# Report as of FY2006 for 2006ND74B: "Stoichiometry and the Transfer of Mercury from Benthic Microinvertebrates into Game Fish"

# **Publications**

- Conference Proceedings:
  - McEwen, Daniel C. and M. G. Butler, 2007, "Macroinvertebrate Responses Associated with a Change in Water-Level Regulation of Lakes in Voyageurs National Park, Minnesota", Third International Water Conference, International Water Institute, Grand Forks, March 13-15.

# **Report Follows**

# STOICHIOMETRY AND THE TRANSFER OF MERCURY FROM BENTHIC MACROINVERTEBRATES INTO GAME FISH

#### **REGIONAL WATER PROBLEM**

Mercury (Hg) damages the central nervous system, altering the way that nerves conduct electrical impulses and divide, leading to lowered cognitive and metal functioning or in especially acute circumstances cerebral palsy, mental retardation or death (NRC 2000). Its effects are especially harmful to fetuses or infants during development of the nervous system. Hg emissions have continued to increase since the industrial revolution, entering aquatic food chains via atmospheric precipitation where they suspend in the water column and are uptaken by phytoplankton or settle to the bottom where they become available to bacteria (Swain *et al.* 1992). Phytoplankton, with acquired Hg, is either ingested by zooplankton or sinks to the substrate as detritus. In turn, detritus and bacteria provide a food source to macroinvertebrate benthic organisms (i.e., benthos) and bioaccumulation occurs up through trophic levels eventually to game fish that are consumed by humans (Swain *et al.* 1992, Bodaly *et al.* 1993, Fitzgerald *et al.* 1998). As a result, the EPA and various state agencies issue advisories for fish consumption where impairment occurs. The North Dakota Department of Health currently has consumption advisories listed for Devils Lake, Red River, Lake Oahe/Missouri River, Lake Sakakawea, and other waterbodies (NDDH 2003).

#### LITERATURE REVIEW

Most Hg in fish tissue comes through their diet, and since benthic invertebrates are important to the diets of most fish species, they likely transfer a high proportion of Hg from the environment (Ryder and Kerr 1978, Harris and Snodgrass 1993, Hall et al. 1997). Vander Zanden and Vadeboncoeur (2002) investigated the contribution of zoobenthic organisms to common fish species inhabiting north-temperate lakes. They combined diet data from 470 fish populations (15 species) and stable isotope data from another 90 populations (11 species) and found that on average, across all species considered, zoobenthos were a direct contributor to 50% of fish diet and indirectly provided another 15% as food for zoobenthos-supported fishes, showing that on average greater than 65% of fish diets rely on zoobenthos. Blumenshine et al. (1997) found that for fish across a taxonomic spectrum, feeding ranged from 18-90% on benthos with a mean reliance of 55%, indicating benthos were more important than planktonic resources. In a community of six piscivorous species, for all combined, the three most important prey species were yellow perch (Perca flavescens), amphipods, and dipterans (Liao et al. 2002). Even if benthos are not a primary food source for piscivores or planktivores, they are stabilizing; once a primary food source is gone, fish will feed on benthos (Blumenshine et al. 1997). Not all benthos store Hg in the same amounts with the result that some taxa will have higher concentrations relative to others (Tremblay and Lucotte 1997, Wong et al. 1997, Hall et al. 1998). Benthos concentrate Hg differentially based on size, functional feeding group, and other physiological processes (Feltmate and Williams 1991, Parkman and Meili 1993). As such benthos community structure likely affects the availability of Hg to fishes.

The kinds of benthos and fish in lakes as well as subsequent Hg accumulation rates are likely determined by nutrient limitations according resource competition theory and ecological stoichiometric (i.e., mass balance) principles (Tilman 1982). Resource competition theory, from which ecological stoichiometry is built, predicts that, in a community where two taxa, with differing body stoichiometries, are in competition, the taxon whose stoichiometry is most similar to the resource will prevail (Tilman 1980, Tilman 1981, Tilman 1982). Ecological stoichiometry predicts nutrient limitation, more than energy, determines the reproductive and competitive success of species (Reiners 1986, Sterner 1990, Elser *et al.* 1996, Sterner and Elser 2002). The direction of energy and nutrients is mostly unidirectional from benthos to pelagia, where fish act as an important vector of that transfer through ingestion of energy and nutrients in one habitat and excretion in others (Vanni 1995, Schindler *et al.* 1996, Sarvala *et al.* 1999, Jeppesen *et al.* 2000, Schindler and Scheuerell 2002).

In both terrestrial and aquatic systems, the essential stoichiometric currency is ratios of carbon:nitrogen:phosphorus; carbon because it is such a ubiquitous element in organisms, and phosphorus and nitrogen because these elements are most likely to be limiting. Carbon, nitrogen, and phosphorus are the prime constituents of major biomolecules (i.e., lipids, nucleic acids, proteins). Carbon, although an important element in organisms, is generally not limiting because of its abundance; nitrogen can be limiting, but typically its supply meets the relative needs of organisms. Phosphorus, however, is often scarce relative to needs and is thus limiting, even though it is typically needed in a much lower absolute amount relative to nitrogen or carbon. Most production in lakes is limited by phosphorus (Elser *et al.* 1990).

