USGS

WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: Mercury Levels in Alaskan Rivers: Relationship Between River Hg Levels and Local Atmospheric Levels

Focus Categories: WQL, SW

Keywords: Heavy Metals, Contaminant Transport, Water Quality Monitoring, Toxic Substances

Duration: 1 March 2000 to 28 February 2002

FY 00 Federal Funding: $17,263

FY 00 Non-Federal Funding: $15,317

Principal Investigators:

Dr. Lawrence K. Duffy
Institute of Arctic Biology
University of Alaska Fairbanks
Fairbanks, AK 99775

Congressional District: Alaska

Overview

Global atmospheric chemical cycling of Hg and exchange at air-water, air-soil, and soil-water interfaces are major processes affecting the mobilization of Hg on earth. Once in a water system, Hg bioaccumulation and biomagnification can occur. In Alaska, there is little information on processes and transport pathways related to Hg accumulation in water; however, there is major concern in relation to wildlife and human subsistence. In this project, we propose beginning a long-term investigation of Hg in Alaska rivers and the air above them during high flow and low flow periods. For this, we would measure total mercury and methyl mercury. We would also provide opportunities for local residents to participate in the evaluation and to disseminate our research results by building a comprehensive education effort to inform the public of the changing levels of the mercury in their local environment. This research follows the priorities and direction set by the Arctic Council and AMAP. This proposal will address a data gap in which atmospheric contaminant inputs from river sources are insufficiently known.

This proposal will complement studies in Western Alaska and the Bering Sea in which mercury levels in salmon, crabs and sediment are being measured as well as NOAA atmospheric research in Barrow. Global atmospheric chemical cycling of Hg and

exchange at air-water and soil-water interfaces are major processes affecting the mobilization of Hg on the earth. Human activities may have changed the natural biogeochemical cycle of toxic metals in many ecosystems. Global climate change can increase the risk of exposure of Northern people to this toxic metal by changing its chemical form (species) and its rate of remobilization and bioaccumulation. In this project, we propose beginning a long-term investigation of Hg in Alaskan rivers.

Preliminary Studies

Water samples from local lakes and rivers were analyzed for mercury in order to establish baseline levels for comparison between atmospheric deposition and mineral runoff. Table 1 summarizes the data in which glacial rivers can be distinguished from lakes and non-glacial rivers. The glacial rivers averaged 26.4 ng/L of Hg while the non-glacial fed rivers mean Hg level was 10 fold lower with a Hg mean of 2.0 ng/L. The large variation in the Yukon River should be noted. During the early summer with high flow rate and runoff, mercury levels were 4 fold higher. The lakes around Fairbanks were five to ten fold lower than the Chena River. Differences in geology could be observed when Fairbanks lakes were compared with those around Delta Junction, 50 miles to the southeast where the Hg mean was 2.4 ng/L. In order to understand the effect of global change, local input must be characterized before one can understand the effect of long distance transport.

These baseline studies are a first attempt to begin systematically monitoring the mercury transport in three major Alaskan rivers and selected lakes. From studies in the Lower 48, it is evident that deposition and runoff of mercury into natural waters is a major feature of Hg entering the food web. Our design of three river sites in Alaska will allow us to focus on developing an extensive set of data for the various forms of Hg in these rivers and the air above these sites. Recently, levels of Hg were measured in the Alaskan surface atmosphere was measured by us and are listed in Table 2.

Objective

The data listed in Tables 1 and 2 in the appendix lead to the question, “Are Hg levels in Alaskan glacial rivers a major source of local atmospheric mercury levels?” A corollary of this hypothesis is that seasonal variations in Hg levels will be related to river flow rates. This hypothesis is supported by recent data presented by Brooks et. al. (1999 CIFAR Arctic Research Workshop, “Atmospheric mercury in the Arctic Environment”). They report that: “ The timing and sequence of the episodic depletions and enhancements appear to follow similar patterns for both Barrow and Alert when adjusted for the difference in local polar sunrise and snow melt dates. Both data sets show similar structure, with Barrow showing much greater variability”. However, in their analysis, the effects of neither river flow rates nor aqueous particulate Hg were considered.

