University of Alaska

# **Coastal Marine Institute**



# **Annual Report No. 4**

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**OCS Study MMS 98-0005** 

#### **OCS Study MMS 98-0005**

# **University of Alaska Coastal Marine Institute**

In Cooperation: Minerals Management Service University of Alaska Fairbanks State of Alaska

#### **Annual Report**

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Submitted by Vera Alexander Director, UA CMI

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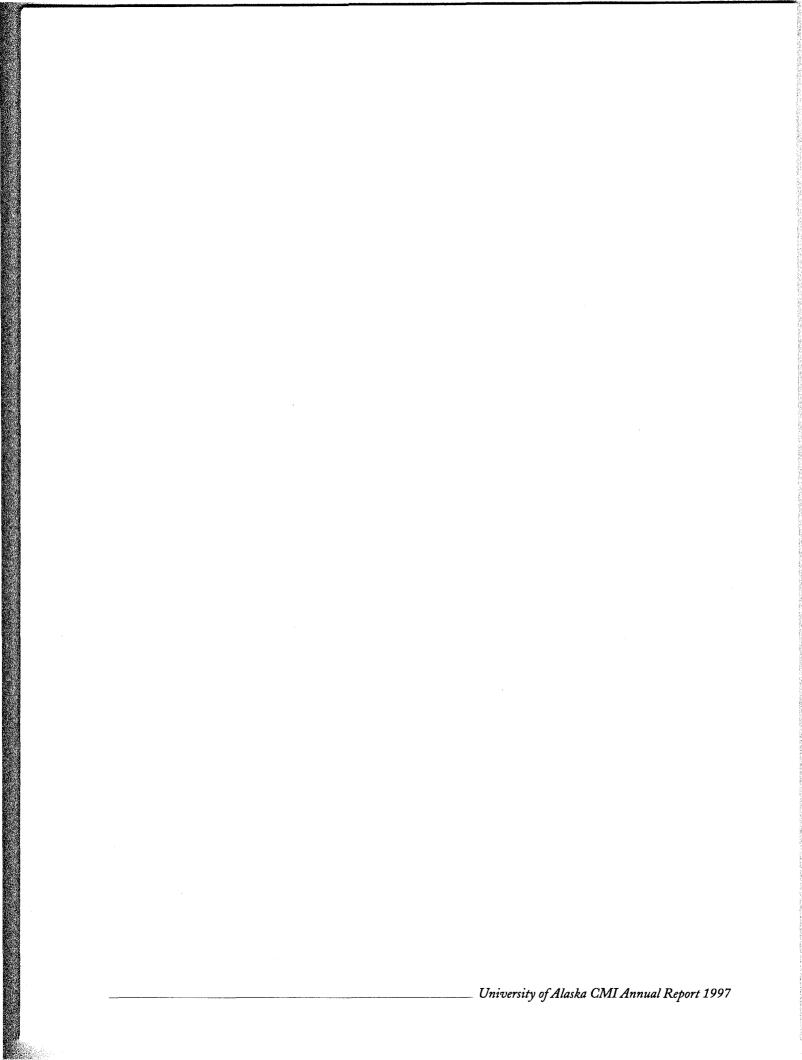


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#### Introduction

The University of Alaska Coastal Marine Institute (CMI) was created by a cooperative agreement between the University of Alaska and the Minerals Management Service (MMS) in June 1993 and the first full funding cycle began late in (federal) fiscal year 1994. CMI is pleased to present this 1997 Annual Report. Of the twelve research projects included in this Annual Report, eight are scheduled to end this federal fiscal year or in the first quarter of the next one. Only abstracts and study products for those projects are included here, as principal investigators are preparing their final reports which will be available soon. An additional five research projects were begun this year. Abstracts for these projects are included in the section titled "New Projects."

MMS administers the outer continental shelf (OCS) natural gas, oil, and marine minerals program in which it oversees the safe and environmentally sound leasing, exploration, and production of these resources within our nation's offshore areas. The Environmental Studies Program (ESP) was formally directed in 1978, under Section 20 of the OCS Lands Act Amendments, to provide information in support of the decisions involved in the planning, leasing, and management of exploration, development, and production activities. The research agenda is driven by the identification of specific issues, concerns, or data gaps by federal decision-makers and the state and local governments who participate in the process. ESP research focuses on the following broad issues associated with development of OCS gas, oil, and minerals:

What are the fates and effects of potential OCS-related pollutants (e.g., oil, noise, drilling muds and cuttings, products of fuel combustion) in the marine and coastal environment and the atmosphere?

What biological resources (such as fish populations) exist and which resources are at risk? What is the nature and extent of the risk? What measures must be taken to allow extraction to take place?

How do OCS activities affect people in terms of jobs and the economy? What are the direct and indirect effects on local culture? What are the psychological effects of the proposed OCS activities?

Because MMS and individual states have distinct but complementary roles in the decision-making process, reliable scientific information is needed by MMS, the state, and localities potentially affected by OCS operations. In light of this, MMS

has developed a locally managed CMI program. Under this program, MMS takes advantage of highly qualified, scientific expertise at local levels in order to:

- 1) Collect and disseminate environmental information needed for OCS oil and gas and marine minerals decisions;
- 2) Address local and regional OCS-related environmental and resource issues of mutual interest; and
- 3) Strengthen the partnership between MMS and the state in addressing OCS oil and gas and marine minerals information needs.

CMI is administered by the University of Alaska Fairbanks School of Fisheries and Ocean Sciences to address some of these mutual concerns and share the cost of research. Alaska was selected as the location for this CMI because it contains some of the major potential offshore oil and gas producing areas in the United States. The University of Alaska Fairbanks is uniquely suited to participate by virtue of its flagship status within the state and its nationally recognized marine and coastal expertise relevant to the broad range of OCS program information needs. In addition, MMS and the University of Alaska have worked cooperatively on ESP studies for many years. Research projects funded by CMI are required to have at least one active University of Alaska investigator. Cooperative research between the University of Alaska and state agency scientists is encouraged.

Framework Issues were developed during the formation of CMI to identify and bracket the concerns to be addressed:

- 1) Studies to improve understanding of the affected marine, coastal, or human environment;
- 2) Modeling studies of environmental, social, and economic processes in order to improve predictive capabilities and define information needs;
- 3) Experimental studies to improve understanding of environmental processes and/or the causes and effects of OCS activities;
- 4) Projects which design or establish mechanisms or protocols for the sharing of data or information regarding marine or coastal resources or human activities to support prudent management of oil and gas and marine mineral resources; and
- 5) Synthesis studies of background information.

Projects funded through CMI are directed towards providing information which can be used by MMS and the state for management decisions specifically relevant to MMS mission responsibilities. Projects must be pertinent to either the OCS oil and gas program or the marine minerals mining program. They should provide useful information for program management or for the scientific understanding of the potential environmental effects of resource development activities in arctic and subarctic environments.

Initial guidelines given to prospective researchers identified the Cook Inlet and Shelikof Strait areas as well as the Beaufort and Chukchi seas as areas of primary concern to MMS and the state. Primary emphasis has subsequently shifted to the Beaufort Sea, and to the Chukchi Sea as it relates to the Beaufort Sea. However, a strong interest remains with Cook Inlet and Shelikof Strait.

The proposal process is initiated each summer with a request for letters of intent to address one or more of the Framework Issues. This request is sent to researchers at the University of Alaska and to various state agencies. The CMI technical steering committee then decides which of the proposed letters of intent should be developed into proposals for more detailed evaluation and possible funding.

Successful investigators are strongly encouraged to publish their results in peer-reviewed journals as well as to present them at national meetings. In addition, some investigators present information directly to the public and MMS staff in seminars.

Alaskans benefit from the examination and increased understanding of those processes unique to Alaskan OCS and coastal waters because this enhanced understanding can be applied to other problems besides oil, gas, and mineral extraction, such as subsistence fisheries and northern shipping.

Many of the CMI-funded projects address some combination of issues related to fisheries, biomonitoring, physical oceanography, and the fates of oil. The ultimate intent of CMI-related research is to identify the ways in which OCS-related activities may affect our environment. Even though work funded to date is primarily related to the physical world, the intent of CMI is to also include studies of the potential economic and social impacts as well.

The CMI project reports have been placed in alphabetic order by lead author. Abstracts for new projects and an overall funding summary follow the reports.

## Microbial Degradation of Aromatic Hydrocarbons in Marine Sediments

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#### **Abstract**

Microbial degradation of petroleum hydrocarbons is a major mechanism for the removal of oil from the environment, yet there are conflicting data regarding how adsorption affects both the rate and extent of biodegradation of hydrocarbon fractions. Polycyclic aromatic hydrocarbons (PAHs) are of significant concern because of their relatively high toxicity. This study focused on the bioavailability in sediment slurries of the aromatic hydrocarbons phenanthrene and naphthalene. Populations of phenanthrene degraders were found to be present in low numbers in sediments collected in Lower Cook Inlet, Alaska. In abiotic experiments, both phenanthrene and naphthalene became more resistant to chemical extraction with time and with increasing organic carbon content. In bioassays, the percent phenanthrene or naphthalene mineralized decreased with increasing sediment concentration and with increasing sediment organic carbon. While organic carbon content explained most of the differences among sediments seen in the mineralization of these aromatic hydrocarbons, some of the variability observed could not be explained by this study. Sediments aged abiotically for 30 days with phenanthrene showed lowered mineralization rates in bioassays. However, the mean mineralization rate for phenanthrene (in both unaged and aged experiments) was greater than that predicted from sediment-free controls, implying utilization of sorbed substrate. In contrast, the mean mineralization rate for naphthalene was less than that predicted from sediment-free controls, implying that some of the naphthalene extracted in abiotic experiments was biologically unavailable. The organic carbon content of the sediment appeared to control strongly the adsorption of these aromatic hydrocarbons and, therefore, their bioavailability. Because the population size of naturally occurring aromatic hydrocarbon degraders is low and because bioavailability generally decreased in the presence of sediment, especially in sediments with a high content of organic carbon compounds, we predict that if oil spills occur in Lower Cook Inlet these compounds are likely to persist for a long period of time.

#### **Student Support**

One M. S. student (Zachary Richter) was supported by this project in 1996.

#### **Study Products**

- Braddock, J. F. 1995. Microbial degradation of aromatic hydrocarbons in marine sediments. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1995, Fairbanks.
- Braddock, J. F. 1996. Microbial degradation of aromatic hydrocarbons in marine sediments. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1996, Fairbanks.
- Braddock, J. F. 1997. Microbial degradation of aromatic hydrocarbons in marine sediments. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1997, Fairbanks.
- Braddock, J. F. and Z. D. Richter. 1995. Microbial degradation of aromatic hydrocarbons in marine sediments. Pages 4 14 *In* V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 2, OCS Study MMS 95-0057. Fairbanks. 122 pp.
- Braddock, J. F. and Z. D. Richter. 1997. Microbial degradation of aromatic hydrocarbons in marine sediments. Pages 5 24 *In* V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 3, OCS Study MMS 97-001. Fairbanks. 191 pp.
- Richter, Z. D. 1996. Bioavailability of phenanthrene in marine intertidal sediment. M. S. Thesis, University of Northern Iowa, Cedar Falls, Iowa.
- Richter, Z. D. and J. F. Braddock. 1995. Bioavailability of phenanthrene in marine intertidal sediments. Page 219 In Abstracts of the 46th Arctic Division of the American Association for the Advancement of Science Conference, Fairbanks, Alaska.
- Richter, Z. D., E. J. Brown and J. F. Braddock. 1996. Bioavailability of phenanthrene in marine intertidal sediment slurries. Page 446 In Abstracts of the 96th General Meeting of the American Society for Microbiology, New Orleans, Louisiana.

# The Alaskan Frozen Tissue Collection and Associated Electronic Database: A Resource for Marine Biotechnology

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#### **Abstract**

The Alaska Frozen Tissue Collection (AFTC) at the University of Alaska Museum in Fairbanks is the primary regional archive for frozen zoological samples and a major source of material for biotechnology studies of the North Pacific and Arctic oceans. It has become the world's third largest collection of frozen tissues of wild mammals and is making excellent progress on one of AFTC's primary goals: to expand the scope of the Collection by recruiting contributions of marine mammal, bird, fish, and invertebrate specimens from throughout the North Pacific and Arctic oceans.

Between 15 May 1996 and 15 May 1997, the AFTC accessioned tissues from 530 marine mammals representing 24 species, as well as fish and marine invertebrate samples (Figure 1). A total of 32 frozen tissue loans representing 576 individual animals were made to ongoing research projects. Cooperative agreements were developed or continued with individual collectors and organizations, including the North Slope Borough, the Alaska Marine Mammal Tissue Archival Project (AMMTAP), and an ongoing Alaska Department of Fish and Game (ADF&G) Subsistence seal harvest project. We also incorporated a collection of dried and preserved specimens of approximately 5,000 seals from more than three decades of field work by ADF&G. This collection includes samples from throughout Alaska's waters, primarily of six species, and is the largest collection of these species worldwide.

Table 1. Marine mammals accessioned into the AFTC from 15 May 1996 to 15 May 1997.

Number	Common Name	Species
2	Cuvier's beaked whale	Ziphius cavirostris
2	Stejneger's beaked whale	Mesoplodon stejnegeri
2	pygmy sperm whale	Kogia breviceps
65	bowhead whale	Balaena mysticetus
3	minke whale	Balaenoptera acutorostrata
1	humpback whale	Megaptera novaeangliae
2	gray whale	Eschrichtius robustus
3	beluga whale	Delphinapterus leucas
1	rough-toothed dolphin	Steno bredanensis
3	Pacific white-sided dolphin	Lagenorhynchus obliquidens
70	northern right-whale dolphin	Lissodelphis borealis
8	striped dolphin	Stenella coeruleoalba
10	white whale	Delphinapterus leucas
1	harbor porpoise	Phocoena phocoena
52	Dall's porpoise	Phocoenoides dalli
70	white-bellied porpoise	Delphinus delphis
24	walrus	Odobenus rosmarus
16	northern fur seal	Callorhinus ursinus
23	Steller sea lion	Eumetopias jubatus
1	northern elephant seal	Mirounga angustirostris
144	hair seals	Phoca sp (vitulina, largha, fasciata, hispid
2	Weddell seal	Leptonychotes weddellii
25	polar bear	Ursus maritimus
530	Total number of marine mamm	als accessioned

#### Introduction

In its second year of support from the University of Alaska Coastal Marine Institute (CMI), the AFTC continued to develop as the primary regional archive for frozen zoological samples and as an inexpensive source of cryogenic tissues for researchers, present and future. Archives such as museum collections are crucial to the study of ecological change because few agencies gather or archive specimens, and while most environmental assessment projects are relatively short-term, significant environmental change is usually long-term. Many projects generate unique and important samples, frequently at tremendous expense, but these are often destroyed or lost after fulfilling their primary function. The AFTC provides a mechanism to ensure that this material is available to the general scientific community in perpetuity.

Recent uses of the AFTC have demonstrated several ways in which new technology can increase the utility of frozen specimens for monitoring long-term trends in marine organisms and, particularly when higher trophic level animals are examined, in the marine environment.

Frozen tissues can be used for genetic investigations. Gene sequences of divergent taxa are becoming crucial to studies of functional biochemistry and physiology, and they are now basic to defining and managing natural populations. Investigations using these techniques provide insight into social systems (Burke, 1989), effective population size (Lande and Barrowclough, 1987), and the effects of inbreeding and outbreeding depression (O'Brien et al., 1985; Ralls et al., 1988). DNA sequencing has eclipsed much of the stock-delimiting work formerly done by electrophoresis of allelic proteins (Moritz, 1994). Improvements in sequencing technology are yielding more data per sample at lower cost and streamlining the processing of larger sample sizes.

Frozen tissue collections are important in studies of epidemiology in wild populations. Crises in the marine environment such as the canine distemper epidemic in North Atlantic grey and harbor seals (Dickson, 1988) suggest that we should build a baseline of tissue samples for Alaskan marine organisms. Hundreds of AFTC samples have been used in three projects screening for hantavirus and babesiosis in Alaskan rodents.

Both frozen samples and samples from standard dry museum specimens are being used to examine carbon and other stable-isotope signatures in several marine species (D. Schell, Institute of Marine Science [IMS], University of Alaska Fairbanks [UAF]); J. Burton, University of Wisconsin; M. Ben-David, Institute of Arctic Biology, UAF). Frozen tissues can also be analyzed for indicators of environmental toxicity (McBee and Bickham, 1990) particularly when tissues from high trophic level organisms are archived. Samples are particularly significant when they represent pre-disturbance, baseline conditions.

In order to provide tissues for such research, it is essential that the AFTC continue to develop and maintain a broad coverage of Alaskan marine organisms. In a state as large as Alaska, this can be done only by coordinating the efforts of potential collectors of samples and by maintaining a resource that is easily accessible to the research community.

#### **Results: Collection Development and Collaborative Projects**

#### **National Marine Mammal Laboratory**

The National Marine Mammal Laboratory (NMML) in Seattle is the agency responsible for managing most marine mammals in Alaska. In the course of their many projects over the past several decades, they have accumulated parts of well over a thousand marine mammals in their large freezers. However, as in many

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agencies not specifically charged with archival functions, development of a system that provides perpetual access to the material has been problematic. With limited resources, it is difficult for agencies to invest in archiving large numbers of specimens. In the past year, we have worked with NMML to subsample and archive selected specimens.

Amy Runck returned in early February from ten days of sampling at NMML with 238 marine mammal tissue samples, including several species new to the AFTC, e.g., northern right-whale dolphin (*Lissodelphis borealis*), Pacific white-sided dolphin (*Lagenorhynchus obliquidens*), and gray whale (*Eschrichtius robustus*). Working with NMML's Jack Cesarone, she assisted in organizing and cataloging a significant portion of the NMML collection. We estimate that portions of 1,100 animals are in their freezers. We expect that this should continue to be an active and productive collaboration.

The National Marine Fisheries Service (NMFS) provided a clear example of how the AFTC can benefit agency operations. Last year we fulfilled a request from NMFS' Southwest Fisheries Science Center for tissue from Stejneger's beaked whale (*Mesoplodon stejnegeri*) for identification purposes in a study of incidental take of marine mammals in fisheries. NMML had two specimens in its freezers but the Southwest Center did not know of their existence.

#### Alaska Department of Fish and Game

In 1996-67, an historically important body of dried and preserved marine mammal specimens was brought into the Collection using CMI support. Last summer, Dr. Ted Miller, a marine mammalogist, marine ornithologist, and museum curator from the Memorial University of Newfoundland, came to Fairbanks to study seal bacula at the University of Alaska Museum. He knew from his own prior work with the Outer Continental Shelf Environmental Assessment Project (OCSEAP) that many more seal bacula had been collected than were cataloged in the Museum. His inquiries revealed that a substantial cache of OCSEAP specimens, as well as specimens collected by ADF&G Subsistence monitoring projects, was stored at the Fairbanks office of ADF&G. Biologists Lloyd Lowry and John Burns agreed to archive specimens at the Museum.