Relevant data for hypothesis testing of stoichiometric theory include nutrient content of consumers, understanding of homeostatic control of those nutrients in the consumer, and nutrient content of consumer resources (Sterner and George 2000). Stoichiometric data are beginning to be generated for common freshwater fish, and are sufficiently constant that published results should give a good estimate for species across environmental gradients (Davis and Boyd 1978, Sterner and George 2000, Tanner *et al.* 2000). Frost *et al.* (2003) made a first effort at stoichiometric analysis of benthic invertebrates, comparing across 9 orders from different lake environments. They found that nutrient ratios for insect orders did not differ substantially among lakes with differential nutrient supply regimes, suggesting similar homeostatic control of nutrient composition as previously found in zooplankton (Andersen and Hessen 1991). N:P ratios from lowest to highest were Amphipoda, Ephemeroptera, Trichoptera, Anisoptera, Diptera, Hemiptera, Zygoptera, Hirudinea, and Coleoptera.

Principles of mass balance apply to Hg as much as any other element in an ecosystem. As such, stoichiometry drives the dynamics of Hg accumulation from benthos to fish. For example, in a phosphorus limited system, for a fish species to maximize growth it will either have to eat high quality food (e.g., low C:P) or a higher amount of low quality food (e.g., high C:P). Suppose that to maximize growth a fish species needs to consume a given amount of phosphorus per year. In such a case, it would have to consume less high quality food compared to the low quality food to sustain maximum growth. Furthermore, consider a scenario where the low quality food has a low P:Hg relative to the high quality food. In this extreme case, Hg would accumulate to high concentrations quickly in fish. These dynamics would affect fish species differently relative to their requirement for phosphorus. These sorts of relationships can be determined with the appropriate data using coupled bioenergetic and mass balance models (Reiners 1986, Kraft 1992).

Benthic macroinvertebrate communities have historically served as good indicators of a variety of environmental conditions (Rosenberg and Resh 1993). The most stable benthos populations occur in habitats whose physical location protects organisms from the effects of near surface perturbations (Brinkhurst 1974). This research will assess the role of using benthos not only for an indicator of nutrient status of a lake, but of the susceptibility of a lake system to Hg accumulation.

## SCOPE AND OBJECTIVES

I propose continuation of a research program addressing taxonomy, stoichiometry, and benthic-pelagic coupling in the context of benthic contribution to Hg accumulation to fisheries in Minnesota and North Dakota lakes along a trophic gradient from oligotrophic to eutrophic. The objectives of this study are as follows:

- 1) Characterize the benthic community of lakes under a variety of nutrient regimes
- 2) Quantify the biomass of the constituent members of the benthic communities in those lakes
- 3) Quantify carbon, nitrogen, phosphorus, and mercury ratios for those communities as a whole
- 4) Model how those ratios impact rates of mercury accumulation and concentrations in piscivorous game fish likely to inhabit those lakes (e.g., lake trout, walleye, smallmouth bass, northern pike, etc.)
- 5) Use appropriate regression models to test whether there is a relationship between Hg and P (as a limiting nutrient) in the benthos
- 6) Provide applicable information for managers of mercury-susceptible systems

## **METHODS**

Twelve lakes will be sampled for benthic invertebrates including 3 deep, oligotrophic trout-lakes in northeast Minnesota, 3 shallow, eutrophic lakes from North Dakota and 6 mesotrophic lakes in Minnesota and North Dakota. Each lake will be sampled using a stratified sampling method, with 20 grabs per lake comprised of 60% of sampling effort at <1 m and the remaining effort split between two strata based on depth. Sampling sites will be randomly chosen using a grid on bathymetric maps, and sites will be located in the field with a GPS and depth finder. All grabs from a lake will be pooled and organisms will be separated to order or family. Samples will be dried for 24 h and dry mass will be recorded for each taxonomic group alone. All organisms will be homogenized and ground and subsamples will be analyzed for carbon, nitrogen, phosphorus, and mercury. These data will be used in a bioenergetics model to predict mercury concentration levels in game fish species, using literature-derived values for parameters not measured in the field.

#### DELIVERABLES

I will provide a framework by which lakes can be assessed for susceptibility to high Hg concentrations in fish. A stoichiometric underpinning can provide managers with a relatively easy method of assessing fish susceptibility to Hg by measuring a subsample of benthos for C:N:P. Manuscripts will be prepared for the bioenergetics models produced in terms of the relationship between nutrient limitation and Hg accumulation.

### **PROGRESS TO DATE**

I have developed our benthic sampling and fauna sorting technique over the summers of 2004-05 in a related project. Computer software has been obtained for bioenergetics modeling, and I have been successful in developing mock models with fictitious data that represent those that will be empirically derived. I am in the process of determining phosphorus concentrations of invertebrates and have contacted laboratories that provide carbon, nitrogen, and mercury analysis services. Presently, I am conducting an in-depth literature review on stoichiometric theory as well as the environmental toxicology of mercury accumulation in aquatic systems.

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