Research Design and Methods

Research Design

The following 3 sites will be sampled 3 times during the summers and winter years. Two years are planned in order to observe the magnitude of year effects. Water will be sampled at several depths and river flow will be recorded.

Yukon River	Bridge Area
Tanana River	Boat Landing Area
Kuskokwim River	Bethel Area

At each site surface air samples will be collected by activity pumping air through a collection tube for 4 hours. Samples of opportunity from other sites will also be collected and analyzed. Standard analytical and statistic techniques will be used.

Air Analysis

The analyses are conducted by the gold amalgamation technique with detection by cold vapor atomic fluorescence spectropscopy (CVAFS) and analysis. Particulate Hg is determined following pyrolysis of a quartz wool plug after collection and CVAFS analysis. Chemical speciation of the gaseous phase is achieved through collection on a gold amalgamation tube, isothermal GC and analysis by CVAFS detection.

River Water Analysis

River water is collected by hand with a Teflon® sampling bottle. To determine volatile Hg species, we will purge fresh, unfiltered water samples onto a Carbotrap™ gold/sand column train, followed by cryogenic gas chromatography and CVAFS detection. Peak height (chart recorder) is measured as a function of mercury concentration. Typical detection limits for this method, using a 1 L sample, are 0.0001 $ng \cdot L^{-1}$ for (CH_3) Hg, and 0.0002 $ng \cdot L^{-1}$ for Hg°.

Quality Control

Selected water samples will be sent to Frontier Geosciences, an EPA certified lab, for comparison with our analysis results.

Milestones

Project Timeline

Project Year	Year 1	Year 2
Project Start Date	Mar – May, 2000	Mar, 2001
Sample Collection in 3 sample sites	June-August 2000	Jan 2001 June-July 2001
Analyses of Hg	Sept-Dec 2000	Mar-May 2001
Data Interpretation, Synthesis and Annual Report	Aug 2000	July 2001
Data to SynCon	Sept 2000	July 2001
Seminar		April 2001
Final Report		May 2001
Journal Publication		Fall 2001

SELECTED BIBLIOGRAPHY:

Seiser, P. E., Duffy, L. K., McGuire, A. D., Roby, D. D., Golet, G. H., and Litzow, M. A. (in press) Comparison of Pigeon guillemot, *Cepphus Columbia*, and blood parameters from oiled and unoiled areas of Alaska eight years after the Exxon Valdez oil Spill. Mar. Pollut. Bull.

Clapp-Lilly, K. L., Roberts, R. C., Duffy, L. K., Irons, K. P., Hu, Y., and Drew, K. L. (1999) An ultrastural analysis of tissue surrounding a microdialysis probe. J. Neurosci. Methods. 90:129-142.

Isbell, M., Ricker, J., Gordian, M.E., and Duffy, L.K. (1999). Use of biomarkers in an indoor air study: lack of correlation between aromatic vocs with respective urinary biomarkers. Science of the Total Environment. 241:151-159.

Duffy, L.K., Scofield, E., Rodgers, T., Patton, M., and Bowyer, R.T. (1999). Comparative Baseline levels of mercury, Hsp 70 and Hsp 60 in subsistence fish from the Yukon-Kuskokwim Delta Region of Alaska. Comp. Biochem. Physiol. 124:181-186.

Scofield, E., Bowyer, R.T. and Duffy, L.K. (1999). Baseline levels of Hsp 70, a stress protein and biomarker, in halibut from the Cook Inlet Region of Alaska. Science of the Total Environment. 226:85-88.

Duffy, L.K., Rodgers, T., Patton, M. 1998. Regional health assessment relating to mercury content of fish caught in the Y-K Delta rivers system. Alaska Medicine 40:75-77.

Duffy, L.K., Hecker, M.K., Blundell, G.M., and Bowyer, R.T. 1999. An analysis of the fur of river otters in PWS, Alaska: Oil related hydrocarbons eight years after the *Exxon Valdez* oilspill. Polar Biology, 21:56-58..

Ben-David, M., Bowyer, R.T., Duffy, L.K., Roby, D.D. and Schell, D.M. 1998. Social Behavior and Ecosystem processes: river otter latrines and nutrient dynamics of terrestrial vegetation. Ecology 79:2567-2571.