The accession contains about 7,500 pieces from at least 5,000 animals collected over a span of more than three decades from all coastal regions of Alaska. Included are ringed seals, harbor seals, spotted seals, ribbon seals, bearded seals, and walruses. About 440 bacula, 800 mandibles, 100 embryos, 3,500 claws, 2,500 teeth, and 25 skulls comprised the accession. A related accession includes approximately 300 hyoid bones prepared by Dr. Francis H. Fay for a study he did not live to complete. The bones are mostly from his own OCSEAP work, and match parts of the huge ADF&G accession. In addition, John Burns provided more than 300 seal skulls collected during his career as a marine mammal

biologist with ADF&G. All of this material was accessioned in 1996; much of it is directly related to specimens already in the Museum.

These pinniped specimens may be critical to long-term studies which require large samples in both time and space. One example of this is continued analysis of the changing stable-isotope signatures at different trophic levels in the Bering Sea (Schell, 1996). Material is now available from as far back as 1932, and is available in quantity for every year from 1957 through the mid-1980s. Figure 1 shows the extent to which this accession enhanced the previous chronological sample for just one of the six main species.

CMI funding allowed Amy Runck to catalog this accession. (She also provided 150 hours of volunteer effort to the project, and Dani DeViche volunteered more than 300 hours.) Several hundred pieces came from seals that were already cataloged in the Mammal Collection in the late 1970s, which greatly complicated the task of cataloging the accession. Ms. Runck had worked extensively with OCSEAP specimens as an undergraduate assistant in the Mammal Collection from 1992 to 1994 and was uniquely suited for this large and complex task of cross-referencing.

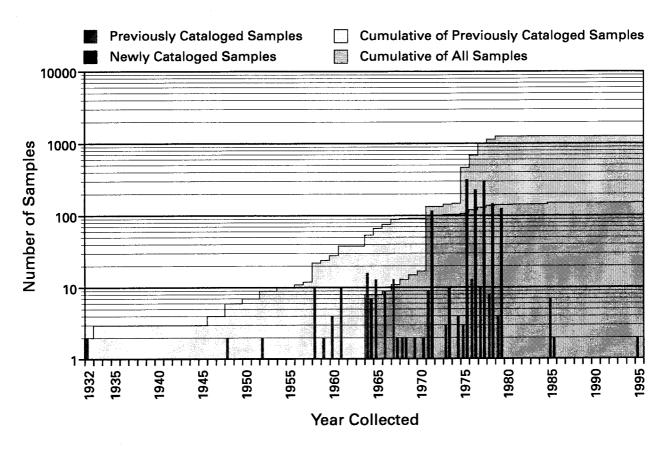


Figure 1. Number of bearded seal specimens (*Erignathus barbatus*) in the University of Alaska Mammal Collection by year of collection. The total number of specimens is 1,376 as of 15 May 1997. Note log scale.

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Some of the samples are voucher specimens for frozen tissues already in the AFTC and approximately 800 are parts from animals that were already cataloged as skulls in the Mammal Collection. To date, 3,764 specimens represent new individuals. We are awaiting data for the walrus specimens, but otherwise the cataloging of these accessions is nearly complete.

#### Alaska Department of Fish and Game Subsistence Project

Subsistence hunters cooperating with ADF&G (Fall et al., 1997) provided harbor and spotted seal tissues and skulls from 140 animals this past year. Archiving tissue samples in the AFTC has become standard operating procedure for marine mammal projects in Alaska, and the subsistence project now uses the AFTC catalog number as their own specimen tracking number.

We received whole frozen heads and organ tissue samples directly from ADF&G Subsistence biologists and immediately provided samples to projects in the laboratories of Dr. Michael Castellini and Dr. Don Schell. Frozen organ tissues were archived in the AFTC, and the skulls were cleaned and cataloged in the Mammal Collection.

#### **Alaska Marine Mammal Tissue Archival Project**

We received tissue samples from two polar bears and seven bowhead whales from AMMTAP.

#### **Other Contributors**

Additional accessions to the AFTC and Mammal Collection this year included tissues from 18 walruses provided by Joel Miller (Marine Mammal Management, U.S. Fish and Wildlife Service [USF&WS], Anchorage), 21 polar bears and 6 walruses from the Alaska Science Center (Biological Resources Division, U.S. Geological Survey, Anchorage), 6 Steller sea lion and 2 harbor seal skulls and tissues from Dr. Alan Springer (IMS, UAF), 58 bowhead whale baleen plates from Dr. Don Schell (IMS, UAF), and a beachcast minke whale skull.

Other individuals and organizations who provided tissues this year include Todd O'Hara (Wildlife Management, North Slope Borough, Barrow), Betsy Webb (Pratt Museum, Homer), Gary Freitag (Tongass Coastal Aquarium, Ketchikan), Lori Quakenbush, (USF&WS, Fairbanks), Kate Wynne (Marine Advisory Program, Kodiak), and Linda Shaw (NMFS, Juneau). These accessions and collaborations added significant material to the AFTC and Mammal Collection at the University of Alaska Museum.

#### **Collection Usage**

The AFTC provided 32 tissue loans representing 576 individuals and 8 species during the year (Table 2). Seal tissues were provided to Brian Fadely who is working with Dr. Michael Castellini to develop physiological condition indices

Table 2. AFTC marine mammal tissue loans from 15 May 1996 to 15 May 1997.

Species	No. of Loans	No. of Individuals
Callorhinus ursinus	3	11
Eumetopias jubatus	3	10
Erignathus barbatus	1	21
Phoca sp (vitulina, largha, fasciata, hispida	24	511
Ursus maritimus	1	23
Totals	32	576

for harbor seals to monitor changes in Gulf of Alaska ecosystems. Amy Hirons, working with Dr. Donald Schell, used tissues from the AFTC to gain insight into ecogeographic and trophic aspects of harbor seals through stable isotope analyses. We sent more than 50 teeth from harbor seals to Mike Turek and John Lewis at ADF&G for cementum annuli aging. Dr. Michael Henshaw of the NMFS Southwest Fisheries Center used tissues from a beaked whale in a study designed to provide positive identifications of marine mammals accidentally taken in fisheries or stranded on California beaches.

Michelle Szepanski, working with Dr. James Peek at the University of Idaho, is using stable isotope analysis to determine the importance of marine organisms in the diets of coastal wolves in southeastern Alaska.

Dr. Masao Amano from the Otsuchi Marine Research Center (Ocean Research Institute, University of Tokyo) spent a week at the Museum in early February measuring the skulls of more than 100 ringed seals.

Examples of publications that have resulted from marine-related studies which used the AFTC and/or Mammal Collection are listed in the appendix.

#### **Computerization and Information Technology**

In 1996 we achieved our second objective of CMI support which was to develop a Worldwide Web site for the AFTC. Protocols for tissue collecting and labeling as well as policies for users of the Collection are available on the University of Alaska Museum's web site (www.uaf.edu/museum). Web users can interrogate a summary database of the Museum's Mammal Collection which provides information on all AFTC samples and conventional Museum specimens. The web site also provides information for contributors to the Alaska Marine Mammal Stranding Network (NMFS, Juneau). A listserver address for the AFTC (AFTC-L@galileo.uafadm.uaf.edu) forwards email inquiries to appropriate museum personnel, assuring prompt responses. Reorganization and consolida-

tion of the AFTC freezers was completed this year. Our database management system tracks the location of samples. Between increased efficiency of new boxes acquired with CMI funding and the increased flexibility of the new storage system, the space requirements of the existing collection were reduced by more than 30%.

#### **Future Work**

During the third year of CMI support for the AFTC, we will continue to reinforce and consolidate the practice of archiving marine zoological samples among the several agencies involved in ecological sampling in Alaska. We will also change the AFTC coordinator position to state funding.

We await the release of additional samples of sea otters collected by USF&W after the Exxon Valdez oil spill; the specimens probably will be in our hands by September 1997. This accession will complement skeletal material deposited in the Mammal Collection by USF&WS in 1992.

The coming year will undoubtedly see a substantial increase in the number of marine birds archived in the AFTC. Dr. Kevin Winker joined the Museum as curator of birds in March 1997, having spent five years at the Smithsonian's Laboratory of Molecular Systematics where he made substantial use of, and contribution to, that frozen tissue collection.

#### **Preliminary Conclusions**

The AFTC continues to make excellent progress on a goal related to one of the CMI's Framework Issues: "establishing mechanisms and protocols for the sharing of data regarding marine or coastal resources." Major contributions of specimens have been made this year by ADF&G, the North Slope Borough, and NMFS. The Collection is expanding rapidly because of CMI funding and is now the third largest collection for wild mammals in the world (Hafner et al., 1997).

Marine mammal tissues, in particular, have been extensively archived and widely used by the scientific community. The Mammal Collection database is now available through the internet, and other electronic communication systems have been established to provide easier access to the AFTC for both contributors and users of tissues. A number of investigations with significant implications for the management of marine mammals are using material from the AFTC.

#### References

- Burke, T. 1989. DNA fingerprinting and other methods for the study of mating success. Trends in Ecology and Evolution 4: 139-144.
- Dickson, D. 1988. Canine distemper may be killing North Sea seals. Science 241: 1284.
- Fall, J. A., M. Riedel and K. Wynne. 1997. Community-based harbor seal management and biological sampling. Exxon Valdez Oil Spill Restoration Project Annual Report (Restoration Project 96244).
- Hafner, M. S., W. L. Gannon, J. Salazar-Bravo and S. T. Alvarez-Castaneda. 1997. Survey of mammal collections in the Western Hemisphere. Journal of Mammalogy. 78: Supplement.
- Lande, R. and G. Barrowclough. 1987. Effective population size, genetic variation, and their use in population management. Pages 87-124 *In* M. Soule [ed.], Viable populations for conservation. Cambridge University Press.
- McBee, K. and J. W. Bickham. 1990. Mammals as bioindicators of environmental toxicity. Current Mammalogy, Vol. 2, Plenum.
- Moritz, C. 1994. Applications of mitochondrial DNA analysis in conservation: a critical review. Molecular Ecology 3: 401-411.
- O'Brien, S. J., M. E. Roelke and L. Marker. 1985. Genetic basis for species vulnerability in the cheetah. Science 227: 1428-1434.
- Ralls, K., J. D. Ballou and A. Templeton. 1988. Estimates of lethal equivalents and the cost of inbreeding in mammals. Conservation Biology 2: 185-193.
- Schell, D. M. 1996. A decadal record of primary productivity in the Bering Sea inferred from isotope ratios. Abstracts of the 47th Arctic Division of the American Association for the Advancement of Science Conference, Girdwood, Alaska.

#### Appendix: Studies Using the AFTC and Mammal Collection

- Ben-David, M. 1997. Timing of reproduction in wild mink: the influence of spawning Pacific salmon. Canadian Journal of Zoology 75: 376-382.
- Ben-David, M., R. T. Bowyer and J. B. Faro. 1996. Niche separation by mink (*Mustela vison*) and river otters (*Lutra canadensis*): co-existence in a marine environment. Oikos 75: 41-48.
- Ben-David, M., T. A. Hanley, D. R. Klein and D. M. Schell. (in press). Seasonal changes in diets of coastal and riverine mink: the role of spawning Pacific salmon. Canadian Journal of Zoology.
- Ben-David, M., R. W. Flynn and D. M. Schell. (in press). Annual and seasonal changes in diets of martens: evidence from stable isotope analysis. Oecologia.

- Best, P. B. and D. M. Schell. 1996. Stable isotopes in southern right whale (*Eubalaena australis*) baleen as indicators of seasonal movements, feeding and growth. Marine Biology 124: 483-494.
- Fadely, B. S. 1996. Developing physiological condition indices of harbor seals to monitor changes in Gulf of Alaska marine ecosystems. Global Glimpses 4: 2-3.
- Fadely, B. S., M. A. Castellini and J. M. Castellini. 1996. Harbor seals and the EVOS: blubber and lipids as indices of food limitation. Exxon Valdez Oil Spill Restoration Project Annual Report (Restoration Project 95117-BAA).
- Ledje, C. and U. Arnason. 1996. Phylogenetic analyses of complete cytochrome b genes of the order Carnivora with particular emphasis on the Caniforma. Journal of Molecular Evolution 42: 135-144.
- O'Corry-Crow, G. M., R. F. Suydam, A. Rosenberg, K. J. Frost and A. E. Dizon. (in press). Phylogeography, population structure, and dispersal patterns of the belukha whale, *Delphinapterus leucas*, in the western Nearctic as revealed by mitochondrial DNA. Molecular Ecology (Accepted May 17).
- O' Corry-Crowe, G. M. and R. L. Westlake. (in press). Molecular investigations of spotted seals (*Phoca largha*) and harbor seals (*P. vitulina*) and their relationship in areas of sympatry. *In A. E. Dizon*, S. J. Chivers and W. F. Perrin [eds.]. Molecular genetics of marine mammals, symposium issue of Marine Mammal Science.
- Talbot, S. L. and G. F. Shields. 1996. Phylogeography of brown bears (*Ursus arctos*) of Alaska and paraphyly within the Ursidae. Molecular Phylogenetics and Evolution 5: 477-494.

# **Assessment of Top-trophic Level Predators as Bioindicators of Pollution**

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#### **Abstract**

Growth rate, foraging ecology, and breeding biology of nestling pigeon guillemots (Cepphus columba) were studied during the breeding seasons of 1994 through 1996 in Kachemak Bay, Alaska. Large differences were observed in diet, growth rates, and nest success among locations within Kachemak Bay. Nest success was low, mostly due to high predation rates during incubation.

Clutch size and nest success did not differ significantly between years, but survival rates of nestlings did vary among nesting colonies within Kachemak Bay. Although productivity was higher in areas where the diet included sandlance (Ammodytes hexapterus), nest predation was also a major factor in reproductive success. The proportion of sandlance in the diet ranged from 2% to 86% at different locations. Growth rates of guillemot nestlings increased with the proportion of sandlance in the diet. Nest success could be predicted by several nest attributes including length of nest entrance, height above mean high tide, and number of exits. Overall productivity was 0.313 fledglings/nest in 1994, 0.457 fledglings/nest in 1995, and 0.560 fledglings/nest in 1996, with most losses occurring during incubation.

Haptoglobin, total protein, alanine aminotransferase (ALT), aspartate aminotransferase (AST), and sodium in sera were measured as potential biomarkers of oil ingestion. Differences in mean levels of biomarkers were observed between years, and between nestlings and adults, as well as among locations within Kachemak Bay. Location effects on the biomarkers may be related to the quality of the diet.

During summer 1995, a controlled dose-response experiment was conducted with weathered Prudhoe Bay crude oil. Fifty-one nestlings were divided into three groups: controls, nestlings fed 0.05 ml of oil, and nestlings fed 0.20 ml of oil. Each experimental nestling was fed the dose of weathered oil twice: once at approximately Day 20 post-hatching, and again 5 days later at approximately Day 25. Blood samples were collected immediately before dosing on Days 20 and 25, and again on Day 30.

No treatment effect was found for total protein, sodium, ALT, or AST levels in sera, or growth in body mass. Levels of haptoglobin differed among treatments, but there were significant location and provisioning rate effects that confounded treatment effects. These results suggest that the low doses of weathered oil were not sufficient to induce a persistent inflammatory response.

#### **Study Products**

- Duffy, L. 1995. Assessment of top-trophic level predators as bioindicators of pollution. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1995, Fairbanks.
- Duffy, L. 1996. Assessment of top-trophic level predators as bioindicators of pollution. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1996, Fairbanks.
- Duffy, L. 1997. Assessment of top-trophic level predators as bioindicators of pollution. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1997, Fairbanks.
- Duffy, L. K., R. T. Bowyer, D. D. Roby and J. B. Faro. 1995. Assessment of top-trophic level predators as bioindicators. Pages 15-31 *In* V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 2, OCS Study MMS 95-0057. Fairbanks. 122 pp.
- Duffy, L. K., R. T. Bowyer, D. D. Roby and J. B. Faro. 1997. Assessment of top-trophic level predators as bioindicators. Pages 33-48 *In* V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 3, OCS Study MMS 97-001. Fairbanks. 191 pp.
- Duffy, L. K., R. T. Bowyer, D. D. Roby and J. B. Faro. 1997. Intertidal and subtidal effects of pollution: Assessment of top-trophic level predators as bioindicators. Draft Final Report for Task Order 11987, University of Alaska Coastal Marine Institute, MMS Cooperative Agreement Number 14-35-0001-30661. Fairbanks. 113 pp.

## A Study of the Adsorption of Aromatic Hydrocarbons by Marine Sediments

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#### **Abstract**

Three aromatic hydrocarbons—benzene, naphthalene, and phenanthrene—were rapidly and strongly adsorbed by intertidal sediments from Jakolof Bay, Lower Cook Inlet, Alaska. Adsorption of phenanthrene was more than twice that of naphthalene and benzene. Adsorption was not completely, rapidly reversible by suspension of the sediment in clean seawater. Longer adsorption reaction times led to decreased desorption, except for benzene. Partition coefficients did not vary with dissolved aromatic concentration nor, in most cases, with the addition of a watersoluble fraction of hydrocarbons from crude oil. Therefore, all sites for adsorption on the sediment surface appeared to be equivalent, and availability of adsorption sites did not limit adsorption over the concentration range studied. Adsorption coefficients for phenanthrene varied among sediment samples by as much as a factor of three. This variability was not correlated with sediment organic carbon content, indicating that organic matter was not solely responsible for the adsorption properties of these sediments. There was no evidence of adsorption or complexation of phenanthrene by colloidal or dissolved organic matter. Cooperating Coastal Marine Institute research by Dr. Joan Braddock and Mr. Zachary Richter (see this volume) showed that, overall, the bioavailability of phenanthrene was decreased by adsorption to sediment. Combined with the finding that adsorption is not completely reversible, these results indicate that adsorption could contribute to the persistence of aromatic hydrocarbons in Lower Cook Inlet sediments.

#### **Study Products**

- Henrichs, S. 1995. A study of the adsorption and biodegradation of aromatic hydrocarbons by marine sediments. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1995, Fairbanks.
- Henrichs, S. 1996. A study of the adsorption and biodegradation of aromatic hydrocarbons by marine sediments. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1996, Fairbanks.
- Henrichs, S. 1997. A study of the adsorption and biodegradation of aromatic hydrocarbons by marine sediments. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1997, Fairbanks.
- Henrichs, S. and M. Luoma. 1995. A study of the adsorption and biodegradation of aromatic hydrocarbons by marine sediments. Pages 32 43 *In V. Alexander*, [dir.] University of Alaska Coastal Marine Institute Annual Report No. 2, OCS Study MMS 95-0057. Fairbanks. 122 pp.
- Henrichs, S., M. Luoma, and S. Smith. 1996. A study of the adsorption and biodegradation of aromatic hydrocarbons by marine sediments. Pages 49 62 In V. Alexander, [dir.] University of Alaska Coastal Marine Institute Annual Report No. 3, OCS Study MMS 97-001. Fairbanks. 191 pp.
- Henrichs, S., M. Luoma, and S. Smith. 1996. A study of the adsorption of aromatic hydrocarbons by marine sediments. Final report for University of Alaska Coastal Marine Institute, Task Order 11981 under Cooperative Agreement No. 14-35-001-30661 with the U.S. Department of the Interior, Minerals Management Service, Alaska OCS Region, Anchorage, Alaska. 47 pp.
- Luoma, Michelle. 1995. Adsorption of phenanthrene by marine sediments. Project report for Master of Arts in Chemistry, University of Alaska Fairbanks. 28 pp.

