Ser. 7.

# APPENDIX G. SOIL CLASSIFICATION

"Soil" is a thin layer of unconsolidated, largely mineral, material on the surface of the earth that has evidence of biological activity. The formation of a soil from its parent material is influenced mainly by (1) climate, particularly temperature and precipitation, (2) nature of the parent material, (3) topography of the area, (4) living matter, particularly native vegetation, and (5) time. The soils of the world have been classified into several systems, of which the Comprehensive Soil Survey System (otherwise known as the 7th Approximation) has been used in the United States since about 1968. Under this system, 10 soil "Orders" are recognized.

The classification of a given soil into an order depends on the soil having particular properties of its horizons. Soil "horizons" are zones or layers within a soil that result from soil-forming processes. Such "diagnostic horizons" are briefly described in Table G.1.

Diagnostic horizon	Major features		
Surface horizons (Epipedons)	·		
Mollic	Thick, dark colored, high base saturation, strong structure		
Umbric	Same as Mollic except low base saturation		
Ochric	Light colored, low organic content, may be hard and massive when dry		
Histic	Very high in organic content, wet during some part of the year		
Subsurface horizons			
Argillic	Accumulation of silicate clay		
Natric	Argillic, high in sodium, columnar or prismatic structure		
Spodic	Organic matter, iron and aluminum oxides accumulations		
Cambic	Changed or altered by physical movement or by chemical reactions		
Agric	Organic and clay accumulation just below plow layer		
Oxic	Primarily mixture of iron and aluminum oxides, and kaolinitic- type clay minerals		

# Table G.1. Diagnostic Soil Horizons

#### SOIL ORDERS

The following section is modified from the description in Brady (1974).

# Entisols

Entisols (or recent soils) are mineral soils without natural genetic horizons or with only the beginnings of such horizons. These soils include highly productive soils on recent alluvium and infertile soils on barren sands, as well as shallow soils on bedrock. These soils are found under a wide variety of climatic conditions.

# Vertisols

Vertisols are mineral soils that have a high content of clays which markedly swell, in dry seasons, causing the soils to develop deep, wide cracks. Due to excessive shrinking, swelling, cracking, and shearing, these soils cause difficulties if used for building foundations, highways, and agriculture. In the United States, areas of these soils occur in eastern Mississippi, western Alabama, the southeastern coast of Texas, and east central and southern Texas.

## Inceptisols

Inceptisols are soils whose profiles contain horizons that are thought to have formed rather quickly from alteration of the parent material. There are no horizons of marked accumulation of clay, and iron and aluminum oxides. The natural productivity of Inceptisols is variable; those of the Pacific Northwest are quite fertile (wheat lands), whereas in southern New York and northern Pennsylvania they are not naturally productive.

# Aridisols

Aridisols are mineral soils found mostly in dry climates, and are dry throughout most of the year except where there is irrigation or shallow groundwater. These soils have not been subjected to extensive leaching, and are generally light in color and low in organic matter. These soils may have a horizon of calcium carbonate, gypsum, or soluble-salt accumulation. In the United States, large areas of Aridisols occur in the southern parts of California, Nevada, Arizona, and central New Mexico. Without irrigation, these soils have low productivity and are used for grazing sheep; with irrigation, these soils can be made among the most productive.

## Mollisols

Mollisols are soils having a thick, dark surface horizon, dominated by divalent cations. The surface horizons usually have a granular or crumb structure and are not hard when dry. Most of these soils have developed under prairie vegetation, although there are some forest soils within this classification. Mollisols have high natural fertility, and are among the world's most productive soils. In the United States, mollisols are dominant in the Great Plains states; sizeable areas also occur in Idaho, Utah, Washington, and Oregon.

#### Spodosols

Spodosols are mineral soils which have spodic horizons. These soils form mostly on coarsetextured, acid parent material subject to leaching. These soils occur only in humid climates, usually under forest vegetation.

#### Alfisols

Alfisols are moist mineral soils that have gray to brown surface horizons, medium to high base status, and a horizon in which silicate clays have accumulated. These soils do not have a mollic epipedon, or oxic or spodic horizons. They are formed mainly in humid regions under native deciduous forests, and are, in general, quite productive.

## Ultisols

Ultisols are usually moist soils developed under warm to tropical climates. These soils are highly weathered and acidic, with argillic horizons. They form normally under forest vegetation, although their formation under savannah or swamp vegetation is common. Most of the soils of the southeastern United States belong to this order; other areas of the United States that contain these soils are Hawaii, California, Oregon, and Washington. These soils are not as naturally fertile as Alfisols or Mollisols, but they respond well to good management.

## <u>Oxisols</u>

Oxisols are the most highly weathered soils. They have a deep oxic horizon. Intense leaching has removed most of the silica from the silicate minerals in this horizon, leaving a high proportion of iron and aluminum oxides. These soils are not known to occur in the continental United States.

## Histosols

Histosols are organic soils (bog and half-bog soils) that have developed in a watersaturated environment. These soils contain a minimum of 20% organic matter if the clay content is low, and 30% organic matter if the clay content is > 50%. These soils, when drained and cultivated, are among the most productive, especially for vegetable crops.

# Subcategories of Soil Orders

Soil orders are divided further into smaller categories, as follows (in increasing degree of specificity):

Soil order

Suborder

Great group

Subgroup

Family

Series

A complete description of this system of classification, along with diagnostic criteria, can be found in "Soil Taxonomy" (U.S. Dep. Agric. Soil Conserv. Serv. 1975).

A general soil map of the United States, delineating soil orders and suborders, can be found in the "National Atlas" (U.S. Geol. Surv. 1970).