Bodenstein, Y. and Duffy, L.K. 1998. Expression of HSP60, a stress protein, in human nasal septa cells after exposure to MTBE. Environ. Toxicol. Pharmacol., 5:79-83.

Prichard, A.K., Roby, D.D., Bowyer, R.T., and Duffy, L.K. 1997. Pigeon guillemots as a sentinel species: A dose response experiment with weathered oil in the field. Chemosphere, 35:1531-1548.

Vyas, S.B. and Duffy, L.K. 1997. Characterization of the minor impurities during synthesis of Alzheimer β-protein. Protein and Peptide Lettrs. 4:99-106.

Blajeski, A., Duffy, L.K. and Bowyer, R.T. 1996. Differences in fecal profiles of porphyrins among river otters exposed to the Exxon Valdez oil spill. Biomarkers. 1:262-266.

Vyas, S.B. and Duffy, L.K. 1996. Equilibration of a synthetic Alzheimer β-protein analog during RP-HPLC. Protein and Peptide Lttrs. 3:89-94.

Duffy, L.K., Bowyer, R.T., Testa, J.W. and Faro, J.B. 1996. Acute phase proteins and cytokines in Alaskan mammals as markers of chronic exposure to environmental pollutants. Amer. Fish. Soci. Symposium. 18:809-813.

Vyas, S.B. and Duffy, L.K. 1995. Interaction of synthetic Alzheimer β-protein derived analogs with aqueous aluminum: A low field 27AL NMR investigation. J. Protein Chem. 14:633-644.

Zhao, X. and Duffy, L.K. 1996. Ultrastructural studies on the interaction of β-amyloid peptide and mouse neuroblastoma cells NB41A3. Neurosci. Res. Comm. 18:39-46.

Zhao, X., Smith, S.L. and Duffy, L.K. 1995. Effects of ethanol as an additive on odor detection thresholds of Alaskan gasolines at sub-Arctic temperatures. Chemosphere 31:4531-4540.

Smith, S.L. and Duffy, L.K. 1995. Odor and health complaints with Alaskan gasolines. Chemical Health and Safety. 2:32-38.

Vyas, S.B. and Duffy, L.K. 1995. Stabilization of secondary structure of Alzheimer β-protein by aluminum (III) ions and D-asp substitutions. Biochem. Biophys. Res. Commun. 206(2):718-723.

Levine, M.E., Duffy, L.K., Moore, D. and Matej, L. 1995. Acclimation of a non-indigenous sub-arctic population: Seasonal variation in thyroid function in interior Alaska. Comp. Biochem. Physiol. 111A:209-214.

Duffy, L.K. 1993. Oxyfuel in Alaska: Use of interleukins to monitor effects on the immune system. Sci. Total. Environ. 151:253-256.

Duffy, L.K., Bowyer, R.T., Testa, F.W. and Faro, J.B. 1994. Evidence for recovery of body mass and haptoglobin values of river otters following the *Exxon Valdez* oil spill. J. Wildlife Dis. 30:421-425.

Danilenko, K.V., Putilov, A.A., Russkikh, G.S., Duffy, L.K., Barnes, B.M. and Ebbesson, S.O.E. 1994. Diurnal and seasonal variations of melatonin and serotonin in women with seasonal affectie disorder. Arct. Med. Res. 53:137-145.

Zhao, X., Valantas, J.A., Vyas, S. and Duffy, L.K. 1993. Comparative toxicity of amyloid β-peptides in neuroblastoma cell lines: Effects of albumin and physalaemin. Comp. Biochem. Physiol. 106C:165-170.

Duffy, L.K., Bowyer, R.T., Testa, J.W. and Faro, J.B. 1993. Chronic effects of the *Exxon Valdez* oil spill on blood and enzyme chemistry of river otters. Environ. Toxicol. Chem. 13:643-647.

Duffy, L.K., Testa, J.W., Bowyer, R.T. and Faro, J.B. 1993. Differences in blood haptoglobin and length-mass relationships in river otter *(Luttra canadensis)* from oiled and nonoiled areas of PWS. J. Wildlife Dis. 29:353-359.