# **Kachemak Bay Experimental and Monitoring Studies**

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#### **Abstract**

This study in lower Kachemak Bay, Alaska, was designed to obtain baseline data on abundance and distribution of intertidal invertebrates and algae and to gather information throughout the year on community-structuring mechanisms such as recruitment and succession. Specific objectives were: 1) to gain an understanding of the seasonal and interannual relationships among intertidal invertebrates and plants, 2) to assess community relationships when recovering from seasonal disturbances in the form of cleared substrate, and 3) to determine the role of wave exposure in differences found in the first two objectives. Quadrats in rocky intertidal habitat on eight sites were cleared of all invertebrates and algae during four visits in 1994 and 1995.

Control, or uncleared, quadrats were also established to provide community assemblages for determining recovery on each site. The dates for creating the quadrats were selected to provide substrate for organisms that recruit in different seasons. The quadrats were subsequently monitored for organism abundance and percent cover. The acorn barnacles Semibalanus balanoides and Balanus glandula first colonized the quadrats in the high and middle tidal zones, often with >80% cover. Fucus gardneri colonized the plots only after barnacles were established. The recovery rates of quadrats scraped on different dates were driven by the timing of barnacle recruitment relative to the timing of bare substrate availability.

Recovery of the dominant algae in the low intertidal zone, Alaria flocossa, was dependent on recruitment of the thatched barnacle, S. cariosis. Bray-Curtis dissimilarity matrices were calculated on community-level data to compare recovery rates of scraped quadrats among sites, quadrat scrape dates, and data collection dates. Multi-dimensional scaling (MDS) ordination plots of the dissimilarity data show that scraped quadrats had not fully converged with control quadrats by the last sampling date, 30 months after the first set of quadrats were scraped in March 1994.

Recovery rates varied by the season that quadrats were scraped, with quadrats scraped in July and October 1994 showing slower recovery rates than quadrats scraped in March 1994 or 1995. MDS ordinations indicate that the extent of recovery on disturbed quadrats compared to control quadrats varied among sites. Differences in wave-exposures on the sites do not account for the differences found for recovery.

#### **Study Products**

- Highsmith, R. C. and S. M Saupe. 1997. Kachemak Bay experimental and monitoring studies. Pages 63-84 In V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 3, OCS Study MMS 97-001. Fairbanks. 191 pp.
- Highsmith, R. C. and S. M Saupe. 1997. Kachemak Bay experimental and monitoring studies. Draft Final Report for Task Order 11982, University of Alaska Coastal Marine Institute, MMS Cooperative Agreement Number 14-35-0001-30661. Fairbanks.
- Highsmith, R. C., T. L. Rucker, and S. M Saupe. 1995. Kachemak Bay experimental and monitoring studies Pages 44 54 *In V.* Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 2, OCS Study MMS 95-0057. Fairbanks. 122 pp.
- Saupe, S. M 1995. Kachemak Bay experimental and monitoring studies. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1995, Fairbanks.
- Saupe, S. M 1996. Kachemak Bay experimental and monitoring studies. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1996, Fairbanks.
- Saupe, S. M 1997. Kachemak Bay experimental and monitoring studies. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1997, Fairbanks.

### **North Slope Amphidromy Assessment**

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#### **Abstract**

Fishes of the genus Coregonus numerically dominate coastal and fresh waters of the Alaskan arctic coastline. They are obligate freshwater spawners but they migrate to coastal waters to feed during the summer. The migration passages used by these fishes have been subjected to physical alterations as a result of the industrial development necessary for oil exploration and extraction. Considerable effort has been made to ascertain whether structures such as causeways located in migration routes have had a detrimental effect on these species. Thus far, no detrimental effects have been detected using conventional research tools. However, subtle effects on lifehistory and migrational behavior with long-term consequences may not be detectable with the technologies currently being employed. In Teshekpuk Lake, for example, a portion of the least cisco and broad whitefish populations are thought to be non-migratory because they grow at a slower rate compared with migratory populations. A consequence of industrial development could be increased dwarfism if migration is restricted. Fecundity loss and thus population reduction is another possible consequence if access to spawning ground becomes more difficult. New methods such as stable isotope ratio measurement may assess subtle changes in the migrational behaviors of these fishes to evaluate these hypotheses.

Large gradients in the natural abundance of <sup>13</sup>C/<sup>12</sup>C and <sup>15</sup>N/<sup>14</sup>N exist between freshwater and marine habitats on the Alaskan arctic coast. The massive terrestrial peat deposits that provide an important carbon source to food chains (directly via peat-consuming insects and indirectly via respiration of peat carbon) have distinctive isotopic signatures. Because stable isotope ratios are conserved during feeding processes, they make effective tracers of food sources, enabling distinction between peat- and marine-derived carbon. Food-source isotopic signatures enables one to determine whether migration has taken place by observing where the sample was collected in relation to potential feeding locations.

#### **Objectives**

The purpose of this project was to develop stable isotope measurement as a proxy for amphidromous behavior. The goal was to determine recent migrational behavior by measuring the <sup>13</sup>C/<sup>12</sup>C and <sup>15</sup>N/<sup>14</sup>N of samples of fish.

The objectives of this study were:

- 1) To establish baseline isotope attributes of a population of fishes before development occurred, so that during and following development fish populations could be monitored to determine if they were excluded from usual feeding habitats as evidenced by alterations in their isotope ratios.
- 2) To sample fishes in the developed area of the Sagavanirktok River (Sag River) delta, Prudhoe Bay, Alaska, and analyze their isotope ratios for comparison with the fishes collected in Objective 1.

#### **Description**

Objective 1 was met by sampling in the Chipp River, an undeveloped area to the west of Prudhoe Bay. Species sampled included least cisco, broad whitefish, humpback whitefish, other fishes including obligate freshwater species, and potential forage species. Sampling in the Chipp River system took place in July 1994 and 1995 in collaboration with the North Slope Borough Department of Wildlife Management. Objective 2 was met through collaboration with BPX and their contractor LGL Alaska Research Associates, Inc., who, in 1994, collected samples of least cisco, Arctic cisco, broad whitefish, Dolly Varden, Arctic grayling, and Arctic flounder for this project, and in 1995 collected Arctic cisco and broad whitefish.

#### Results

Stable isotope abundance characterized the recent feeding of the individual fishes sampled since they incorporated this natural tracer by having fed in habitats with characteristic isotopic signatures. Characteristic isotopic signatures of feeding in fresh- and saltwater habitats were established. A sample size of about 100 fish, broadly distributed in age, enabled the assessment of how a fish population shifts in feeding migratory behavior over its life history. This project demonstrated that if life history migratory behavior changes over time, a concomitant isotope shift can be used to quantitatively assess the change. No other method currently exists that provides such data or analysis.

#### Conclusion

Stable isotope analysis elucidated aspects of North Slope fish populations not available by other methods through 1) the isotopic characterization of fish populations which enabled determination of spatial and temporal patterns, 2) assessment of interaction among populations by trophic status and food web characterization, and 3) assessment of habitats important as nurseries for recruitment.

#### Study Products

- Goering, J. J. 1996. North slope amphidromy assessment. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1996, Fairbanks.
- Kline, T. C. 1997. North Slope Amphidromy Assessment. Final Report for Task Order 11984, University of Alaska Coastal Marine Institute, MMS Cooperative Agreement Number 14-35-0001-30661.
- Kline, T. C. 1995. Assessing the role of amphidromy in the production of North Slope Alaska coregonine fishes using  $\delta^{13}$ C and  $\delta^{13}$ N. Presentation at the annual meeting of the American Society of Limnology and Oceanography, Reno, Nevada.
- Kline, T. C. 1995. North slope amphidromy assessment. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1995, Fairbanks.
- Kline, T. C. 1996. Natural stable isotope abundance used for assessment of anadromous and amphidromous migrations in fish ecology: implications for fisheries management and habitat protection. Pages 118-119 In D. A. Hancock and J. P. Beumer [eds]. Developing and sustaining world fisheries resources: the state of science and management, Proceedings of the second world fisheries congress. Vol. 1.
- Kline, T. C. 1997. North slope amphidromy assessment. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, 25 February 1997, Fairbanks.
- Kline, T. C. and J. J. Goering. 1995. North Slope amphidromy assessment. Pages 55 67 *In* V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 2, OCS Study MMS 95-0057. Fairbanks. 121 pp.
- Kline, T. C. and J. J. Goering. 1996. North Slope amphidromy assessment. Pages 85 101 *In* V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 3, OCS Study MMS 97-0001. Fairbanks. 191 pp.
- Kline, T. C., W. J. Wilson, and J. J. Goering. Natural isotope indicators of fish migration at Prudhoe Bay, Alaska. Manuscript for submission to the Canadian Journal of Fisheries and Aquatic Sciences.

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# Physical-biological Numerical Modeling on Alaskan Arctic Shelves

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#### **Abstract**

The arctic shelves north of Bering Strait and the north coast of Alaska are regions of important benthic and marine mammal resources. These are areas that may be impacted by offshore oil, gas, and mining operations. These shelves are also regions of seasonal sea-ice cover that is mobile and dynamic. Physical (including ice), biological, and chemical oceanographic conditions in both summer and winter are such that several types of both natural and anthropogenic "particles" (e.g., from primary production or phytoplankton, detritus, petroleum, mining, radionuclides) may interact, aggregate, and ultimately be transported deeper into the ocean, into the arctic halocline, onto the shelf bottoms, and into the benthic and marine mammal ecosystems. In this study, I have been using numerical models to address the generation, flux, and fate of the natural primary production phytoplankton particles and their interaction with each other and with physical processes. I have modeled the air-ice-ocean interaction numerically in a relatively fine-scale crosssectional model, and simultaneously modeled physical interaction with both primary production and the aggregation of phytoplankton. The modeling so far has shown that two main sources, pathways, or processes for the formation and flux of particles are brine rejection from ice formation in fall and winter, and primary production blooms in spring and summer. I have used available hydrographic data for initial and boundary conditions and for preliminary verification. The preliminary verification from limited data appears to be good. The goal is to gain a predictive capability of the flux and fate of natural material on the Alaska arctic shelves.

#### Introduction and Background

The circulation on the Chukchi Sea shelf north of Bering Strait (Figure 1) is not well understood although considerable progress is being made (e.g., Weingartner et al., 1997). This broad, shallow shelf bordering the deep basin of the Arctic Ocean is an area of confluence of ocean flow from the Bering Sea to the south,

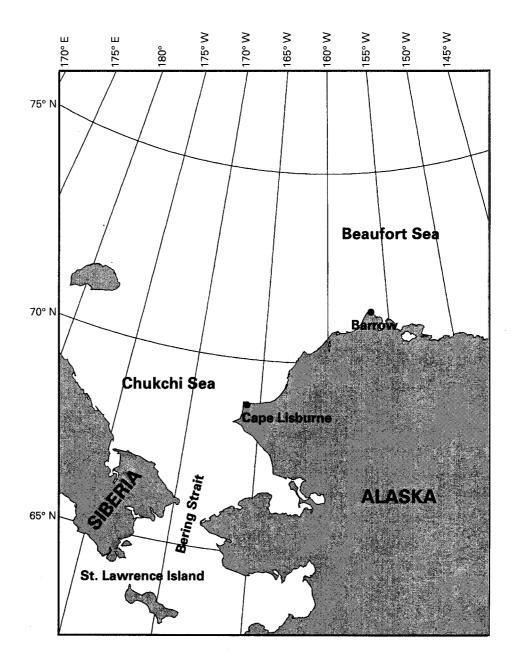


Figure 1. Chart of the Chukchi and Beaufort seas around Alaska. The location of the modeling is primarily off Point Barrow, Alaska, which is the approximate boundary between the Chukchi and Beaufort seas.

from the Siberian shelf to the west, and from the Beaufort Sea to the east. This confluent flow tends to spread out toward the deep Arctic Ocean where it meets westward flow from the Beaufort Sea moving past Point Barrow, some of which continues westward along the Siberian shelf. There is also subsurface flow which moves off the shelf and/or down the shelf break canyons, such as Barrow Canyon, feeding the Arctic Ocean halocline or deeper water. Some of this subsurface flow moves around Point Barrow and continues east along the Beaufort shelf break.

The circulation and dynamics of the Alaska Beaufort and Chukchi sea shelves are further complicated by the cover of mobile and dynamic sea ice in winter that is reduced to a partial cover in summer (although in some summers the area of open water between the ice and the north Alaska coast is very narrow). In spring and summer, increased insolation and the resulting melt water causes low-salinity surface stratification that leads to increased primary production. That is, the stratification holds phytoplankton in the photic zone, resulting in a net increase in primary production (Alexander and Niebauer, 1981; Niebauer et al., 1990, 1995). In fall and winter, ice formation in the various leads, cracks, shear zones, and polynyas as well as in open water resulting from episodic wind events leads to brine formation (Cavalieri and Martin, 1994). This brine convectively sinks to the shelf bottom and feeds into the Arctic Ocean halocline through, for example, Barrow Canyon (Weingartner et al., 1997).

Although biological production in the permanently ice-covered Arctic Ocean is low, biological production can be quite high in the seasonally ice-free shelf regions surrounding the Arctic Ocean, and interaction of the ocean and biological organisms with ice is very important (Alexander and Niebauer, 1981; Grebmeier and Cooper, 1995; Niebauer et al., 1990, 1995; Walsh et al., 1989). Arctic marine food webs are greatly influenced by the interdependency of sea ice, water density, and nutrient availability. The currents and ice may carry materials derived from human activity (e.g., petroleum, offshore mining materials, radionuclides) as well as natural materials (nutrients, detritus, and petroleum particles) into the region where they may interact with biological processes. For example, the flow from the Bering Sea into the Chukchi Sea is particularly rich in nutrients which fuel high primary production in the southern Chukchi Sea (Walsh et al., 1989). It also has been suggested that a primary source of nutrients found in Fram Strait of the eastern arctic is the western arctic Bering Sea (W. O. Smith, Jr., pers. comm.) and that these nutrients must cross the Chukchi and Beaufort shelves to get there.

Primary production particles (i.e., phytoplankton) aggregate, incorporate, and otherwise interact with each other, forming larger, more dense particles which sink faster. Single cell background sinking is ~0.5 m day¹ while aggregate sinking speeds are on the order of ~10 m day¹, although speeds of up to 100 m day¹ have been reported (Hill, 1992). Aggregation and sinking carry these particles out of the photic zone and surface layers, and deeper into the ocean. Because low temperatures tend to retard zooplankton development, phytoplankton are not heavily grazed in cold water areas (Coyle and Cooney, 1988) and so can sink to the bottom. This primary production directly feeds the substantial benthic communities of the arctic shelves, and both directly and indirectly feeds the substantial marine mammal populations in the area. It is the biological-physical-chemical interactions of the primary production and their fluxes and fates that I am modeling with the aim of predictive capability.

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In addition to the aggregation and sinking of spring blooms, the dense water (brine) generated during ice formation can also carry particulate material to the benthos, to the Arctic Ocean halocline, or to deeper waters. The Arctic Ocean halocline, which begins at depths of 30–60 m and is ~100 m thick, is thought to result from the lateral input of cold, high-salinity water from ice formation in polynyas, leads, and other open waters on the adjacent shelves. This process undoubtedly, at times, entrains particulate material of "new" production from the seasonal ice edge and open water blooms on the arctic shelves and Bering Sea (Walsh et al., 1989).

The aim of this project is to use numerical models of air-ice-ocean interaction with biological production and nutrient chemistry to understand, model, and quantify energy and material (i.e., biological or primary production, chemical nutrients, brine) interaction, pathways, fluxes, and fates on the Alaska arctic shelves.

#### **Methods**

The model (Niebauer and Smith, 1989; Smith and Niebauer, 1993) is a cross-sectional, multilayered, time-dependent, finite difference numerical model that is composed of physical, biological, and sea-ice submodels. At present, the space dimensions are ~100 km on the horizontal axis by ~300 m on the vertical axis with  $\delta x$  of 3 km and  $\delta z$  of 5 m. Recent simulation durations have been 12 weeks with  $\delta t$  of 20 min (Smith et al., 1997). These dimensions are fairly arbitrary and depend upon computer power. The physical and biochemical ocean and ice submodels are a series of time- and space-dependent coupled nonlinear equations of motion. The equations include the effects of Coriolis, wind and heat forcing, ice motion as well as melting and freezing, vertical and horizontal density gradients, and ocean currents.

Ocean density is a function of salinity, temperature, and pressure. The model is a circulation model and is what is sometimes called a 2½-D model in that parameters such as currents can vary in time and space in the vertical and in the horizontal dimension parallel to the section. Perpendicular to the section, currents can exist and can vary in time but not in space along this dimension. That is to say, the dimension perpendicular to the cross-section is modeled as very long and, for example, waves cannot propagate in this direction. The biological submodel includes two separate nutrient pools (nitrate and ammonium), phytoplankton nutrient uptake, grazing by zooplankton, and nutrient recycling and regeneration. The primary production is driven by an insolation submodel as a function of date, latitude, nutrients, and physical parameters such as depth, temperature, and stratification. Details of the model are found in Niebauer and Smith (1989).

I added code to the model on biological particle aggregation (modified after Riebesell and Wolf-Gladrow, 1992), as aggregation appears to be an important process for transporting biological products deeper into the ocean (i.e., bigger aggregations are more dense and so sink faster).

Although the physical sea-ice submodel is a simple balance among Coriolis force, wind drag, and ocean drag, thermodynamics are included to connect ice and water to permit change of state between water and ice. The submodel allows for sea ice formation and thickening (and brine formation), melting and thinning (and associated ocean freshening), and differential advection (and associated mechanical thinning and thickening of sea ice from both wind stress from above and current stress from below). Therefore, both latent heat and sensible heat polynyas can form. In the present model, leads with widths on the order of meters can not form explicitly because the horizontal grid spacing is 3 km, a dimension closer to that of polynyas. However, the model does allow 0–100% ice cover in each grid space so that leads can be simulated to some extent.

I am modeling sea water freezing/brine rejection and associated penetrative convection during the freeze-up period as well as during winter wind events which cause large-scale ice divergence and open water along the north Alaska coast. One of these wind events was captured by satellite in December 1994 when the ocean was ~20% open water over hundreds of kilometers. Substantial amounts of brine must have formed and sunk, becoming part of the arctic halocline. This brine probably carried at least a portion of whatever particles were in the surface water. I am comparing the model results with data presently being gathered on the shelf and in Barrow Canyon by Dr. T. Weingartner of the Institute of Marine Science, University of Alaska, and Cota et al. (1996).

Finally, I am modeling the spring primary production bloom associated with ice melt and ocean stratification. More importantly, the model includes the interaction of the phytoplankton production in aggregation and I am beginning to follow particle paths through the ecosystem.