## REFERENCES

Brady, N. C. 1974. The Nature and Properties of Soils, 8th ed. Macmillan Publishing Co., Inc., New York. 639 pp.

- U.S. Department of Agriculture, Soil Conservation Service, Soil Survey Staff. 1975. Soil Taxonomy. Agriculture Handbook No. 436. U.S. Government Printing Office, Washington, D.C. 754 pp.
- U.S. Geological Survey. 1970. National Atlas of the United States of America. Washington, D.C. 417 pp.

# CREDITS

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# Figure

4

Babcock and Wilcox Co. 1972. Steam, Its Generation and Use, 38th ed. Copyright 1972 by The Babcock and Wilcox Company. Figure 4 reprinted with permission of the Babcock and Wilcox Co., New York. p. 8-16 (Fig. 19).

Ottmers, D. M., Jr., P. S. Lowell, and J. G. Noblett. 1975. Energy and water requirements for air quality control, pp. 358-370. <u>In</u> E. F. Gloyna, H. H. Woodson, and H. R. Drew (eds.), Water Management by the Electric Power Industry. Water Resources Symposium No. 8, Center for Research in Water Resources, The University of Texas at Austin. Figures 5, 6, 7, and 8 reprinted with permission of the Center for Research in Water Resources.

- 5 p. 363 (Fig. 1). 6 p. 363 (Fig. 2). 7 p. 365 (Fig. 3). 8 p. 365 (Fig. 4).
- 9 Cooper, H. B. 1975. The ultimate disposal of ash and other solids from electric power generation, pp. 183-195. In E. F. Gloyna, H. H. Woodson, and H. R. Drew (eds.), Water Management by the Electric Power Industry. Water Resources Symposium No. 8, Center for Research in Water Resources, The University of Texas at Austin. Figure 9 reprinted with permission of the Center for Research in Water Resources. p. 190 (Fig. 4).

American Society of Mechanical Engineers. 1973. Recommended Guide for the Prediction of the Dispersion of Airborne Effluents, 2nd ed. Copyright 1973 by the American Society of Mechanical Engineers. Figures 10 and 11 reprinted with permission of the American Society of Mechanical Engineers, New York.

- 10 p. 30 (Fig. 11-15).
- 11 p. 31 (Fig. 11-16).

Strom, G. H. 1976. Transport and diffusion of stack effluents, pp. 401-501. <u>In</u> A. C. Stern (ed.), Air Pollution, 3rd ed. Copyright 1976 by Academic Press, Inc. Figures 13 and 14 reprinted with permission of Academic Press, Inc., New York.

- 13 p. 406 (Fig. 1 top half).
- 14 p. 406 (Fig. 1 bottom half).
- 19 Brady, N. C. 1974. The Nature and Properties of Soils, 8th ed. Copyright 1974, Macmillian Publishing Co., Inc. Figure 19 reprinted with permission of Macmillian Publishing Co., New York. p. 52 (Fig. 3.8).
- 20 Stumm, W., and H. Bilinski. 1973. Trace metals in natural waters; difficulties of interpretation arising from our ignorance of their speciation. Adv. Water Pollut. Res. 6:39-52. Figure 20 reprinted with permission of Pergamon Press, Inc., Elmsford, N. Y. p. 40 (Fig. 1).

Guthrie, R. K., and D. S. Cherry. 1976. Pollutant removal from coal-ash basin effluent. Water Resour. Bull. 12(5):889-902. Figures 21, 22, and 23 reprinted with permission of the American Water Resources Association, Minneapolis, Minnesota.

- 21 p. 896 (Fig. 2).
- 22 p. 897 (Fig. 3).
- 23 p. 898 (Fig. 4).
- 26 DiGioia, A. M., Jr., J. F. Meyers, and J. E. Niece. 1977. Design and construction of bituminous fly ash disposal sites, pp. 267-284. <u>In</u> Geotechnical Practice for Disposal of Solid Waste Materials. ASCE Specialty Conference of the Geotechnical Engineering Division, American Society of Civil Engineers. Figure 26 reprinted with permission of the American Society of Civil Engineers. p. 284 (Fig. 9).

Kubota, J., and W. H. Allaway. 1973. Geographic distribution of trace element problems, pp. 525-554. In Micronutrients in Agriculture. Soil Science Society of America, Inc. Figures E.1, E.4, and E.5 reprinted with permission of the Soil Science Society of America, Inc., Madison, Wisconsin.

- E.1 p. 530 (Fig. 1).
- E.4 p. 538 (Fig. 3).
- E.5 p. 542 (Fig. 4).

Hodgson, J. R., W. H. Allaway, and R. B. Lockman. 1971. Regional plant chemistry as a reflection of environment, pp. 55-72. <u>In</u> H. L. Cannon and H. C. Hopps (eds.). Environmental Geochemistry in Health and Disease. Geol. Soc. Am. Memoir 123. Figures E.2 and E.7 reprinted with permission of the Geological Society of America, Boulder, Colorado.

- E.2 p. 66 (Fig. 3).
- E.7 p. 66 (Fig. 4).
- E.3 Figure E.3 provided courtesy of Dr. J. Kubota, Soil Conservation Service, U.S. Plant, Soil and Nutrition Laboratory, Cornell University, Ithaca, New York.
- E.6 Rosenfeld, I., and O. A. Beath. 1964. Selenium: Geobotany, Biochemistry, Toxicity, and Nutrition. Copyright 1964 by Academic Press, Inc. Figure E.6 reprinted with permission of Academic Press, Inc., New York. p. 10 (Fig. 2).



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