Segal, A. and Duffy, L.K. 1992 Ethanol elimination among different racial groups. Alcohol: Clinical and Exp. Res. 9:213-217.

Borgese, T.A., Harrington, J.P., Duffy, L.K. and Bourke, S. 1992. Function studies on goosefish hemoglobin. Comp. Biochem. Physiol. 101B:535-539.

Zhao, X., Schoenheit, C. and Duffy, L.K. 1991. A heparin-binding protein from neuroblastoma cells: Immunological comparison to β-amyloid precursor protein, Comp. Biochem. Physiol. 100A(3): 715-718.

Kowall, N.W., Beal, M.F., Busciglio, J., Duffy, L.K. and Yankner, B.A. 1991. An in vivo model for the neurodegenerative effects of β-amyloid and protection by substance. Proc. Natl. Acad. Sci. (USA). 88:7247-7251.

Yankner, B.A., Caceres, A. and Duffy, L.K. 1990. Nerve growth factor potentiates the neurotoxicity of β-amyloid. Proc. Natl. Acad. Sci. USA. 87:9020-9023.

Yankner, B.A., Duffy, L.K. and Kirschner, D.A. 1990. Neurotrophic and neurotoxic effects of β-amyloid: Reversal by tachykinin neuropeptides. Science. 250:279-282.

Atmospheric Mercury in the Arctic Environment

Steven B. Brooks and Tilden P. Meyers, NOAA/ERL/ARL, Atmospheric Turbulence and Diffusion Division, 456 S. Illinois Avenue, P.O. Box 2456, Oak Ridge, TN 37831-2456, phone 423-576-1245; fax 576-1327, brooks@atdd.noaagov ; Steven L. Lindberg, Environmental Sciences Division, Oak Ridge National Laboratory, Bethel Valley Road, P.O. Box 2008, Oak. Ridge, TN 37831-6038, phone 423-574-7857; fax 576-8646, sll@oml.gov

Atmospheric mercury is deposited by wet and dry processes to environmental surfaces, and the importance of air/surface exchange processes in the cycling of mercury in ecosystems is well known. Gaseous elemental mercury has been continuously monitored at Barrow by our group since September 8, 1998. Temperature controlled ambient air is passed through a Tekran 2537A cold vapor atomic fluorescence spectrometer sensor equipped with a Tekran model 1120 standard addition controller. The instrument is self calibrating from an internal mercury permeation source, and the controller periodically substitutes clean air or permeation source mercury into the measurement cycle to confirm the proper function of the instrument.

An important recent observation at the Canadian Arctic research site at Alert is the existence of so called mercury depletion events, in which total gaseous mercury decreases rapidly from normal background levels (1.5 1.8 ng m 3) to levels <0. I ng m 3 during polar springtime (Environment Canada). An important objective of the Barrow project is to confirm such events at a more southern Arctic site. We have found that such events do occur at Barrow and may be widespread Arctic or polar phenomena. The timing and sequence of the episodic depletions and enhancements appear to follow similar patterns for both Barrow and Alert when adjusted for the difference in local polar sunrise and snow melt dates. Both data sets show similar structure, with Barrow showing much greater variability. In addition, in both the Barrow and Alert datasets, the episodic depletions/ enhancements are strongly correlated to surface ozone concentrations and at least at Barrow are strong functions of wind speed (boundary layer entrainment rate) and temperature (chemical reaction rate).

SynCon: An Arctic Contaminants Knowledge Base System

Kara Nance, Dept. of Mathematical Sciences, University of Alaska Fairbanks, Fairbanks, AK 99775 6660; Shari George, Alaska Data Visualization and Analysis Lab, University of Alaska Fairbanks, Fairbanks, AK 99775-7320

The SynCon System is a knowledge base data system for the SYNthesis of CONtamination data. Focusing on Arctic data, the SynCon System was designed with the needs of the Arctic scientist in mind. Utilizing the latest technologies in geographic information systems and data organization, it provides foundational data support for scientists including the ability to serve as a permanent data repository for Arctic contamination data. Scientists can contribute their data to the system in a variety of formats, where it can then be made accessible in graphical or textual output. Multiple data sets can be combined to provide additional research support and scientific insight.