#### **Results and Discussion**

Of the four objectives listed in the original proposal, the first objective is to modify the model (Niebauer and Smith, 1989; Smith and Niebauer, 1993) to simulate realistically the vertical flux of phytoplankton as aggregates of cells. This objective has two parts: to get the particles or cells to aggregate realistically, and to model the vertical flux of the various particle size classes realistically, making the larger, more dense particles sink faster. A constraint is that if particles aggregate too quickly and sink out of the photic zone too fast, the bloom is extinguished for lack of light. If the particles aggregate too slowly, the bloom sinks more slowly than has been observed.

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Initially, ten size classes were chosen with particles ranging from 30 phytoplankton cells per aggregate (or cells per particle) to 300 cells per particle. For a single cell of size 10 µm, this gives a particle diameter range of 45–123 µm and a corresponding sinking range of ~1.7–5.5 m day<sup>-1</sup> (Riebesell and Wolf-Gladrow, 1992). Many numerical experiments were run to "tune" the aggregation parameter "stickiness" which dictates how rapidly smaller, slower-sinking particles aggregate to form larger, faster-sinking particles. The results of tuning experiments were compared with experimental and observational data. Open ocean estimates range from almost zero to >100 m day<sup>-1</sup> (Hill, 1992). Sinking data from ice-related blooms is sparse and sinking observations are not available for the Chukchi and Beaufort seas. However, data from ice-edge-related blooms on the Bering Sea shelf suggest sinking rates of ~7 m day<sup>-1</sup> (Niebauer et al., 1995). Sinking rates ~5.5 m day<sup>-1</sup> have been observed in the Ross Sea, Antarctica (Smith and Dunbar, 1997).

The first objective has basically been accomplished. Some additional work remains in that I would like to expand the number of size classes of particles to increase the maximum particle diameter to ~500 µm to fit the range of particle sizes observed in the ocean. Also, this will increase the range of sinking speeds to a maximum of ~30 m day<sup>-1</sup> which is closer to that observed in the ocean in general.

The second objective is to model spring phytoplankton blooms on arctic shelves. This includes the blooming, aggregation, and vertical transport of chlorophyll and phytoplankton as a function of physical processes of melt water and/or solar heated surface stratification, wind mixing, and wind-driven coastal upwelling of nutrients into the photic zone. The model has successfully generated a spring phytoplankton bloom from the melt water and solar-heated stratification (Figure 2) with subsequent aggregation of phytoplankton into larger, denser particles which sink faster. For the experiment from which Figure 2 was taken, integrated primary production (chlorophyll, Chl) was ~27 mg Chl m<sup>-2</sup> over 40 m, and primary productivity was ~360 mg C m<sup>-2</sup> day<sup>-1</sup>. Integrated field data for comparison and verification are available from Cota et al. (1996) from an icebreaker cruise in the eastern Chukchi and Beaufort seas. They measured ~27 mg Chl m<sup>-2</sup> for primary production and ~300 mg C m<sup>-2</sup> day<sup>-1</sup> for primary productivity. The average photic zone depth for their cruise was 37 m. Modeled vertical fluxes of aggregates were ~15 mg C m<sup>-2</sup> day<sup>-1</sup> through 250 m. Although there are no field estimates of vertical flux for this region of the arctic, Smith and Dunbar (1997) reported fluxes of 2-92 mg C m<sup>-2</sup> day<sup>-1</sup> in the Ross Sea. This verification of the modeling results is preliminary but encouraging.

The wind-driven upwelling experiments are the next task for this second objective. Wind-driven upwelling probably enhances primary production and may increase vertical convection.

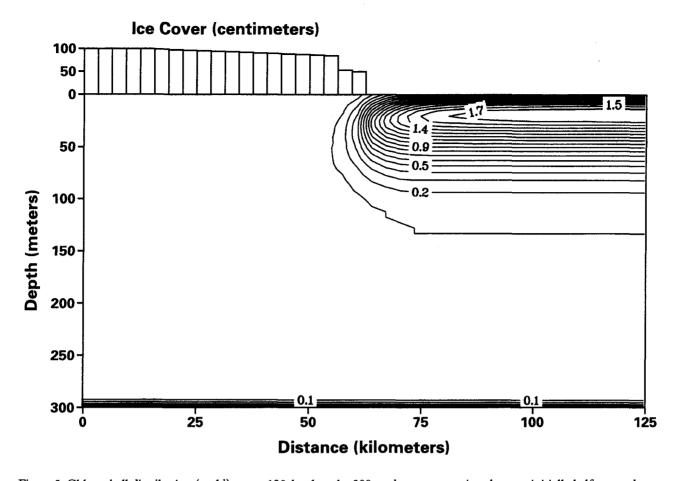


Figure 2. Chlorophyll distribution ( $\mu g \, l^{-1}$ ) over a 120-km long by 300-m deep cross-section that was initially half-covered with sea ice 100 cm thick. The chlorophyll is the sum of all phytoplankton size classes. This "snapshot" is taken after 4 weeks of simulating a spring bloom driven by sunlight for April 1–28 at 71°N. Initial conditions of nutrient, salinity, and temperature are taken from Cota et al. (1996). Initial chlorophyll was 0.19  $\mu g \, l^{-1}$ . The water is warmed by assuming ~5°C air temperature over –1.7°C water.

The third objective is to model the convective sinking of water, both in conjunction with, and as a separate process from, the flux of natural and primary production particles and particle aggregation. Studies (e.g., Cavalieri and Martin, 1994) suggest that brine rejection over the Arctic Ocean shelf is the source of the cold, salty water that maintains the Arctic Ocean halocline via convective sinking. Probably this usually involves low speed convection (known as convective mixed layer deepening) with speeds on the order of meters per day rather than advective or penetrative convection with speeds of tens to thousands of meters per day. Although thousands of meters per day is a very high velocity for vertical flow in the ocean, penetrative velocities of up to 8 cm sec<sup>-1</sup> (almost 7000 m day<sup>-1</sup>) have been observed (Denbo and Skyllingstad, 1996). However, Drijfhout et al. (1996) suggested that in this region off Alaska, at least one event per year occurs in which a penetrative column caused by surface cooling reaches a depth of at least 200 m. Such events are probably penetrative convection.

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My physical emphasis in the model included modeling higher density surface water formation and deep convection through processes such as ocean surface cooling, ice formation, and brine rejection, and possible interaction with eddies and upwelling as preconditioning to convection. Vertical motion of water can be divided arbitrarily into broad categories of ordinary or convective mixed layer deepening convection (downward) with speeds of two to three meters per day as opposed to downward advective or penetrative convection with speeds of tens to thousands of meters per day. A third velocity scale is that of upwelling with speeds of approximately ten meters per day. Figures 3 and 4 show results from the model for a hypothetical case of cooling for two weeks (air temperature of -10°C over water of 0°C under a coupling coefficient of 40 watts m<sup>-2</sup> °C<sup>-1</sup>, Drijfhout et al., 1996). Convective mixed layer deepening is observed for about the first three weeks with maximum convective speeds of 2.5 m day-1. An advective or penetrative convective event occurs at approximately the fourth and fifth weeks when there is transport of higher salinity water and higher chlorophyll to depth at speeds of up to 40 m day-1. After the convective event, vertical speeds drop back to 1 m day-1 for the rest of the experiment. An important point in

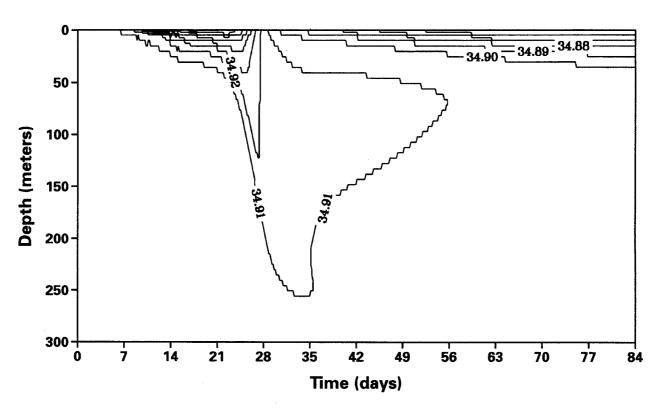


Figure 3. Time series of salinity (‰) over a 3-month (April, May, and June) model experiment in which temperature and salinity were initially 0°C and 34.9‰ but the air temperature was held at -10°C for the first 2 weeks. The cooling in the first 2 weeks resulted in ice formation and brine rejection which in turn resulted in deep penetrative convection during the fourth and fifth weeks. Maximum vertical velocities were 40 m day<sup>-1</sup>.

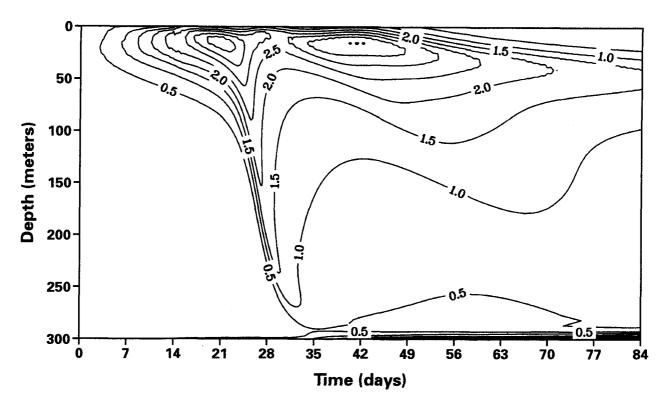


Figure 4. Time series of chlorophyll ( $\mu$ g l<sup>-1</sup>) over the 3-month model experiment described in Figure 3. A surface spring bloom begins in the first weeks but is interrupted by deep convection shown centered on about day 28. Maximum bloom primary production is ~800 mg C m<sup>-2</sup> day<sup>-1</sup> while the vertical flux at depth (250 m) was ~70 mg C m<sup>-2</sup> day<sup>-1</sup> associated with the penetrative convection. The slow sinking of the chlorophyll is seen after about day 35 with maximum vertical flux of ~120 mg C m<sup>-2</sup> day<sup>-1</sup> occurring on day 78. Note also the accumulation of chlorophyll on the bottom after day 35.

these experiments is that penetrative convection does not occur without the inclusion of both the earth's rotation (Coriolis force) and the density of sea water as a function of temperature, salinity, and pressure. Not including the effect of pressure on density precludes penetrative convection.

The transport of carbon differs from the transport of water because, while the vertical flux of carbon depends on the advection of water, it also depends upon the sinking of more dense particles and the timing of the bloom. In Figure 4, at a depth of 250 m, the vertical flux of carbon is ~11 mg C m<sup>-2</sup> day<sup>-1</sup> on day 14, rises to ~70 mg C m<sup>-2</sup> day<sup>-1</sup> by day 31 during the penetrative convection, but then decreases after that. For comparison, maximum integrated (40 m) primary production, the source of the carbon, is ~800 mg C m<sup>-2</sup> day<sup>-1</sup>. Later, after at least 7 weeks, when vertical speeds are very low (1 m day<sup>-1</sup>), vertical flux reaches a maximum of ~120 mg C m<sup>-2</sup> day<sup>-1</sup> which is due to the sinking of the larger, aggregated chlorophyll particles. The magnitude of the vertical flux of carbon can be highly variable depending on the timing of the bloom. For example, during a penetrative convective event in the winter when there is little light and primary production, the flux of carbon will be nil.

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The next step under this third objective is to run experiments with observed initial conditions of salinity and temperature profiles as is being done for the second objective. Included will be experiments of wind-driven upwelling bringing warmer, more saline water to the surface where it will be cooled, becoming cold, saline water which should convect strongly. Another set of winter experiments will be done in which wind will create polynyas exposing relatively warm water to cold air temperatures which should also drive convection through ice formation.

The fourth objective is to interact with field data groups and individuals who are working on different aspects of the Alaska arctic shelves, as recommended by the National Academy of Science. Real data are required for initial and boundary conditions as well as for verification of the model. That is, modelers should interact with field and data processing groups to ground models in reality. Money and support are insufficient to study every aspect of the whole region in detail, therefore, models must be used to fill these needs. I am using available data and interacting with field researchers such as Dr. Tom Weingartner of the University of Alaska Fairbanks and Dr. Walker O. Smith, Jr. of the University of Tennessee.

## **Preliminary Conclusions**

The work to date suggests that I can model the spring bloom driven by physical stratification (either thermal or melt water). This is supported by comparison with field data in the form of primary production (chlorophyll) and primary productivity (rates of carbon fixing in mg C m<sup>-2</sup> day<sup>-1</sup>). I can also model the aggregation and sinking of particles with sinking rates and flux of carbon within observed ranges. A problem is the lack of data from the Chukchi-Beaufort region to verify the aggregation of phytoplankton cells and the vertical flux to depth.

I can model convection due to surface cooling and brine rejection from ice formation on at least two convection velocity scales: convective mixed layer deepening (1–2 m day<sup>-1</sup>) and penetrative convection (10s–1000s m day<sup>-1</sup>). Using the model I can separate the flux of carbon due to aggregation and sinking from the flux due to vertical convection/advection of water. There is some field evidence of a sinking bolus of water in the data set of Cota et al. (1996).

## **Future Work**

Future work includes wind-driven experiments including 1) wind-driven upwelling experiments in spring to bring nutrients to the photic zone to drive primary production, 2) wind to drive ice off the ocean in spring/summer to expose the ocean to light in order to drive primary production, and 3) wind to drive ice off the ocean in winter to expose the ocean to freezing air temperatures in order to drive convection through ice formation.

Additional work and experiments, and especially verification with actual data, are required on all the objectives.

Finally, more work is needed on the ice algorithm for heat and momentum transfer among air, ice, and ocean. The aggregation of phytoplankton cells needs to be expanded to include more size classes to allow better simulation of vertical flux of biological material.

## Acknowledgments

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## References

- Alexander, V. and H. J. Niebauer. 1981. Oceanography of the eastern Bering Sea ice edge zone in spring. Limnology and Oceanography 26: 1111-1125.
- Cavalieri D. J. and S. Martin. 1994. The contribution of Alaskan, Siberian, and Canadian coastal polynyas to the cold halocline layer of the Arctic Ocean. Journal of Geophysical Research 99: 18343-18362.
- Cota, G. F., L. R. Pomeroy, W. G. Harrison, E. P. Jones, F. Peters, W. M. Shelton, Jr. and T. R. Weingartner. 1996. Nutrients, primary production and microbial heterotrophy in the southeastern Chukchi Sea: Arctic summer nutrient depletion and heterotrophy. Marine Ecology Progress Series 135: 247-258.
- Coyle, K. O. and R. T. Cooney. 1988. Trophic implications of cross-shelf copepod distributions in the southeastern Bering Sea. Marine Biology 70: 187-196.
- Denbo, D. W. and E. D. Skyllingstad. 1996. An ocean large-eddy simulation model with application to deep convection in the Greenland Sea. Journal of Geophysical Research 101: 1095-1110.
- Drijfhout, S. S., E. Maier-Reimer and U. Mikolajewicz. 1996. Tracing the conveyor belt in the Hamburg large-scale geostrophic ocean general circulation model. Journal of Geophysical Research 101: 22563-22575.
- Grebmeier, J. M. and L. W. Cooper. 1995. Influence of the St. Lawrence Island Polynya upon the Bering Sea benthos. Journal of Geophysical Research. 100: 4439-4460.
- Hill, P. 1992. Reconciling aggregation theory with observed vertical fluxes following phytoplankton blooms. Journal of Geophysical Research 97: 2295-2308.

Niebauer \_\_\_\_\_\_ 37 \_\_\_

- Niebauer, H. J. and W. O. Smith, Jr. 1989. A mesoscale model of the physical-biological interactions in the Fram Strait marginal ice zone. Journal of Geophysical Research 94: 16151-16175.
- Niebauer, H. J., V. Alexander and S. Henrichs. 1990. Physical and biological oceanographic interaction in the spring bloom at the Bering Sea marginal ice zone. Journal of Geophysical Research 95: 22229- 22241.
- Niebauer, H. J., V. Alexander and S. Henrichs. 1995. A time-series study of the spring bloom at the Bering Sea ice edge I. Physical processes, chlorophyll and nutrient chemistry. Continental Shelf Research 15: 1859-1877.
- Payne, J. R., L. E. Hachmeister, G. D. McNabb, Jr., H. E. Sharep, G. S. Smith and C. A. Manen. 1991. Brine-induced advection of dissolved aromatic hydrocarbons to Arctic bottom waters. Environmental Science and Technology 25: 940-951.
- Riebesell, U. and D. A. Wolf-Gladrow. 1992. The relationship between physical aggregation of phytoplankton and particle flux: A numerical model. Deep-Sea Research 39: 1085-1102.
- Smith, W. O., Jr. and R. B. Dunbar. 1997. The relationship between new production and vertical flux on the Ross Sea continental shelf. Journal of Marine Systems (in press).
- Smith, W. O., Jr. and H. J. Niebauer. 1993. Interactions between biological and physical processes in Arctic seas: Investigations using numerical models. Review of Geophysics 31: 189-209.
- Smith, W. O., Jr., H. J. Niebauer and V. L. Asper. 1997. Coupling of surface layer biological processes and vertical flux in the Ross Sea. *In* Faranda, F., L. Guglielmo and A. Ianora [eds], Ross Sea Ecology. (Submitted)
- Walsh, J. J., C. P. McRoy, L. K. Coachman, J. J. Goering, J. J. Nihoul, T. E.
  Whitledge, T. H. Blackburn, P. L. Parker, C. D. Wirick, P. G. Shuert, J. M.
  Grebmeier, A. M. Springer, R. B. Tripp, D. A. Hansell, S. Djenidi, E.
  Deleersnijder, K. Henriksen, B. A. Lund, P. Andersen, F. E. Muller-Karger and K. Dean. 1989. Carbon and nitrogen cycling within the Bering/Chukchi Seas: Source regions for organic matter effecting AOU demands of the Arctic Ocean. Progress in Oceanography 22: 277-359.
- Weingartner, T. J., D. J. Cavalieri, K. Aagaard and Y. Sasaki. 1997. Circulation, dense water formation and outflow on the Northeast Chukchi shelf. Journal of Geophysical Research (Submitted).

# Defining Habitats for Juvenile Flatfishes in Southcentral Alaska

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## **Abstract**

Significant progress has been made on studies of juvenile flatfish distribution and abundance within Chiniak Bay, Kodiak Island and Kachemak Bay, Kenai Peninsula in the past year. The final collection activities for this project were completed August 1996, and recent efforts have been focused on analysis of the annual data (1991–96) from Chiniak Bay and seasonal data (1994–96) from Kachemak Bay. This annual report summarizes and gives preliminary conclusions by area for three research products of this project: the development of a habitat-focused survey design for the assessment of interannual fluctuations in juvenile flatfish abundances within Chiniak Bay; the effects of seasonal temperature and salinity patterns on distribution, abundance, and growth of juvenile flathead sole (Hippoglossoides elassodon) and rock sole (Pleuronectes bilineatus) within Kachemak Bay; and the use of depth and sediment as determinants of distribution of juvenile flathead sole and rock sole within Kachemak Bay.

