Mercury Bioaccumulation and Methylation in Stream Ecosystems

Background - The elevated level of mercury in the contemporary environment compared to pre-industrial levels is mainly due to the anthropogenic emissions such as coal burning and mining activities. Because mercury can travel around the globe and be deposited by precipitation, mercury can be found in virtually any aquatic ecosystem on the planet. Although mercury is present in extremely trace amounts in natural waters, it can be found in considerably higher concentrations in fish tissues. Elevated mercury concentrations in fish and other animals compared to water are the result of strong binding capability of mercury to biological tissues (termed as "*bioaccumulation*"), and subsequent increases of mercury concentrations with each link in the food chain (e.g. mercury concentrations follow as: fish > invertebrates > algae). As a consequence, mercury concentrations peak in the highest trophic level such as carnivorous fish, and therefore humans and wildlife species that consume fish will often be exposed to high levels of mercury [1].

However, not all chemical forms of mercury have equal tendency to bioaccumulate. In fact, it is a single organic form of mercury (i.e. methylmercury) that is responsible for the majority of mercury bioaccumulation in nature [2]. The predominant form of mercury in the environment is inorganic, and many natural processes such as anaerobic sulfate reduction can transform inorganic mercury into methylmercury (a process called "*methylation*"). Thus the process of methylation may be the most important factor regulating mercury transfer into food webs. However, the processes of mercury methylation are complex and controlled by multiple environmental factors, and as a consequence, remain poorly understood in many natural environments [2].

In the past three decades, the processes mediating bioaccumulation and methylation of mercury have largely been studied in lakes and wetlands. Very little work has been done on streams, despite the fact that mercury contamination in the flowing waters is of similar magnitude and frequency as the standing waters. In streams, many physical, chemical and biological processes are highly influenced by surrounding watersheds (e.g. canopy cover, land use patterns) [3], which may have direct or indirect effects on mercury bioaccumulation and methylation in streams. Nevertheless, these processes are not well understood and need to be fully characterized if we want to predict which types of stream ecosystem are particularly prone to high contamination of mercury.

Goals and objectives - The two main goals of my dissertation research are: (i) to identify the spatial patterns of mercury bioaccumulation in stream food webs; & (ii) to elucidate the environmental controls on mercury methylation via two most important organic materials in streams (i.e. algae and leaf litter). There are four specific objectives of this dissertation:

1) To determine the spatial variability of mercury bioaccumulation in streams along a stream size gradient;
2) To examine the effect of land use in the watershed on mercury bioaccumulation in streams;
3) To identify the rates and mechanisms of stream algae in methylating mercury; &
4) To investigate the environmental controls on mercury methylation in streams via leaf litter.

Design, methodology & results - In this research, I chose to study two typical environmental gradients of streams. The first is stream size which increases downstream in watersheds. Since canopy cover decreases as stream size increases, stream algal productivity increases downstream, and inputs of terrestrial leaf litter decrease. The second is land use patterns in the watershed which can determine the water chemistry in the streams as well as the types of food sources available to stream organisms [3].

[1] Wiener JG, Krabbenhoft DP, Heinz GH, Scheuhammer AM (2003) Ecotoxicology of mercury. In *Handbook of Ecotoxicology*; Hoffman DJ, Rattner BA, Burton GA, Cairns J, Eds.; CRC: Boca Raton, FL, pp 409-463.
[2] Benoit JM, Gilmour CC, Heyes A, Mason RP, Miller CL (2003) Geochemical and biological controls over methylmercury production and degradation in aquatic systems. In *Biogeochemistry of Environmentally Important Trace Metals*; ACS Symposium Series 835; Cai Y, Braids OC, Eds.; American Chemical Society: Washington, DC, pp 262-297.
[3] Allan JD, Castillo MM (2007) *Stream Ecology*, second edition. Springer Press.

I use these two environmental gradients to disentangle the underlying processes leading to spatial differences in mercury bioaccumulation across streams. Moreover, I examine two of the most important organic materials (i.e. algae and leaf litters) in stream ecosystems and how they contribute to the in-situ production of methylmercury. In fact, algae dominate as food sources in large or nutrient-rich streams while litters dominate as food sources in small or nutrient-poor streams [3], thus the inclusion of both organic materials in this study is important to understand the in-situ production of methylmercury via organic materials in different stream types. While the majority of studies have focused on mercury methylation in the surface sediment, these organic materials have a high potential for contributing methylmercury to stream ecosystems [4], it is especially true as these materials contain high quality organic carbon that can fuel the microbes for methylating mercury.

Location of study sites - For *specific objectives (1) and (3)*, study sites include a network of streams (11 sites) located in the headwaters of the South Fork Eel River in northern California (Angelo Coast Range Reserve, managed by UC Berkeley). Much of the watershed is maintained as a protected reserve, and habitats encompass a range of stream size and algal productivity. For *specific objectives (2) and (4)*, study sites are located mainly from south to north in the eastern part of Minnesota where there is a transition in land cover, from predominantly agricultural in the south, to a mix of urban, forest and agricultural covers in Twin Cities Metro Area, and predominantly forested and wetland-associated land cover in the north.

Specific objective (1) - Spatial variation of mercury bioaccumulation in a stream network

In summer of 2007, I sampled water and dominant invertebrates in 11 streams with different sizes of drainage basins (from 0.5 to 150 km^2). I analyzed samples for total-mercury and methylmercury using standardized methods and found that methylmercury in water and invertebrates increased as stream size increased [5]. Therefore, more mercury bioaccumulation occurs in larger and more productive streams than small tributaries, which may be a result of higher in-situ mercury methylation.