#### Introduction

Habitat is one of the primary factors determining survival of early life history stages of marine fishes (Gadomski and Caddell, 1991; Reichert and van der Veer, 1991; Sogard, 1992; Moles and Norcross, 1995), thereby affecting the level of recruitment to commercial and sport fisheries. Assessment of habitat characteristics in relation to fish distribution and abundance is necessary to begin to understand variations in species abundance. Physical characteristics which affect the distribution and habitat quality of flatfishes may include distance from shore or bay mouth, depth (Ronholt et al., 1982; Weinberg et al., 1984; Walters et al., 1985), sediment type (Tanda, 1990; Gibson and Robb, 1992; Moles and Norcross, 1995), temperature (Pihl, 1990; Gadomski and Caddell, 1991;

Henderson and Seaby, 1994), salinity (Rosenberg, 1982), winds, and currents (Tyler, 1971; Krygier and Pearcy, 1986; Pihl, 1990). The physical parameters which most strongly affect the distribution and abundance of juvenile flatfishes within nursery areas near Kodiak Island have been described by Norcross et al. (1997). These investigators determined that age-0 flathead sole (*Hippoglossoides elassodon*) are found at temperatures <8.9°C on mud and mixed mud sediments. Age-0 Pacific halibut (*Hippoglossus stenolepis*) are <7.9 km inside bays and at depths <40 m. Age-1 yellowfin sole (*Pleuronectes asper*) are at depths <28 m on mixed sediments. Age-0 rock sole (*Pleuronectes bilineatus*) are on sand and muddy sand sediments at temperatures >8.7°C. The determination by Norcross et al. (1997) of key parameters for the nursery habitats of these species will be applied in the data analyses now underway for this project (see section on future work).

## **Methods**

The gear and method of collection within Chiniak Bay in August 1996 and Kachemak Bay during February, May, and August 1996 were similar to those used in prior sampling by Norcross (Norcross et al., 1995; 1997). At each sampling site (station) sediment was collected using a 0.06-m<sup>3</sup> Ponar grab for proportional grain size analysis, vertical records of salinity and temperature were collected using a SeaBird Seacat Profiler 19 CTD (conductivity, temperature, and depth profiler), and a 3.05-m plumb staff beam trawl was towed for 3.3 to 10 minutes. The body of the trawl net was 7-mm square mesh, with a 4-mm codend liner; the net was equipped with a double tickler chain. In addition, during the August 1995 and 1996 cruises in Chiniak Bay and May 1996 cruise in Kachemak Bay, an underwater camera was used to view the habitat directly. During the February 1996 cruise in Kachemak Bay, two bottom temperature recorders were deployed which measured bottom temperature every 30 minutes until August 1996. Thus, data on depth, bottom temperature, bottom salinity, sediment type, distance from the mouth of the bay, distance from shore, tidal stage, and light stage were collected or measured for use in describing the physical parameters of flatfish habitat and comparing with previous collections.

Fishes were identified to species and total lengths were measured (mm), using either a Limnoterra electronic fish measuring board (FMB IV) or rulers and manual data entry. Flatfish ages were estimated using length frequency data and literature references (as described in Norcross et al., 1993; 1994). Catch-per-unit-effort (CPUE) values were standardized to a 1000-m² tow area for comparison of fish abundances.

Data analysis was a focus during the past year. Structuring the database to include all previously collected data; data entry, checking, and analysis were components of this effort. Data from 1991 through 1996 were analyzed for the

interannual study in Chiniak Bay, and 1994-96 data were analyzed for the seasonal study in Kachemak Bay.

## Results

## I. A habitat-focused survey design for the assessment of interannual fluctuations in juvenile flatfish abundance

Six years of annual trawl data and physical parameter measurements have been collected in Chiniak Bay, Kodiak Island (Figure 1). The focus of these surveys was to assess the distribution and abundance of juvenile flatfishes in relation to habitat characteristics and to develop a multistep survey design based on these characteristics to identify sites for assessing interannual variation (Dressel, pers. comm.). From 1991 to 1994, sampling sites were distributed across a wide range of habitat types throughout Chiniak Bay. Statistical analysis of 1991 and 1992

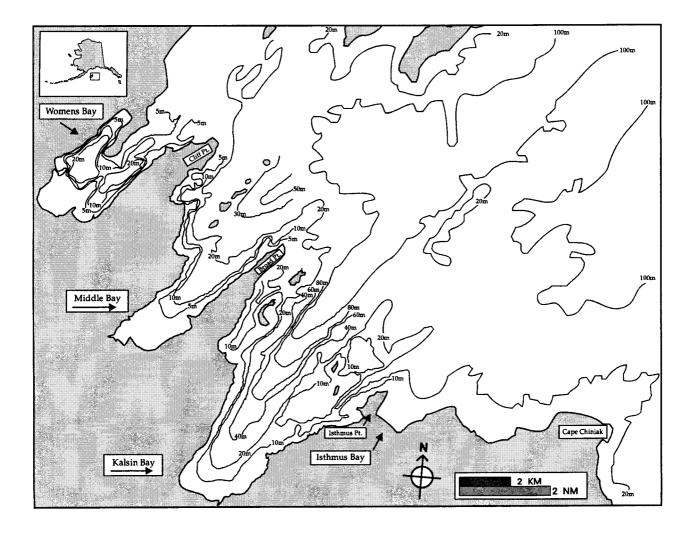


Figure 1. Chiniak Bay, northeast Kodiak Island, Alaska.

data in Chiniak Bay and around Kodiak Island showed depth and sediment to be the two habitat parameters most closely related to the distribution of the four species targeted in this study: age-0 flathead sole and Pacific halibut, age-1 yellowfin sole, and age-0 rock sole (Norcross et al., 1997). Depth and sediment parameters were then used to stratify sampling in 1995.

In the 1995 survey, multiple samples were taken on the predominant sediment types within each 10-m depth interval for a total of thirteen strata. Each of the four target species had distinct habitat preferences (Norcross et al., 1995). Variances of species abundance estimates were less within strata than across strata. While abundances of these four species have varied interannually, the locations of centers of abundance for each species remained relatively consistent among years. This trend appears to be due to the strong association with habitat type as defined by depth and sediment type. Interannual changes in abundance resulted in spreading and shrinking distributions around the centers of abundance, and is consistent with the "basin model" of MacCall (1990).

The final stage of the survey design was implemented during 1996. Prior to the 1996 collections, sampling effort was reallocated into a total of five strata, and relative sample sizes were predicted for each species in each strata according to the method of optimal allocation (Thompson, 1992). Since the strata with the highest mean fish abundances had the highest variances, and since the optimum allocation method assigns a greater sample size to strata with higher variances and higher costs, strata closer to the center of each species' abundance required more samples than strata on the outskirts. Sampling in 1996 was conducted primarily on the outskirts of each species' distribution range where interannual changes in abundance could be assessed from data with minimal sampling variance. The result of this multistep habitat based survey design is that interannual variations in abundance for juvenile flatfish in this region can be assessed and monitored with less effort and cost.

## II. The effects of seasonal temperature and salinity patterns on distribution, abundance, and growth of juvenile flathead sole and rock sole in Kachemak Bay, Alaska

Seasonal and interannual distributions in bottom temperature and salinity in Kachemak Bay were investigated in spring, summer, and winter from September 1994 to August 1996 (Abookire, 1997). Bottom temperatures in both May and August 1996 were higher than in 1995. Differences in bottom temperatures, but not salinities, were present among transects within the bay in May 1995, February 1996, and August 1995 and 1996. In the winter, deep mixing of the water column was observed.

Distribution and abundance of flatfishes were not related to bottom water temperatures or salinities. The seasonal offshore movement of rock sole could not be attributed to changes in bottom temperatures; thus, other unmeasured factors such as winter mixing, competition, or food availability may have influenced their distribution. Temperature did not define habitats for these species beyond previously defined models based on depth and sediment (Abookire and Norcross, in press). Differences in fish abundance were not related to seasonal or interannual temperature differences.

Mean length increases of flathead sole and rock sole 1994 and 1995 year-classes were compared within and between species to examine the relationship between growth rate and temperature. Among seasons, growth was greatest from spring to summer, and temperature had a positive effect on growth. However, temperature differences between years had a positive relationship with growth only for flathead sole age-1. The results indicate that other unmeasured factors such as food quality or quantity may be important for growth of flathead sole and rock sole in Kachemak Bay. To monitor year-class strength of flathead sole and rock sole, it is recommended that specific habitats be sampled in mid-August when abundances are high.

## III. Depth and sediment as determinants of distribution of juvenile flathead sole and rock sole

Three transects in Kachemak Bay (Figure 2) were sampled in September 1994, May and August 1995, and February, May, and August 1996 (Abookire and Norcross, in press). Juvenile flathead sole and rock sole were the most abundant flatfishes, comprising 65-85% of all flatfishes captured at any period. Collections of fish and sediments were made at regular depth contour intervals of 10 meters. Habitat distribution was described by depth at 10-m increments and sediment percent weights of gravel, sand, and mud. Year-round habitat of flathead sole age-0 was primarily from 40 m to 60 m, and age-1 habitat was primarily from 40 m to 80 m. Summer habitat of rock sole ages-0 and -1 was from 10 m to 30 m, and in winter they moved offshore to depths up to 150 m. Both age classes of flathead sole were most abundant on mixed mud sediments, while age-1 were also in high abundance on muddy sand sediments. Rock sole ages-0 and -1 were most abundant on sand, though age-1 were also found on a variety of sediments both finer- and coarser-grained than sand. Flathead sole and rock sole had distinctive depth and sediment habitats. When habitat overlap occurred between the species, it was most often due to rock sole moving offshore in the winter. Abundances were not significantly different among seasons for age-1 flatfishes.

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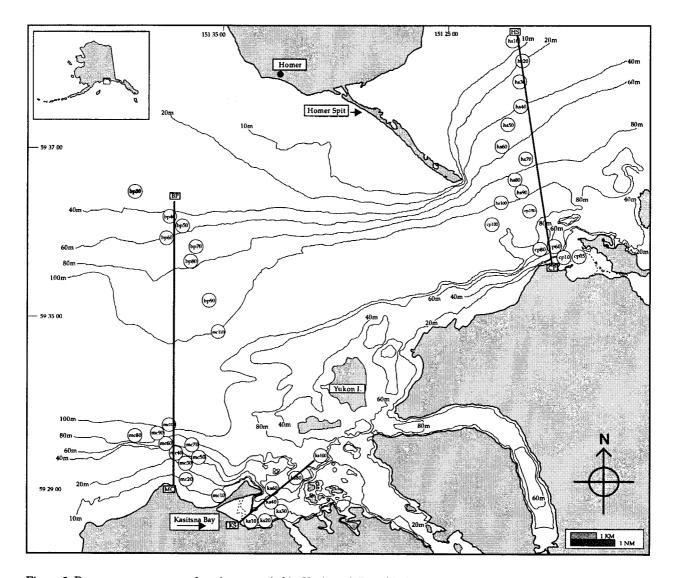


Figure 2. Permanent transects and stations sampled in Kachemak Bay, Alaska.

## **Preliminary Conclusions**

## **Chiniak Bay**

- Variances of juvenile flatfish abundances are less within depth/sediment strata than between depth/sediment strata.
- Strata with the highest mean fish abundances had the highest variances of fish abundance.
- The centers of abundance for each species are found at locations with that species' preferred depth and sediment characteristics.
- While the abundances of flathead sole, Pacific halibut, yellowfin sole, and rock sole varied interannually, the location of centers of abundance for each species remained relatively consistent among years.

- More samples are required to reduce sampling variance when the strata being assessed are closer to each species' center of abundance than are required to reduce sampling variance in strata on the outskirts of a species' abundance.
- When monitoring for interannual changes in abundance, sampling on the outskirts of each species' abundance reduces sampling variance and thus provides assessments with greater precision and reduced cost.

## Kachemak Bay

- Depth and sediment defined habitat of flathead sole and rock sole better than temperature and salinity.
- Flathead sole and rock sole had different depth and sediment habitats.
- Rock sole moved offshore during winter; this movement could not be attributed solely to changes in bottom temperatures.
- Growth of flathead sole and rock sole was correlated with temperature and was highest from spring to summer.

## **Progress Toward Objectives**

- 1) To sample juvenile flatfishes in Kachemak Bay over three oceanographic seasons (spring, summer, winter) and measure associated physical oceanographic parameters. This analysis has been completed; the seasonal distribution, abundance, and growth of flathead sole and rock sole are summarized above in section II and reported fully by Abookire (1997).
- 2) To monitor juvenile flatfish distribution, abundance, and associated physical parameters at index stations in Chiniak Bay, Kodiak Island, during August 1995 and 1996. These analyses are in progress.
- 3) To conduct graphical and statistical analyses of abundance and distribution of juvenile flatfishes in Kachemak Bay (1994–1996) and Chiniak Bay (1991–96) with respect to physical variables of location within bay, distance from shore, depth, sediment type, temperature, and salinity, plus season in Kachemak Bay and year in Chiniak Bay. Chiniak data are currently being analyzed as indicated in section I above. The use of depth and sediment as determinants of distribution of juvenile flathead sole and rock sole within Kachemak Bay are summarized above and are reported fully by Abookire and Norcross (in press).
- 4) To compare summer species composition, abundance, and distribution of juvenile flatfishes in Kachemak Bay with that of juvenile flatfishes in Chiniak Bay. These analyses are dependent upon results from the other objectives and thus are just beginning.

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## References

- Abookire, A. A. 1997. Environmental factors affecting seasonal habitat and distribution of flathead sole and rock sole in Kachemak Bay, Alaska. M.S. Thesis, University of Alaska Fairbanks. Fairbanks. 87 pp.
- Abookire, A. A. and B. L. Norcross. In press. Depth and substrate as determinants of distribution of juvenile flathead sole (*Hippoglossoides elassodon*) and rock sole (*Pleuronectes bilineatus*), in Kachemak Bay, Alaska. Netherlands Journal of Sea Research.
- Bollens, S. M., B. W. Frost, H. R. Schwaninger, C. S. Davis, K. J. Way and M. C. Landsteiner. 1992. Seasonal plankton cycles in a temperate fjord and comments on the match-mismatch hypothesis. Journal of Plankton Research 14: 1279–1305.
- Gadomski, D. M. and S. M. Caddell. 1991. Effects of temperature on early life-history stages of California halibut *Paralichthys californicus*. Fisheries Bulletin U.S. 89: 567–576.
- Gibson, R. N. and L. Robb. 1992. The relationship between body size, sediment grain size and the burying ability of juvenile plaice, *Pleuronectes platessa* L. Journal of Fisheries Biology 40: 771-778.
- Henderson, P. A. and R. M. H. Seaby. 1994. On the factors influencing juvenile flatfish abundance in the lower Severn Estuary, England. Netherlands Journal of Sea Research 32: 321-330.
- Krygier, E. E. and W. G. Pearcy. 1986. The role of estuarine and offshore nursery areas for young English sole, *Parophrys vetulus* Girard, off Oregon. Fisheries Bulletin U.S. 84: 119-132.
- MacCall, A. D. 1990. Dynamic geography of marine fish populations. University of Washington Press, Seattle. 153 pp.
- Moles, A. and B. L. Norcross. 1995. Sediment preference in juvenile Pacific flatfishes. Netherlands Journal of Sea Research 34: 177-182.

- Norcross, B. L., B. A. Holladay and M. Frandsen. 1993. Recruitment of juvenile flatfish in Alaska, Phase 1. Final Contract Report, NOAA #NA 16FD0216-01. Institute of Marine Science, School of Fisheries and Ocean Sciences, University of Alaska Fairbanks, Fairbanks. 504 pp.
- Norcross, B. L., B. A. Holladay and F.J. Müter, 1995. Nursery area characteristics of pleuronectids in coastal Alaska, USA. Netherlands Journal of Sea Research 34(1-3): 161-175.
- Norcross, B. L., B. A. Holladay, F. J. Müter and M. Frandsen. 1994. Recruitment of juvenile flatfish in Alaska, Phase 2. Final Contract Report, NOAA #NA 26FD0156-01. Institute of Marine Science, School of Fisheries and Ocean Sciences, University of Alaska Fairbanks, Fairbanks. 653 pp.
- Norcross, B. L., F. J. Müter and B. A. Holladay, 1997. Habitat models for juvenile pleuronectids around Kodiak Island, Alaska, USA. Fisheries Bulletin U.S. 95: 504-520.
- Pihl, L. 1990. Year class strength regulation in plaice (*Pleuronectes platessa* L.) on the Swedish west coast. Hydrobiology 195: 79-88.
- Reichert, M. J. M. and H. W. van der Veer. 1991. Settlement, abundance, growth and mortality of juvenile flatfish in a subtropical tidal estuary (Georgia, U.S.A.). Netherlands Journal of Sea Research 27: 375-391.
- Ronholt, L. L., F. R. Shaw and T. K. Wilderbuer. 1982. Trawl survey of ground-fish resources off the Aleutian Islands, July-August 1980. NOAA Technical Memorandum NMFS F/NWC-23. Seattle, Washington.
- Rosenberg, A. A. 1982. Growth of juvenile English sole, *Parophrys vetulus*, in estuarine and open coastal nursery grounds. Fisheries Bulletin U.S. 80: 245-252.
- Sogard, S. M. 1992. Variability in growth rates of juvenile fishes in different estuarine habitats. Marine Ecology Progress Series 85: 35-53.
- Tanda, M. 1990. Studies on burying ability in sand and selection to the grain size for hatchery-reared marbled sole and Japanese flounder. Nippon Suisan Gakkaishi 56: 1543-1548.
- Thompson, S. K. 1992. Sampling. Wiley and Sons, New York. 343 pp.
- Tyler, A. V. 1971. Surges of winter flounder, *Pseudopleuronectes americanus*, into the intertidal zone. Journal of the Fisheries Research Board of Canada 28: 1727-1732.
- van der Veer, H. W., R. Berghahn and A. D. Rijnsdorp. 1994. Impact of juvenile growth on recruitment in flatfish. Netherlands Journal of Sea Research 32: 153-173.
- Walsh, S. J. 1992. Factors influencing distribution of juvenile yellowtail flounder (*Limanda ferruginea*) on the Grand Bank of Newfoundland. Netherlands Journal of Sea Research 29: 193-203.

Norcross et al. \_\_\_\_\_\_\_47 \_\_\_\_

- Walters, G. E., G. B. Smith, P. A. Raymore Jr. and W. Hirschberger. 1985. Studies of the distribution and abundance of juvenile groundfish in the northwest Gulf of Alaska, 1980-82: Part II, Biological characteristics in the extended region. U.S. Department of Commerce, NOAA Technical Memorandum. NMFS F/NWC-77. Seattle, Washington. 95 pp.
- Weinberg, K. L., M. E. Wilkins and T. A. Dark. 1984. The 1983 Pacific west coast bottom trawl survey of groundfish resources: estimates of distribution, abundance, age and length composition. U.S. Department of Commerce, NOAA Technical Memorandum. NMFS F/NWC-70. Seattle, Washington. 376 pp.

## Testing Conceptual Models Of Marine Mammal Trophic Dynamics Using Carbon and Nitrogen Stable Isotope Ratios

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## **Abstract**

Stable isotope tracer techniques were used to investigate the ecological functioning of Steller sea lions, northern fur seals, and harbor seals in the Alaskan marine ecosystem (Figure 1). The goals were to better define the isotope ratio gradients in the environment, to test whether marine mammals have undergone changes in trophic status within the environment over the past decades, and to seek isotopic evidence of changes in primary productivity in the ecosystem.

Carbon and nitrogen isotope data for major zooplankton taxa in Alaskan waters were synthesized into contour maps defining the isotope ratio gradients in the ecosystem. The data show that the pelagic waters of the Bering Sea, Arctic Ocean, and Beaufort Sea are characterized by food chains depleted in the heavy isotopes of carbon and nitrogen whereas the regions of very high primary production on the continental shelf of the Bering Sea have the most isotope-enriched biota. The transition from low to high isotope ratios occurs across the shelf break in a band less than 100 km wide and explains the sharp changes observed in isotope ratios in marine mammal vibrissae. The zooplankton with high isotope ratios are advected northward from the Bering Sea into the Chukchi Sea and western Beaufort Sea.

Nitrogen isotope ratios within an environment are excellent indicators of trophic status of consumer organisms. I analyzed tissues from museum specimens and from more recently collected animals to test the hypothesis that the trophic status of Steller sea lions, northern fur seals, and harbor seals have changed in the past three decades in the Bering Sea. Nitrogen isotope ratios revealed no change in trophic status of the marine mammals whereas concurrent fisheries data indicated that major shifts in species composition occurred over the same period. If prey switching occurred, it appears to have taken place at the same trophic level. Some individual harbor seals as well as the northern fur seals and Steller sea lions have isotope ratios indicative of movements between continental shelf and offshore pelagic waters.

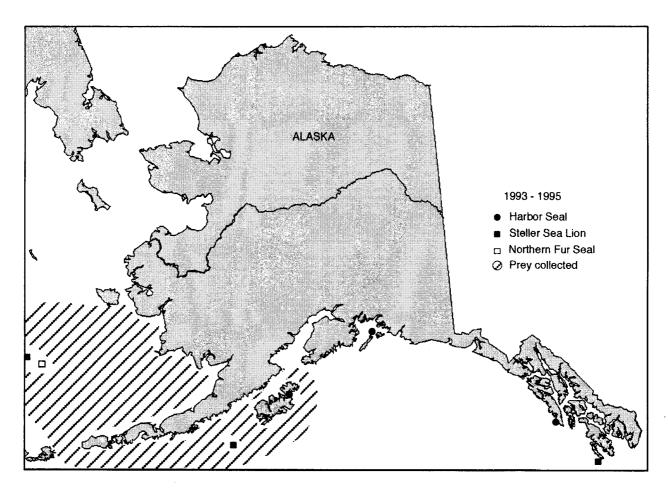


Figure 1. Locations of pinniped and prey sampling.

In this study, I constructed a long-term carbon isotope record that provides strong evidence of decreased primary productivity in the western Gulf of Alaska and Bering Sea over the past two decades. These changes are indicated by long-term shifts in the carbon isotope ratios in bowhead whale baleen and pinniped skeletal remains. By sampling bowhead whale baleen archived at the Los Angeles County Museum and baleen from whales taken in recent years, a continuous record of carbon and nitrogen isotope ratios in baleen has been constructed from 1947 to 1995. The baleen isotope ratios are a proxy for primary producers and provide indirect evidence that primary productivity was relatively stable in the Bering Sea between 1947 and 1964, increased to maximum productivity in 1966, then began to decline by approximately 2.5% per year through the last sample. The carbon isotope ratios for 1994 and 1995 are the lowest in the baleen record for the Bering Sea and imply a decrease of 30-40% in primary productivity from 1965-96 levels. Body tissues of Steller sea lions, northern fur seals, and harbor seals collected from 1950 through 1996 reflect the decrease in carbon isotope ratios. Correlative climatic and fisheries data support the possibility of a major regime shift in the biota of the region over this period.

## **Students Supported**

Two students have been supported in part by this project. Ph.D. student Amy Hirons has been studying the long-term changes in isotope ratios via use of archived tissues and modern collections. Her work is being prepared for inclusion in the final report and is abstracted above. Sang Heon Lee, an M.S. student, is currently being supported by this project. Mr. Lee is assisting in the mass spectrometry laboratory with sample preparation and weighing.

Ms. Patricia Rivera, M.S., is temporarily being supported by this project and is working in the mass spectrometry laboratory as an assistant to technician Norma Haubenstock in machine operations.

## **Study Products**

- Barnett, B. A. and D. M. Schell. 1995. Winter feeding of bowhead whales in the western Arctic: a dilemma delineated by stable isotope ratios. Eleventh Biennial Conference on the Biology of Marine Mammals, Orlando, FL, December 14-18, 1995.
- Hirons, A. C. and D. M. Schell. 1995. Prey sources and seasonal distribution of Alaskan pinnipeds as indicated by stable carbon and nitrogen isotope ratios. Eleventh Biennial Conference on the Biology of Marine Mammals, Orlando, FL, December 14-18, 1995.
- Hirons, A. C. and D. M. Schell. 1996. Trophic relationships of Alaskan pinnipeds in the Bering Sea and Gulf of Alaska as indicated by stable carbon and nitrogen isotopes. Abstracts of the 47th Arctic Division of the American Association for the Advancement of Science Conference, Girdwood, AK, September 19-21, 1996.
- Hirons, A. and D. M. Schell. 1997. Testing conceptual models of marine mammal trophic dynamics using carbon and nitrogen stable isotope ratios.

  Presentation at University of Alaska Coastal Marine Institute Annual Symposium, 25 February 1997, Fairbanks.
- Schell, D. M. 1995. Testing conceptual models of marine mammal trophic dynamics using carbon and nitrogen stable isotope ratios. Pages 86-96 In V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 2, OCS Study MMS 95-0057. Fairbanks. 121 pp.
- Schell, D. M. 1995. Testing conceptual models of marine mammal trophic dynamics using carbon and nitrogen stable isotope ratios. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1995, Fairbanks.
- Schell, D. M.1996. Testing conceptual models of marine mammal trophic dynamics using carbon and nitrogen stable isotope ratios. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1996, Fairbanks.

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- Schell, D. M. 1996. A decadal record of primary productivity in the Bering Sea inferred from stable isotopes. Abstracts of the 47<sup>th</sup> Arctic Division of the American Association for the Advancement of Science Conference, Girdwood, AK, September 19-21, 1996.
- Schell, D. M. 1996. Primary productivity in the Bering Sea: a long-term view. Climate Change and Cetaceans. Presentation at a meeting of the International Whaling Commission, Oahu, HI, 25-27 March 1996
- Schell, D. M. 1997. Testing conceptual models of marine mammal trophic dynamics using carbon and nitrogen stable isotope ratios. Pages 119-158 *In* V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 3, OCS Study MMS 97-0001. Fairbanks. 191 pp.
- Schell, D. M. 1998. Marine Ecology Progress Series.
- Schell, D. M. and A. C. Hirons. 1997. The decline of pinniped populations in the northwestern Pacific Ocean: a top-down or bottom-up response? Presentation at the North Pacific Marine Science Organization. Fifth Annual meeting, Nanaimo, BC 11-20 Oct 1996. PICES.

# Interaction Between Marine Humic Acids and Polycyclic Aromatic Hydrocarbons in Lower Cook Inlet and Port Valdez, Alaska

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## **Abstract**

Humic acid is a major component of naturally occurring organic matter which interacts strongly with organic pollutants including polycyclic aromatic hydrocarbons (PAHs). PAHs are present in petroleum and associated with significant long-term environmental impacts and public health problems. The resulting chemical associations influence the fate and effects of PAHs in the marine environment. This project investigates the interaction of marine humic acids from sediments of Lower Cook Inlet and Port Valdez, Alaska, with PAHs. Geochemical characterization of sediments and humic acids from the study area shows that their chemical composition is nonuniform, probably reflecting differences in both source materials and post-depositional alterations. This may account for the fact that the relationship between the concentration of sediment humic acid and the amount of PAHs associated with sediments in the areas studied does not fit a simple linear model. Based on this and two other studies supported by the University of Alaska Coastal Marine Institute (CMI), Braddock and Richter (1997) and Henrichs et al. (1997), humic acids appear likely to be involved in the sorption of PAHs by sediments in Lower Cook Inlet and Port Valdez.

## Introduction

This study uses sediments collected from the CMI focus region in Lower Cook Inlet and from Port Valdez, Alaska, to improve our understanding of the nature and extent of the role of naturally occurring organic material, specifically humic acids, in the association of PAHs with marine sediments.

Petroleum hydrocarbons are significant pollutants to the marine environment on a global basis (NRC, 1981) and are of great concern in coastal regions such as Cook Inlet where petroleum production and transportation coexist with productive fisheries as well as other renewable resources and environmental values. PAHs are of particular concern because many molecules in this class degrade slowly and are highly toxic or carcinogenic. Because hydrocarbons have very low solubilities in both freshwater and seawater (Shaw et al., 1986), they tend to partition into other available organic phases. One important organic phase in this regard is the naturally occurring organic matter which is a constituent of marine sediments. Humic acids are a major refractory portion of this organic matter. Sorption or other association of PAHs and other petroleum hydrocarbons with humic acid has been observed to remove these contaminants from the water column, reduce their bioavailability, and increase their persistence.

Humic acid may be defined as the fraction of organic material isolated from natural waters, soils, and sediments that is soluble in aqueous base but insoluble in aqueous acid (Parsons, 1988). Thus, humic acids are a class of organic compounds defined by solubility characteristics. Materials with a considerable range of molecular structures are all classified as humic acids. The sources of marine humic acids are generally well understood, although many of the details are unclear. Large amounts of detrital plant material together with lesser amounts of a wide variety of metabolic and excretory compounds are released to the aquatic environment during normal physiological processes and on the death of all organisms. Once in the environment, most of these materials reenter the biological cycle directly as substrates for other organisms; however, a portion undergoes a wide variety of chemical condensation reactions with other organic materials. In the condensation process, reactive portions of the molecules combine, usually without enzymatic control. This gradually leads to large (molecular weight [MW] > 1000 daltons) organic molecules with few reactive sites remaining for further condensation and little chance of being consumed by organisms. The resulting humic acids have a variable structure, reflecting the structural characteristics and origin of the initial constituent molecules.

In coastal environments, soil humic acids along with humic acid source material in the form of both flora (leaf litter, forest detritus, etc.) and fauna (excrement and decomposing remains) can be washed into the aquatic environment (Nissenbaum and Kaplan, 1972). Isotopic ratios can be used as an indicator of humic acid source locations. Humic acids derived from marine detritus are similar to, but structurally distinct from, terrestrially derived humic acids (Sastre et al., 1994). Structural differences in humic acids appear to affect their interactions with PAHs.

Seawater and marine sediments contain considerable amounts of organic material, mostly of natural origin. Because this organic material has a much greater affinity for organic compounds such as PAHs than does the water itself or the

mineral portion of sediments, the particular chemical nature of the organic matter strongly influences the fate and effect of pollutants, including petroleum and petroleum-related compounds. Humic acid material, whether dissolved in the water column or associated with mineral particles in the sediment, often shows a marked tendency to associate chemically with other organic molecules, including organic pollutants (Piccolo, 1994; Karickhoff and Morris, 1985; Karickhoff et al., 1979). Various studies involving bioavailability of hydrophobic pollutants in the presence of sediments exist (Fisher et al., 1993; Kauss and Hamdy, 1991; Moll and Mansfield, 1991); however, only a few begin to take into account the role of humic acids (McCarthy et al., 1994; Landrum et al., 1985).

Characteristics of the sediment that are thought to be important qualities influencing the binding of PAHs to sediments include the amount of organic matter present, the fraction of that organic matter that is humic acid, and the aromaticity of the humic acid present. Aromaticity is the proportion of the structural humic acid fraction that is composed of aromatic (benzene-like) rings. This quality has been hypothesized to be important because of probable binding interactions between the ring systems of the humic acids and the hydrocarbons. Humic acids have a much greater affinity for nonpolar organic pollutants than either water itself or the mineral portion of sediments (Boehm and Farrington, 1984). The humic acid–PAH association appears to result from weak dipole interactions between aromatic rings of the PAHs and similar rings which are part of many humic acids, particularly those derived from lignins and related materials of woody terrigenous plants (Chin et al., 1994).

One widely used method for the characterization of humic acids is the E4/E6 ratio. This is the ratio of two absorption bands in the visible region of the electromagnetic spectrum (wavelengths of 465 nm and 665 nm). Ratios for humic acids are usually less than 5.0 and decrease with increasing molecular weight and aromatic condensation. Thus the E4/E6 ratio has been proposed as an index of humification (Stevenson, 1994). A low ratio indicates a relatively high degree of condensation of aromatic constituents, while a high ratio implies the presence of relatively more aliphatic structures. An inverse relationship has been observed between the ratio and mean residence time of humic acid in the sediments: higher ratios have lower residence times. This leads to the conclusion that older material is more highly condensed and aromatic in nature (Campbell et al., 1958). In practice, the E4/E6 ratio can be difficult to interpret because several factors contribute to an observed value. Although from the E4/E6 value alone it is difficult or impossible to separate the effects of source material and post-depositional alteration, the ratio can be informative when used with other indicators.

Related work sponsored by CMI (Henrichs et al., 1997) has examined the sorption and desorption of radiolabeled phenanthrene and bulk sediment from Jakolof Bay in Lower Cook Inlet. They showed that sorption is linear with

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phenanthrene concentration and that sorption on the sediment surface is equivalent at all sites. In addition, they found that on a time-scale of days, sorption is rapid but desorption is slow and incomplete and that sorption coefficients vary by a factor of three among the sediments examined.

In another related CMI-sponsored project (Braddock and Richter, 1997), the microbial degradation of phenanthrene in slurries of sediment from Lower Cook Inlet was investigated. This work found that phenanthrene degraders are naturally present in low numbers in Cook Inlet sediments, that the percentage of phenanthrene mineralized decreases as its concentration in the sediment increases, that the initial rate of mineralization is dependent not on the concentration of phenanthrene sorbed to sediment but on the fraction dissolved in the aqueous phase, and, overall, that the sorption of phenanthrene to sediment decreases its bioavailability.

## **Methods**

Sediments collected in Port Valdez during 1995 (Feder and Shaw, 1996) were used in this study; locations are shown in Figure 1. Stations PV-16, PV-25, PV-33, PV-51, PV-77, PV-80, and PV-82 are subtidal locations near the Alyeska marine terminal. Stations PV-11, PV-45, and PV-50 are on a transect along the center line of Port Valdez. Stations PV-2, PV-5, PV-7, and PV-8 are located near fish processing plant discharges adjacent to the Valdez municipal boat harbor, and station PV-37 is located in northcentral Port Valdez. PV-91 and Anderson

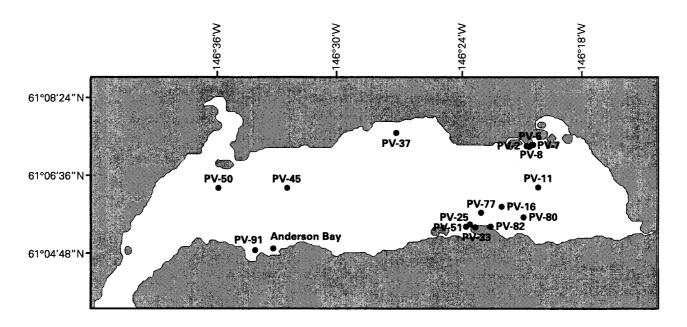


Figure 1. Sampling locations in Port Valdez, Alaska, used in this study.

Bay are in southwest Port Valdez. Stations were chosen to provide a range of anthropogenic influence, particularly in respect to petroleum input.

Samples for this study were also taken from Lower Cook Inlet during August 1996 (Figure 2). Homer Boat Harbor sediment was taken from directly below the harbor master's office. The Homer Mud Flat station is in Coal Bay on Homer Spit. Bishop Beach is located at the end of Bunnel Street in Homer. Jakolof Bay sediments (Jakolof-1, Jakolof-2, Jakolof-3, Jakolof-4, and Jakolof-5) were collected from the head of Jakolof Bay (Henrichs et al., 1997; Braddock and Richter, 1997). The Tutka Bay sample is from the head of Tutka Bay and Seldovia Beach sediment is from the head of Seldovia Bay. Stations were selected to provide a range of anthropogenic influence, sediment grain size, and organic matter content.

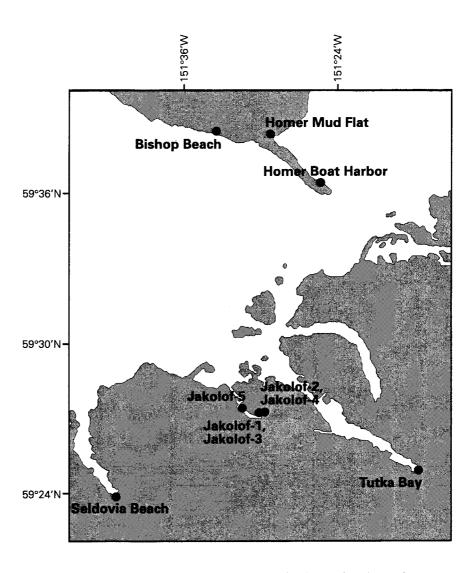


Figure 2. Sampling locations in Lower Cook Inlet, Alaska, used in this study.

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Humic acids were obtained using an extraction procedure based on Anderson and Schoenau (1993). Approximately 30 g of weighed, wet sediment was added to a 250-mL Nalgene centrifuge bottle with a sealing cap containing 150 mL of 0.5M HCl and shaken on a wrist-action shaker for 10 min to remove floating plant debris and acid-volatile inorganic forms of C, N, P, and S. The sample was then centrifuged for 20 min at low speed (g force unknown). Next, the sediment was washed with 150 mL of double-distilled water and centrifuged again as described above. The supernatant solutions from both washes were discarded. Then 150 mL of freshly prepared 0.5M NaOH was added to the washed sediment sample and the headspace was flushed with N2 gas to minimize hydrolysis and oxidation of humic and fulvic acids. The sample was then shaken for 20 hours and centrifuged as above. The supernatant was decanted into a tared centrifuge bottle and the residual sediment was discarded. The humic acid portion of the supernatant was precipitated by adding 6M HCl until a pH of 1.5 was obtained. Approximately 23 mL of acid was required. The precipitated extract was allowed to stand for 15 min and then centrifuged for 30 min as described above. After centrifugation, the fulvic acid supernatant was decanted and a portion was stored in a glass scintillation vial. The precipitated humic acid was lyophilized at -85° C for 24 hours. The resulting dry humic acid was weighed and stored in a glass vial. The water content of the sediment was determined by drying a weighed aliquot of sediment and reweighing. Each sample was extracted in duplicate and the mean percentage humic acid was reported.

Determination of total polycyclic aromatic hydrocarbons (TARO) and total organic carbon (TOC) followed Feder and Shaw (1996). TARO is the sum of the concentrations of eighteen individually quantified two- to five-ring PAHs.