Specific objective (2) – Effects of land use patterns on mercury bioaccumulation in streams

In summer of 2008, I surveyed 31 streams in a range of land use patterns in the watersheds in the eastern part of Minnesota and collected monthly water samples (from July to October) and dominant stream invertebrates in August to determine their total-mercury and methylmercury concentrations. From the results obtained so far, I observe a general increase of methylmercury concentrations in both water and invertebrates in streams from the south to the north of Minnesota, which I attribute to greater coverage by wetlands in northern watersheds as wetlands are well-known as hotspots of methylmercury production [2]. Therefore, as observed in lakes, watershed land cover is important in determining mercury bioaccumulation in streams [1].

Specific objective (3) - Mediation of mercury methylation by stream algae

The increasing concentration of methylmercury in water with stream size (from *specific objective 1)* is positively related to the abundance of stream algae. Therefore, stream algae potentially play a role in hosting microbes responsible for mercury methylation, as observed in lakes [6]. In summers of 2007 & 2008, I found very high levels of methylmercury concentrations in a ubiquitous algal species called *Cladophora glomerata* which are highly abundant in the mainstem of the South Fork Eel River watershed in northern California. Therefore, it is feasible that for this dominant alga could mediate the mercury methylation processes. In summer of 2009, I will investigate whether mercury methylation occurs with *Cladophora* biomass and if so, whether in-situ production of methylmercury in the stream would coincide with the abundance and growth stages of *Cladophora*. This work has important implications for understanding how eutrophication (i.e. excessive nutrients) of streams may influence mercury contamination, since eutrophication commonly leads to large and excessive growth of algae.

[4] Balogh SJ, Huang Y, Offerman HJ, Meyer ML, Johnson DK (2002) Episodes of elevated methylmercury concentrations in prairie streams. *Environmental Science and Technology* 36: 1665-1670.

[5] **Tsui MTK**, Finlay JC, Nater EA (In revision) Spatial variation of mercury bioavailability in a river network. *Environmental Science and Technology*

[6] Desrosiers M, Planas D, Mucci A (2006) Mercury methylation in the epilithon of boreal shield aquatic ecosystems. *Environmental Science and Technology* 40: 1540-1546.

Specific objective 4 – Environmental controls of leaf litter as source of mercury to stream ecosystems

In autumn of 2007, I performed a series of laboratory experiments by incubating leaf litter in different stream water types in order to examine whether inorganic mercury release from leaf litter (which takes up atmospheric mercury during growth) would be different across water chemistry, and whether methylmercury production associated with the litter would be different. This was novel because litter has long been recognized as a source of mercury to aquatic environments [4], but how the environmental factors control such release and subsequent methylation was not known. Interestingly, I found a large contrast between water types in releasing and methylating litter mercury, with water from agricultural streams releasing and methylating more mercury than water from pristine groundwater-fed streams [7]. Therefore, in autumn of 2009 I will perform a field experiment across streams in Minnesota to verify if streams with different land use patterns in the watershed would result in different mercury methylation in leaf litter with in-situ incubation. Specifically, I will place litterbags of freshly collected leaf litter in 12 streams of contrasting land use patterns in the watershed and monitor changes in litter mercury concentrations and methylation over 3 months (September-November). This work will increase our understanding on how the contribution of leaf litter to the mercury pools in stream ecosystems is mediated by the stream environments and their watersheds.

Potential significance of the research - Although mercury contamination is recognized in many natural streams, there is no study fully examining underlying controls of mercury bioaccumulation and methylation in these important habitats. This research has two significant aspects. First, it attempts to disentangle the different factors governing spatial variability of mercury bioaccumulation in streams in a local scale, which includes stream size and land use patterns. This would allow us to better understand and predict how landscape factors (e.g. presence of wetlands, canopy cover, surface runoff, etc.) or stream variables (e.g. light illumination, nutrient availability, etc.) influence mercury bioaccumulation in the flowing waters. Second, it is novel in investigating how algae and leaf litter contribute to mercury inputs in stream ecosystems; most other studies focus only on surface sediments in lakes and wetlands [2]. These organic materials are dominant food sources to stream ecosystems [3], and with the new information generated from this research may provide a new paradigm on how these food sources participate in mercury cycling. In summary, this dissertation research will substantially increase our current understanding of the environmental controls of transformation and bioaccumulation of this global contaminant in natural stream ecosystems, and the results are applicable in predicting consequences of different anthropogenic activities such as conversion of land covers and eutrophication of streams on mercury contamination in stream ecosystems.

Progress to date and schedule for completion - Research associated with *specific objective (1)* was completed and a manuscript is currently under revision for a leading journal in the field [5]. All sampling has been performed for *specific objective (2)*, and laboratory analyses will be completed by the end of Spring 2009. This work will also be presented at the upcoming Minnesota Water Resources Conference in St. Paul (MN) in October, 2009. For *specific objective (3)*, the manipulative experiments will be performed from May to September, 2009. For *specific objective (4)*, the first phase, laboratory incubation experiment, is finished and recently published [7], while the field experiment (second phase) will be carried out in Fall 2009. Therefore, upon finishing all field work, laboratory analyses and data processing by the end of Fall 2009, I will write my dissertation in Spring 2010 and plan to defend it by Summer 2010!

[7] **Tsui MTK**, Finlay JC, Nater EA (2008) Effects of stream water chemistry and tree species on release and methylation of mercury during litter decomposition. *Environmental Science and Technology* 42: 8692-8697.