Cross-polarized magic angle spinning <sup>13</sup>C nuclear magnetic resonance (nmr) spectroscopic data were obtained from Florida State University in Tallahassee on six of the samples (PV-25, PV-82, PV-91, Homer Boat Harbor, Jakolof-4, and Tutka Bay). Aromaticity was calculated by integrating the area between 100 and 160 ppm (aromatic region) and dividing it by the area between 0 and 200 ppm (entire spectrum) minus the area between 160 and 190 ppm (carbonyl region). This gives carbonyl-free aromaticity as a percent of the entire humic acid fraction. The aromaticity was then multiplied by the percent humic acid found in the sediment to give aromatic abundance.

Fourier transform infrared spectra were obtained using a Nicolet model 560 FT-spectrometer with an infrared source, KBr beamsplitter, and a MCT/B detector. The operating software, OMNIC, was used to acquire and process the spectra. Signals were averaged from 200 scans and a resolution of 0.121 cm<sup>-1</sup> processed against a background of KBr. Humic acid samples were prepared as KBr pellets (0.200 g KBr and 0.005 g humic acid) and spectra obtained between 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup>. After baseline correction, a ratio of peak heights corre-

sponding to aliphatic carbon deformation modes (1535 cm<sup>-1</sup>) and aromatic carbon stretching (1658 cm<sup>-1</sup>) was found. By plotting these ratios against the aromaticity from nmr, the empirical relationship was obtained and used to calculate aromaticities for the remaining humic acids samples.

The E4/E6 ratio of the extracted humic acids was calculated using ultra-violet-visible (uv-visible) light spectroscopy. A Milton Roy Spectronic 21D uv-visible spectrometer was used to determine the light absorbance characteristics of the humic acids. Humic acid (2–4 mg) was dissolved in 10 mL of 0.05 N sodium bicarbonate (Chen et al., 1977) and light absorbance readings were taken at 465 nm and 665 nm. The ratio of these two absorbances is the E4/E6 ratio.

Isotopic analysis for  $\delta^{13}$ C and  $\delta^{15}$ N of the humic acids was done by Dr. Donald Schell's laboratory at the University of Alaska Fairbanks using a Europa 20/20 mass spectrometer equipped with Roboprep.

## **Results and Discussion**

#### **Characterization of the Sediments**

Geochemical measurements (Table 1) were made to characterize the relationship of PAHs and humic acids in 32 sediment samples (22 from Port Valdez and 10 from Lower Cook Inlet). The sediments were representative of those occurring widely in coastal marine areas of southcentral Alaska including sands and glacially derived silt-clay mixtures which are low in organic material (less than 1.0% TOC) as well as higher organic intertidal and shallow subtidal muck (1.8–5.7% TOC). Most of the sediment sampling locations have relatively low human impact, but two (the Homer Boat Harbor and PV-33, the discharge site for treated ballast water for Alyeska) were adjacent to identifiable sources of petroleum contamination. The carbon nitrogen ratios (C/N) were all less than 12.3 and generally in the range 6.5 to 10.0, indicating that the predominant source of organic matter to most of these sediments was marine algae but that vascular plants (probably including both seagrasses and terrigenous plants) also contributed to the accumulating organic matter.

The percentage of TOC ranged from 0.09 in sand from Bishop Beach in Cook Inlet to 5.66 in an intertidal sediment from Jakolof Bay. Values between 0.4 and 0.8 were common for subtidal sediments of glacial origin. The percentages of humic acid ranged from 0.17 to 7.29 with humic acid exceeding TOC at 14 of the 32 locations. This is not unexpected, as humic acids typically contain substantial quantities of oxygen. In the humic acids isolated from these sediments, carbon never exceeded 25% of the total weight. In all samples the amount of carbon in the humic acid fraction is less than the TOC value.

Concentrations of 18 PAHs were determined for each sample. Table 1 shows the concentrations of naphthalene, phenanthrene, and TARO for each sediment, all

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Table 1. Bulk characteristics of sediments studied in this project. The percentages of humic acids (% HA) and organic carbon (% TOC) are expressed relative to sediment dry weight. The weight ratio of carbon to nitrogen (C/N) is a dimensionless number, and the concentrations of aromatic hydrocarbons (naphthalene, phenanthrene, and the sum of all aromatic hydrocarbons measured, TARO) are expressed as ng of hydrocarbon per gram of dry sediment, or parts per billion, dry weight (ppb).

Site	% HA	% TOC	C/N	Napthalene	Phenanthrene	TARO
PV-2	0.61	0.65	6.69	1.7	31.1	156.7
PV-5	0.44	0.52	7.59	1.1	17.5	88.2
PV-7	0.49	0.60	7.94	<1.0	11.2	49.4
PV-8	0.46	0.57	7.08	1.2	12.4	38.2
PV-11a	0.24	0.39	8.98	<1.0	3.0	18.2
PV-11b	0.21	0.36	7.68	<1.0	1.6	13.0
PV-16	0.20	0.37	7.52	<1.0	2.7	18.3
PV-25a	0.55	0.77	11.06	<1.0	18.3	308.6
PV-25b	1.49	0.64	9.65	<1.0	6.9	91.9
PV-33a	0.54	0.71	10.97	3.4	80.2	517.4
PV-33b	0.60	0.65	9.77	1.0	16.6	137.3
PV-37	0.45	0.47	8.15	<1.0	5.4	23.8
PV-45	0.44	0.56	8.01	1.9	5.7	30.2
PV-50a	0.61	0.59	9.09	1.1	7.1	68.1
PV-50b	0.71	0.63	7.92	1.2	8.1	40.9
PV-51	0.53	0.6	9.28	<1.0	5.7	56.1
PV-77	0.30	0.41	8.07	<1.0	2.4	17.9
PV-80	0.53	0.55	8.72	<1.0	4.1	108.9
PV-82a	0.67	0.61	11.56	2.0	15.5	80.1
PV-82b	0.60	0.62	10.13	<1.0	8.1	73.1
PV-91	0.89	0.69	8.49	<1.0	6.5	36.3
Anderson Bay	0.70	0.68	8.61	<1.0	7.3	41.5
Bishop Beach	0.17	0.09	6.78	<1.0	<1.0	10.8
Homer Boat Harbor	3.75	1.76	10.35	1.7	12.3	707.5
Homer Mud Flat	2.79	2.42	10.95	<1.0	4.2	128.1
Jakolof-1	5.30	2.85	8.07	1.3	<1.0	66.5
Jakolof-2	4.80	3.20	8.78	2.1	8.0	112.2
Jakolof-3	4.07	2.70	8.08	3.1	10.3	358.6
Jakolof-4	7.29	5.66	8.76	1.8	8.7	489.3
Jakolof-5	3.30	4.48	7.59	3.3	228.6	914.4
Seldovia Beach	3.72	3.03	12.21	<1.0	12.1	109.2
Tutka Bay	1.60	1.99	6.68	2.4	4.0	52.8

reported in the units ng of hydrocarbon per g of dry sediment (parts per billion, dry weight). All of the PAH concentrations were low. The highest was 914 ng g<sup>-1</sup> (that is, less than one part per million) at Jakolof-5. The concentrations of naphthalene and phenanthrene were also low. At 16 of the 32 sites, naphthalene was below 1.0 ng g<sup>-1</sup>, the limit of quantification. Phenanthrene was below the same quantification limit at two of the sites.

## **Characterization of the Humic Acids**

Chemical characterization of the humic acid extracts from the 32 sites was made in order to assess aromatic character of the humic acids and other properties which might influence the humic acid's ability to associate with and sequester PAHs. The results of these characterizations are shown in Table 2.

The determination of percent aromaticity (the percentage of humic acid carbon atoms in aromatic rings) by nmr spectroscopy is generally thought to be more accurate than by ir spectroscopy since the peak area in nmr spectroscopy is proportional to the number of carbon atoms present; this is not the case for ir spectroscopy. However, because measurement of aromaticity by nmr consumes relatively large quantities of humic acid, nmr was used for only six samples. A preliminary estimate of aromaticity was made by ir for all samples.

Aromaticity, however it is measured, gives information about the fraction of the humic acid in a sediment which is aromatic without consideration of whether humic acid is abundant or depleted in that sediment. To obtain information about the relative amounts (as opposed to fractions) of aromatic humic acid carbon in the sediments, we multiplied the percentage of humic acid (Table 1) by the aromaticity by ir (expressed as a decimal fraction) to give a quantity we called aromatic abundance which is the percentage of humic aromatic carbon in the sediment. Although the aromatic abundance was low, typically about one part per thousand, it was much higher that the concentration of PAHs which was always less than one part per million.

Carbon and nitrogen isotope ratios were determined for the humic acids (Table 2) to determine the source of organic matter (Parker et al., 1972; Schell, 1997).  $\delta^{13}$ C values ranged from -17.4 to -27.6 and the  $\delta^{15}$ N values ranged from 1.3 to 9.4. These values are consistent with the C/N data for the bulk sediment (Table 1) and suggest that the major source of organic matter from which the humic acids were derived was marine. However, vascular plants also contributed. The mean values of both isotopes in sediments from Port Valdez were isotopically lighter ( $\delta^{13}$ C = -24.0,  $\delta^{15}$ N = 6.5) than for Cook Inlet sediments ( $\delta^{13}$ C = -20.0,  $\delta^{15}$ N = 7.3). These isotopic differences probably reflect different sources of humic acids from the two areas. Since marine algae contain less lignin and other aromatic-containing structures than do vascular plants, these source differences may give rise to structural differences and differences in the ability of the humic acids to associate with PAHs.

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Further support for structural differences between humic acids from Port Valdez and Cook Inlet sediments comes from their E4/E6 ratios (Table 2).

The mean value for sediments from Port Valdez was significantly lower than that from Cook Inlet. This suggests that the humic acids from Port Valdez are more highly condensed and aromatized, have fewer aliphatic structures, and have

Table 2. Characteristics of humic acid isolates studied in this project. The quantities and their units are discussed in the text.

Site	Aromaticity by nmr	Aromaticity by ir	Aromatic Abundance	$\delta^{15}N$	δ <sup>13</sup> C	E4/E6
PV-2		29.9	0.18	8.9	-23.8	1.31
PV-5		36.3	0.16	8.6	-24.0	1.26
PV-7		30.4	0.15	7.6	-23.7	1.28
PV-8		28.3	0.13	9.2	-23.8	1.32
PV-11a		46.0	0.11		-24.9	1.40
PV-11b		34.0	0.07		-24.9	1.37
PV-16		38.1	0.08		-24.2	1.37
PV-25a		39.4	0.22	7.1	-24.2	3.27
PV-25b	21.69	24.0	0.36	1.3	-27.6	1.99
PV-33a		30.6	0.17	5.3	-24.6	3.29
PV-33b		24.9	0.15	6.6	-24.0	1.50
PV-37		28.4	0.13	8.6	-24.1	1.32
PV-45		33.0	0.15	7.8	-23.5	1.98
PV-50a		33.4	0.20	6.5	-22.9	1.92
PV-50b		28.8	0.21	7.2	-23.0	1.37
PV-51		15.1	0.08	8.0	-23.9	1.42
PV-77		39.2	0.12		-24.0	1.35
PV-80		22.7	0.12	5.2	-23.4	1.86
PV-82a		34.0	0.23	4.7	-24.2	1.55
PV-82b	27.06	27.6	0.17	4.3	-24.4	1.62
PV-91	24.06	21.7	0.19	5.5	-22.6	1.42
Anderson Bay		36.6	0.26	5.4	-22.7	2.42
Bishop Beach		15.3	0.03			4.17
Homer Boat Harbor	33.86	29.8	1.11	8.6	-21.0	2.87
Homer Mud Flat		21.6	0.60	7.9	-21.9	3.01
Jakolof-1		22.5	1.19	7.1	-20.2	3.90
Jakolof–2		19.8	0.95	7.2	-21.1	4.03
Jakolof-3		20.5	0.83	6.9	-21.1	3.83
Jakolof-4	19.07	21.5	1.57	6.9	-17.4	3.30
Jakolof-5		23.3	0.77	9.4	-18.6	3.20
Seldovia Beach		22.1	0.82	5.6	-20.5	3.30
Tutka Bay	14.64	21.6	0.35	5.7	-18.2	2.52

longer residence times than the humic acids from Cook Inlet. All of the sediments from Port Valdez used in this study are subtidal while the sediments from Cook Inlet include intertidal and subtidal sediments collected with the intent of studying sediments with higher amounts of organic matter. It is possible, perhaps likely, that subtidal sediments from Cook Inlet contain humic acid similar to the material found in Port Valdez. In any case it is clear that there exist significant differences in the character of humic acid from different locations in southcentral Alaska. Caution should be exercised in the geographical extrapolation of conclusions.

## Relationship Between Humic Acids and PAHs

We began this project with two working hypotheses:

- 1. The amount of sediment humic acids are directly correlated with the concentration of PAHs in the sediments of Lower Cook Inlet and Port Valdez.
- 2. The aromatic character of sediment humic acids are directly correlated with the concentration of PAHs in the sediments of Lower Cook Inlet and Port Valdez.

These hypotheses were investigated with a series of correlations. Figure 3 examines the first hypothesis with a scatter plot of total PAH concentration (TARO) against percentage of humic acid in the sediments examined. The least squares best fit line has a positive slope, but the correlation is poor ( $r^2 = 0.25$ ). A scatter plot of TARO against TOC (Figure 4) shows a similar relationship with a slightly stronger correlation ( $r^2 = 0.37$ ). These two figures show that the relationship between in situ concentrations of organic carbon or humic acid and PAH concentration is more complex than can be accounted for with a simple linear correlation. The three points farthest from the line are from stations at the discharge site for treated ballast water at the Alyeska marine terminal in Port Valdez (PV-33), the Homer Boat Harbor, and a high-organic intertidal site in Jakolof Bay (Jakolof-5). These sites had relatively high concentrations of PAHs without correspondingly elevated concentrations of humic acid. These results emphasize the importance of distinguishing between standing stocks of PAHs and sediments and their potential for association.

Figure 5 shows a similar scatter plot of TARO against aromatic abundance. Again, there is a weak positive correlation ( $r^2 = 0.32$ ). The aromatic abundance values used in Figure 5 are derived from the determinations of percent aromaticity from ir data. As noted above, these are likely to have greater scatter than percent aromaticity data from nmr.

In Figure 6, aromatic abundance data derived from the nmr data are plotted against TARO. Here the data set is small (n = 6) but the correlation is stronger than in the previous scatter plots ( $r^2 = 0.90$ ).

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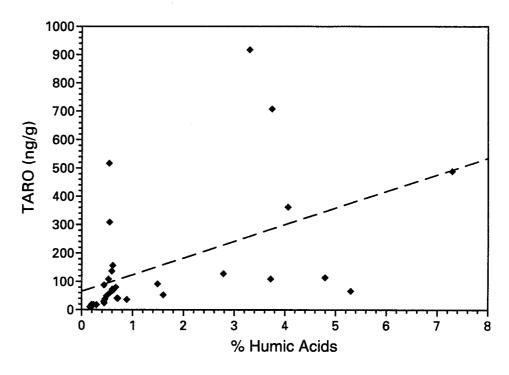


Figure 3. Correlation of total PAHs concentration (TARO) with percentage of humic acid in sediment. The dotted line represents the least squares best fit line.

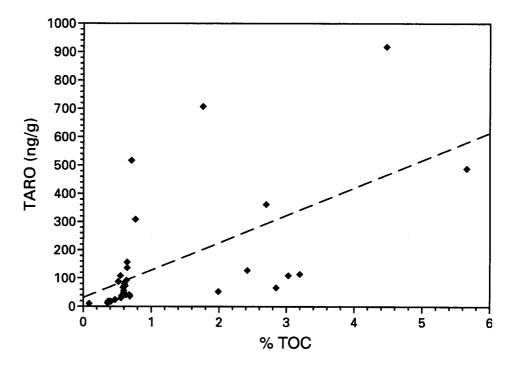


Figure 4. Correlation of total PAHs concentration (TARO) with percentage of total organic carbon (TOC) in sediment. The dotted line represents the least squares best fit line.

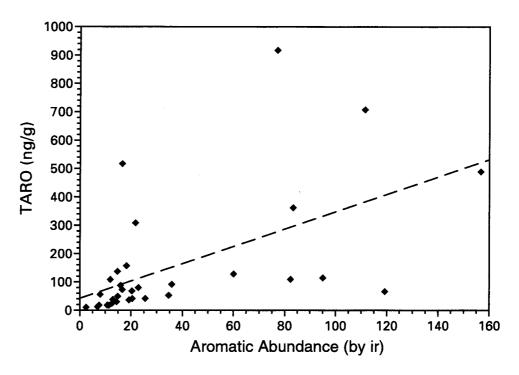


Figure 5. Correlation of total PAHs concentration (TARO) with concentration of aromatic humic carbon in sediment (aromatic abundance) determined by infrared analysis (ir). The dotted line represents the least squares best fit line.

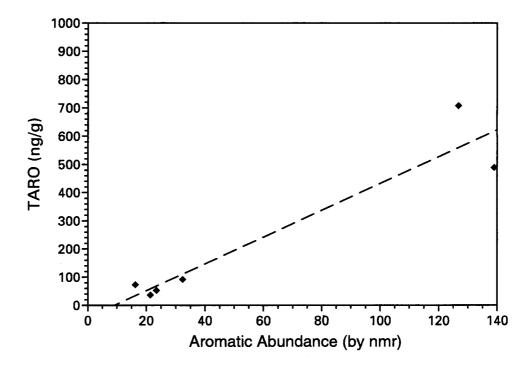


Figure 6. Correlation of total PAHs concentration (TARO) with concentration of aromatic humic carbon in sediment (aromatic abundance) determined by nuclear magnetic resonance analysis (nmr). The dotted line represents the least squares best fit line.

## **Preliminary Conclusions**

Humic acids are major components of the organic matter in all sediments from Lower Cook Inlet and Port Valdez examined in this study. Geochemical measurements including C/N ratio, isotopic composition, E4/E6, and aromaticity as determined by nmr show that the chemical composition of these humic acids is nonuniform, probably reflecting differences in both source materials and post-depositional alterations.

The relationship between the concentration of sediment humic acid and the amount of PAHs associated with sediments in the areas studied does not fit a simple linear model. Whether this reflects differences in chemical character of the humic acids, differences in the available concentrations of PAHs or some combination of these and other factors is not known.

Based on limited data (n = 6), the aromatic content of humic acids as determined by nmr appears to correlate strongly with the sediment concentrations of PAHs.

Based on this study and the studies of Braddock and Richter (1997) and of Henrichs et al. (1997), humic acids appear likely to be involved in the sorption of PAHs by sediments in Lower Cook Inlet.

## **Future Work**

The final year of this project will concentrate on obtaining additional measurements of humic acid aromaticity by nmr and on direct measurements of PAH sorption to humic acids from study area sediments. These latter measurements will be designed as an extension of measurements already performed by Henrichs et al. (1997) of the sorption of radiolabeled PAHs to bulk sediments. Humic acid isolates will be deposited onto the surface of a mineral substrate and the phenanthrene sorption coefficients will be determined for both coated and uncoated substrate. If possible, the desorption characteristics of these systems will also be investigated.

## **Acknowledgments**

We are indebted to S. Henrichs, J. Braddock, and D. Schell for advice and assistance in this work. We also wish to thank the University of Alaska Coastal Marine Institute and Alyeska Pipeline Service Company for financial support of this study.

#### References

- Anderson, D. W. and J. J. Schoenau. 1993. Soil humus fractions, p. 391-395 In
  M. R. Carter [ed.], Soil Sampling and Methods of Analysis. Canadian
  Society of Soil Science, Lewis.
- Boehm, P. D. and J. W. Farrington. 1984. Aspects of the polycyclic aromatic hydrocarbon geochemistry of recent sediments in the Georges Bank region. Environmental Science and Technology 18: 840-844.
- Braddock, J. F. and Z. D. Richter. 1997. Microbial degradation of aromatic hydrocarbons in marine sediments. Pages 5 24 *In* V. Alexander [dir.] University of Alaska Coastal Marine Institute. Annual Report No. 3, OCS Study MMS 97-0001. Fairbanks. 191 pp.
- Campbell, C. A., E. A. Paul, D. A. Rennie and K. J. McCallum. 1958. Soil Science. 104: 152-158.
- Chen, Y., N. Senesi and M. Schnitzer. 1977. Information provided on humic substances by E4/E6 ratios. Soil Science Society of America Journal 41: 352-358.
- Chin, Y. P., G. Siken and E. O'Loughlin. 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environmental Science and Technology 28: 1853-1858.
- Feder, H. M. and D. G. Shaw. 1996. Environmental studies in Port Valdez, Alaska. Final report to Alyeska Pipeline Service Company, Anchorage, AK., Institute of Marine Sciences, University of Alaska Fairbanks.
- Fisher, S. W., M. J. Lydy, J. Barger and P. F. Landrum. 1993. Quantitative structure-activity relationships for predicting the toxicity of pesticides in aquatic systems with sediment. Environmental Toxicology Chemistry 12: 1307-1318.
- Henrichs, S. M., M. Luoma and S. Smith. 1997. A study of the adsorption and biodegradation of aromatic hydrocarbons by marine sediments. Pages 49-62 *In* V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 3, OCS Study MMS 97-0001. Fairbanks. 191 pp.
- Karickhoff, S. W. and K. R. Morris. 1985. Sorption dynamics of hydrophobic pollutants in sediment suspensions. Environmental Toxicology Chemistry 4: 469-479.
- Karickhoff, S. W., D. S. Brown and T. A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Research 13: 241-248.
- Kauss, P. B. and Y. S. Hamdy. 1991. Polycyclic aromatic hydrocarbons in surficial sediments and caged mussels of the St. Marys River, 1985. Hydrobiologia. 219: 37-62.
- Landrum, P. F., M. D. Reinhold, S. R. Nihart and B. J. Eadie. 1985. Predicting the bioavailability of organic xenobiotics to *Pontoporeia hoyi* in the presence of humic and fulvic materials and natural dissolved organic matter. Environmental Toxicology Chemistry 4: 459-467.

Shaw and Terschak \_\_\_\_\_\_\_67 \_\_\_\_

- McCarthy, J. F., J. Strong-Gunderson and A. V. Palumbo. 1994. The significance of interactions of humic substances and organisms in the environment. Pages 981 997 *In* N. Senesi and T. M. Miano [eds.] Humic Substances in the Global Environment and Implications for Human Health. Elsevier Science.
- Moll, R. A. and P. J. Mansfield.1991. Response of bacteria and phytoplankton to contaminated sediments from Trenton Channel, Detroit River. Hydrobiologia. 219: 281-299.
- National Research Council. 1981. Oil in the sea: inputs, fates, and effects. National Academy Press, Washington, D. C.
- Nissenbaum, A. and I. R. Kaplan. 1972. Chemical and isotopic evidence for the *in situ* origin of marine humic substances. Limnology and Oceanography 17: 570-582.
- Parker, P. L., E. W. Behrens, J. A. Calder and D. Schultz. 1972 Stable carbon isotope ratio variations in Gulf of Mexico sediments. Contributions in Marine Science 16: 139-147.
- Parsons, J. W. 1988. Isolation of humic substances from soil and sediments. Pages 3 14 *In* F. H. Frimmel and R. F. Christman [eds.] Humic Substances and their Role in the Environment. Wiley.
- Piccolo, A. 1994. Interactions between organic pollutants and humic substances in the environment. Pages 961 979. *In N. Senesi and T. M. Miano [eds.]*Humic Substances in the Global Environment and Implications for Human Health. Elsevier Science.
- Sastre, I., M. Martinez, M. A. Vicente and M. C. Lobo. 1994. Characterization of humic substances from a reservoir in central Spain: a comparison of the terrestrial and aquatic sediments. Pages 883 888. *In* N. Senesi and T. M. Miano [eds.] Humic Substances in the Global Environment and Implications for Human Health. Elsevier Science.
- Schell, D. M. 1997. Testing conceptual models of marine mammal trophic dynamics using carbon and nitrogen stable isotope ratios. Pages 119 158 In v. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 3, OCS Study MMS 97-0001. Fairbanks. 121 pp.
- Shaw, D. G., M. Haulait-Pirson, G. T. Hefter, and A. Maczynski [eds.] 1986. The solubility data series, Vol. 38, Hydrocarbons C8 to C36 with water and seawater. Pergamon Press.
- Stevenson, F. J. 1994. Humus chemistry: genesis, composition, reactions, 2nd ed. Wiley.

# Circulation on the North Central Chukchi Sea Shelf

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#### **Abstract**

Current meter moorings (sponsored by the University of Alaska Coastal Marine Institute, the National Science Foundation, the Office of Naval Research, and the Japan Marine Science and Technology Center) were deployed on the north central and northeast shelf of the Chukchi Sea between September 1993 and September 1995 to investigate shelf circulation processes. Data from a portion of this array form the basis of this annual report. The results show that, on average, waters move northward and eastward across the central Chukchi shelf, parallel to the isobaths, but opposite to the prevailing wind direction. The mean circulation is established primarily by the sea-level slope between the Pacific and Arctic oceans. The mean flow probably advects biologically rich water from the central shelf to the Alaskan coast and transports relatively dense shelf waters into the subsurface, eastward-flowing boundary current along the Chukchi-Beaufort continental slope.

The bathymetry markedly influences the flow and, from spring through fall, steers a northward flow of relatively warm water across the shelf. This flow exerts an important thermodynamic control on the ice pack as it retreats across the shelf from spring through fall. These warm waters represent a source of heat to the ice and are likely responsible for the perennial formation of large embayments in the ice edge at several locations along the retreating pack. We found circumstantial evidence for relatively stagnant flow around two important shoal regions on the central shelf. These findings comport with recent results suggesting that Taylor columns forming over the shoals trap water over and along the shoals.

Much of the flow variability is wind-forced, although the effects of seasonal thermohaline processes can be substantial. From fall through early spring, horizontal density gradients (fronts) formed whose strength and sign varied as a result of the seasonal effects of sea-ice formation and advection of different water masses from the southern Chukchi shelf and northern Bering Sea. These gradients appear sufficient to force baroclinic currents with magnitudes comparable to the mean flow.

In the winter of 1993–94, cold, hypersaline waters formed within the extensive coastal polynyas which lie athwart the northwest coast of Alaska. The data suggest that dense water propagates along the bottom into the central Chukchi Sea as eddylike features with speeds of 0.1–0.2 m s<sup>-1</sup> and length scales of 10–20 km. The data corroborate theoretical model results that predict that dense water, formed within polynyas, generates vigorous eddies via baroclinic instability. These findings suggest that bottom-confined eddies are a potentially significant transport mechanism on arctic shelves. These eddies conceivably ventilate the subsurface layers of the Arctic Ocean with shelf waters and they might be precursors to the eddies that populate the Canada Basin.

Considerable interannual variability exists in wintertime thermohaline structure and in production of dense water on the Chukchi Sea shelf. For example, in 1993–94 water column temperatures became isothermal at the freezing point by mid-December and extensive coastal polynyas formed in January. Substantial volumes of hypersaline water (S>34) formed during that winter. By contrast, in 1994–95, water column temperatures were still above freezing on some parts of the shelf through early February, and only small polynyas formed. Consequently, virtually no hypersaline water formed in the winter of 1994–95. The differences between these two years are related to the fall–early winter evolution of the shelf ice cover. In fall 1993, extensive open water areas existed over the Chukchi shelf exposing large areas to freezing temperatures. In fall 1994, thick ice from the previous winter covered much of the shelf and effectively prevented the loss of heat from the water during fall–early winter cooling.

Some of these results were presented at meeting held May 9–12 in Virginia Beach, Virginia. The meeting involved principal investigators and scientists interested in the Ocean-Atmosphere-Ice-Interaction component of the National Science Foundation's Arctic System Science Program.

### Study Products

- Weingartner, T. J. 1995. Circulation on the North Central Chukchi Sea Shelf. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1995, Fairbanks.
- Weingartner, T. J. 1995. Circulation on the North Central Chukchi Sea Shelf. Pages 97-110 *In* V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 2, OCS Study MMS 95-0057. Fairbanks. 121 pp.
- Weingartner, T. J. 1997. Circulation on the North Central Chukchi Sea Shelf. Pages 167-186 *In* V. Alexander [dir.] University of Alaska Coastal Marine Institute Annual Report No. 3, OCS Study MMS 97-0001. Fairbanks. 191 pp.

Weingartner, T. J. 1996. Circulation on the North Central Chukchi Sea Shelf. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, February 1996, Fairbanks.

Weingartner, T. J. 1997. Circulation on the North Central Chukchi Sea Shelf. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, 25 February 1997, Fairbanks, Alaska.

# Modeling the Circulation of the Chukchi Sea Shelf

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#### **Abstract**

We used a two-dimensional, nonlinear, coupled ice-ocean barotropic model to examine variability in the interannual circulation of the Chukchi Sea shelf. The model was forced by the secular pressure gradient between the Arctic and Pacific oceans' regional winds that were estimated from 6-hourly fields of sea level pressure forecast by the Fleet Numerical Meteorological and Oceanographic Center of the U.S. Navy. The model was integrated using the wind field from January 1981 through December 1995. We have found the model particularly useful in diagnosing some of the circulation features of the Chukchi shelf.

We found reasonably good agreement in comparisons of measured and modeled transport through Bering Strait. The model reproduces the major spatial and temporal modes of this shelf's circulation which is a function of the coastal geometry in conjunction with the interaction between the time-invariant secular-pressure gradient and the time-varying wind-induced sea-level gradient. The model reproduces the main flow pathways including 1) the northwestward flow through Hope Sea Valley that turns northward through Herald Valley, 2) a northward flow across the central Chukchi Sea to the east of Herald Shoal and 3) a northeastward flow that leaves the shelf through Barrow Canyon. The model corroborates inferences drawn from current meter measurements that some of the flow entering Herald Valley veers northeastward across the outer Chukchi shelf before entering the Arctic Ocean. It also corroborates data obtained from satellites, shipboard hydrography, acoustic Doppler current profiler, and moored current meters that the flow over Herald and Hanna Shoals is stagnant, possibly due to Taylor column formation.

We have used the model to characterize the transit times and trajectory paths for particles and the statistical properties of storm surges along the Alaskan coast. Finally, we have prepared a video of the mean monthly circulation from 1981 to 1995 which shows many of the features described here.

Although particular model results were not displayed, the results were useful in interpreting other data sets gathered with the support of the Minerals Management Service, the National Science Foundation, and the Office of Naval Research and presented at a meeting held May 9–12, in Virginia Beach, Virginia. The meeting involved principal investigators and scientists interested in the Ocean-Atmosphere-Ice-Interaction component of the National Science Foundation's Arctic System Science Program.

### **Study Products**

Weingartner, T. J. 1997. Modeling the Circulation of the Chukchi Sea Shelf. Presentation at University of Alaska Coastal Marine Institute Annual Symposium, 25 February 1997, Fairbanks.

### **New Projects**

Five new projects are being funded this federal fiscal year along with the ongoing projects reported above. Abstracts are presented here to show the full range of work being supported by the University of Alaska Coastal Marine Institute.

### An Economic Assessment of the Marine Sport Fisheries in Lower Cook Inlet

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While there is considerable information regarding the economic value and impact of commercial fisheries off Alaska, the economic value and impact of sport and subsistence fishing activities have not been rigorously evaluated. The marine sport fisheries of Lower Cook Inlet are the focus of a rapidly expanding tourist economy. Sport fisheries produce nonmonetary benefits to fishers and monetary benefits to tourism related businesses. Outer continental shelf exploration, development, and production activities could affect the quality of recreation opportunities and the demand for tourism related services. We will employ a regional input-output model to measure the impact of marine sport fisheries on the Kenai Peninsula economy.

# Historical Changes in Trace Metals and Hydrocarbon Contaminants on the Inner Shelf, Beaufort Sea: Prior and Subsequent to Petroleum-Related Industrial Development

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The primary purpose of this study is to ascertain whether local enrichment of trace metals and hydrocarbons in marine sediments has resulted from anthropogenic inputs during the past century. The study area is the region of recent industrial development along the Alaskan Beaufort Sea coast. Sediments will be examined for changes in the concentrations of selected trace metals (Cu, Cr, Ni, V, Pb, Zn, Cd, Ba, methyl Hg and As); normal, branched, and cyclic (tricyclic di- and pentacyclic triterpenoid) hydrocarbons; and polynuclear aromatic hydrocarbons

## The Relationship of Diet to Habitat Preferences of Juvenile Flatfishes in Kachemak Bay, Alaska

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The objective of this project is to investigate the feeding differences of the two species of flatfishes, flathead sole and rock sole, which account for 65–85% of the juvenile flatfish community in Kachemak Bay, Alaska. Specimens were collected in 1995 and 1996 in a CMI-funded study to define the habitats for juvenile flatfishes (Task Order #12041). We are examining the stomach contents, developing indices of relative prey importance, and analyzing these indices with respect to size of fish, physical characteristics of habitat of fish, and season of capture. We are also investigating feeding where the two species of fish overlap in occurrence. The study will address the relative importance of biological characteristics versus physical characteristics in defining the habitats of these prominent species.

### **Subsistence Economies and North Slope Oil Development**

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This project is a study of the mixed, subsistence-cash economies of Nuiqsut and Kaktovik, two Inupiat villages located near areas that are impacted by petroleum exploration and development on the North Slope. In order to assess the continuity and change in subsistence and wage employment activities of households, we will analyze comprehensive quantitative data sets on subsistence production and distribution and employment by households, collected over the last decade. The analysis will test for relationships between short-term changes in subsistence and other employment patterns in response to conditions in the natural, social, and economic environments. Additional materials will be collected through key respondent interviews in Nuiqsut and Kaktovik to augment and help interpret the statistical findings. The study will provide information to assess the potential impacts of petroleum development in the North Slope region on the subsistence and wage employment activities of households. The project is a collaboration between the University of Alaska and the Alaska Department of Fish and Game, and includes funding for participatory research training of a student assistant in the Alaska Native and Rural Development program.

## Wind Field Representations and Their Effect on Shelf Circulation Models: A Case Study in the Chukchi Sea

Arctic pollutant transport models use forcing by winds estimated from atmospheric forecasts of the surface pressure field. There are uncertainties inherent in these forecast pressure fields which lead to errors in the surface winds and the circulation models dependent upon these winds. I am investigating the differences between three nominally identifiable wind field representations derived from surface atmospheric pressure fields prepared by 1) the European Center for Medium Weather Range Forecasting, 2) the US Navy's Fleet Numerical Oceanography Center, and 3) Rutgers University. We will:

analyze wind and surface atmospheric pressure data from the National Weather Service' Barrow, Alaska, office to examine differences between observed and estimated winds, and

analyze ice drifting buoy data from the International Arctic Buoy Program to examine differences between observed and interpolated surface atmospheric pressure and differences between observed and simulated ice drift.

We will examine the differences in shelf circulation as predicted by barotropic shelf circulation models (2D and 3D) when forced by these three wind fields. The results of this study will lead to a better understanding of the uncertainty in wind products and the circulation predictions that rely on these wind fields.

### **Funding Summary**

### **Student Support**

The cooperative agreement which formed the University of Alaska Coastal Marine Institute (CMI) stressed the need to support education as well as research. The following student support information is summarized from proposals and may not accurately reflect actual expenditures:

	Funds from MMS	Match from other sources
Fiscal Year 94		
7 Master Students	\$ 67,000	\$ 37,400
2 Doctoral Students	23,000	9,200
Source Totals	\$ 90,000	\$ 46,600
Fiscal Year 95		
7 Master Students	\$ 115,400	\$ 57,200
4 Doctoral Students	59,600	12,800
Source Totals	\$ 175,000	\$ 70,000
Fiscal Year 96		
10 Master Students	\$ 133,000	\$ 31,800
1 Doctoral Student	4,000	0
Source Totals	\$ 137,000	<b>\$</b> 31,800
Fiscal Year 97		
4 Master Students	\$ 76,700	0
1 Doctoral Student	0	\$ 21,500
Undeclared or Undergra	ad 3,900	0
Source Totals	\$ 80,600	\$ 21,500
Totals to Date	\$482,600	\$169,500

These figures show a strong commitment to graduate student education by MMS through CMI. Approximately 13% of the funding provided by MMS has gone directly to support students involved in coastal and OCS-related research in Alaska.

#### **Total CMI Funding**

The total MMS funding available for funding CMI projects through federal fiscal year 1997 is approximately \$4 million. Since all CMI-funded projects require a one-to-one match with non-federal monies, project commitments through fiscal year 1997 have totaled approximately \$8 million.

### **Sources of Matching Funds**

Matching for CMI-funded projects has come from a wide variety of sources. Identifying and verifying match remains a major administrative challenge in the development of CMI proposals. In general, match has been available to those investigators who expend the necessary extra effort to locate and secure the support. The following list of matching support participants demonstrates the breadth of support for CMI-funded programs:

Afognak Native Corporation

Alaska Department of Fish and Game (ADF&G)

Alyeska Pipeline Service Company

Ben A. Thomas Logging Camp

British Petroleum Exploration (BPX)

College of Natural Sciences, University of Alaska Fairbanks (UAF)

Institute of Arctic Biology, UAF

Institute of Marine Science, UAF

Japanese Marine Science and Technology Center (JAMSTEC)

Kodiak Island Borough

North Slope Borough

UAF Equipment Fund

University of Alaska Museum, UAF

University of Northern Iowa

Water Research Center, UAF

Some of the CMI-funded projects are closely related to other federally funded projects which cannot be considered as match but nevertheless augment and expand the value of a CMI project. Related projects have been funded by the

National Science Foundation (NSF), the Office of Naval Research (ONR), the National Aeronautics and Space Administration (NASA), the National Marine Fisheries Service (NMFS), the National Oceanographic and Atmospheric Administration (NOAA), and Alaska Sea Grant.

A positive relationship has been fostered between MMS, the University of Alaska, and the State of Alaska since the formation of CMI. Residents of Alaska, as well as the parties to the agreement, benefit from the cooperative research that has been and continues to be funded through CMI.

