Report as of FY2007 for 2006NV101B: "Modeling Biotic Uptake of Mercury in the Lahontan Resevoir System"

Publications

- Other Publications:
 - Carroll, R.W.H., Memmott, J., Warwick, J., Fritsen, F.H., and J.C. Bonzongo. in review. Biotic sorption of mercury in Lahontan Reservoir phytoplankton: Implications of dynamic loading. Science of the Total Environment.

Report Follows

Modeling Biotic Uptake of Mercury in the Lahontan Reservoir System

Synopsis

Year One Progress Report

Problem and research objectives (year 1):

Most mercury bioaccumulation modeling efforts assume a constant loading of mercury through time and space. These are justifiable assumptions where atmospheric mercury loading is the dominant phenomenon. However, the timing of maximum growth of phytoplankton relative to that of mercury loading could matter greatly if the loading signal varies strongly over time. Therefore, accurate prediction of mercury bioaccumulation may depend upon understanding the interactions of mercury loading and phytoplankton growth at sub-annual time scales (i.e. days to weeks). It was hypothesized that the strong temporally varying signal of mercury loading to Lahontan Reservoir will cascade, albeit with expected dampening, up through the reservoir foodweb with significantly different non-linear responses depending upon the relative timing and duration of peak mercury loading and the rates of phytoplankton and zooplankton growth. The primary objective of the proposed study for the first year of funding was to observe a temporally varying mercury signal in the lower food web, specifically the phytoplankton and zooplankton communities.

<u>Problem and research objectives (year 2):</u>

Note that funding for the second year is contingent on results presented in this progress report. The proposed objectives for the second year of funding include using collected data to parameterize/drive a bioaccumulation model (e.g. Bioaccumulation and Aquatic System Simulator – BASS by the US EPA (Barber, 2004)) to simulate mercury pulse loading on uptake of several trophic levels in Lahontan Reservoir. A verified model will allow model prediction of bioaccumulation based on hypothetical flow/Hg-loading scenarios. Finally, an uncertainty analysis (Monte Carlo simulation) will provide a quantitative assessment of the expected accuracy of model predictions. This will allow a determination of significant differences between simulated scenarios.

Methodology (year 1)

Water column sampling occurred every six weeks at Fisherman's Point, a narrow section separating the southern and middle basins of Lahontan Reservoir. Sampling began in March 2006 to ensure the capture of peak spring runoff from the Carson River and continued until late September 2006 in hope of capturing a secondary zooplankton peak and to witness possible impacts of internal mercury cycling on biotic uptake. Using a YSI 6600 profiler, measurements of temperature, pH, oxidation-reduction potential, specific conductivity, in vivo fluorescence, photosynthetically-active radiation, turbidity, and dissolved oxygen occurred at three equidistant locations across the lake. Water samples were collected at the same three points along the transect. When the lake was stratified, depth integrated samples were collected above and below the thermocline for mercury (total and dissolved), methylmercury (total and dissolved) and phytoplankton

mercury concentrations and biomass (ash free dry mass (AFDM) and chlorophyll-a (chla)), as well for as nutrient analysis (NO₃-, NO₂-, NH₄+,TKN and PO₄³, TP, DOC). When the lake was not stratified, depth integrated samples representing the entire vertical profile (lake bottom to surface) were collected. Nutrient analysis was conducted at the Desert Research Institute water quality lab while mercury samples (water and biota) were analyzed at the University of Florida by J.C. Bonzongo. Zooplankton were collected at each location along the reservoir transect with vertical drags of an 86 µm Nitex net. Collected zooplankton were combined into a single representative sample. Mercury associated with different-sized algal groups was measured to assess if different sizes showed different patterns of mercury affiliation. Differentiating by size is a rough method to designate functional groups such that the smaller-sized algal fraction (in this case, less than 35 µm) was assumed more palatable and more easily consumed by higher trophic levels (Horne and Goldman, 1994). On the other hand, the larger-sized algal fraction (greater than 35 µm) was assumed not as palatable, and any mercury sorption could represent a sink of mercury, or a mechanism for depositing mercury onto the reservoir bed for later cycling in the system.

Mercury loading into Lahontan Reservoir was separated by source: the Carson River, and diffusion from reservoir benthic sediments. Two mercury loading mechanisms were considered: (1) the Carson River, and (2) the diffusion from the benthic sediments. While the former contributes large quantities of Hg-laden sediment, only the dissolved fraction is considered bio-available and discussed in conjunction with dissolved benthic loads. Carson River mass loading into the reservoir was computed as discharge (USGS, 2007) multiplied by USGS concentrations measured at Weeks Bridge (Karen Thomas, USGS, written communication, 2006). Loading of mercury species from reservoir benthic sediments was computed with a constant rate of diffusion from May and June 2001 flux experiments with sediment from the southern lobe of the reservoir (Kuwabara et al., 2002). The amount of surface area available for active diffusion was assumed to equal the surface area of the reservoir as computed from the U.S. Bureau of Reclamation rating curve. The area of active diffusion upstream of FPO was assumed to equal one-third the total area of the reservoir. While assumptions used to compute benthic loads were crude, calculations helped illustrate the time-varying nature of benthic loading and relative importance when compared to Carson River loads.

Data analysis included adjusting mercury concentrations on GF/F filters by subtracting out the mercury content found in a blank filter then normalized by the volume of composite reservoir water used in the filtering process. This established concentrations of phyto-Hg and phyto-MeHg per unit volume of reservoir water. Phytomercury concentrations for particles greater than 35 μ m were derived by subtracting concentrations less than 35 μ m from the total concentration. This calculation maintains mass balance if one assumes no error in the sub-sampling process from the 14-L, Teflon, USGS Water Quality Modified Churn Splitter. Similar calculations were done for all biomass indices (Chla, AFDM) to obtain biomass per volume reservoir water. If one assumes that AFDM increases proportionately to phytoplankton Chla, then any change in the ratio of AFDM to Chla, or the autotrophic index (AI), becomes an indicator of change in either variable relative to the other. Biomass-specific concentrations (mass mercury per biomass) were established by dividing phyto-mercury concentrations (ng/L) by either Chla or AFDM concentrations (μ g/L). Significance of correlation between all

measured/derived parameters was conducted using the *t*-statistic given two degrees of freedom, and assuming highly significant at $p \le 0.05$ and moderately significant at $p \le 0.10$. Bio-concentration factors (BCF) were computed with Equation (1)

$$BCF = \log \left(\frac{C_b}{C_w} \right) \tag{1}$$

where C_b is the concentration of mercury (ng/L) of a given phytoplankton size fraction and C_w is the concentration of dissolved mercury in the water column (ng/L). Negative values imply dilution, while positive values signify increased concentration.

A Monte Carlo uncertainty analysis was conducted to establish 95-percent confidence intervals in mercury and biomass concentrations. One thousand realizations were run in Monte Carlo. Random sampling from Hg and MeHg assumed a normal distribution while random sampling from biomass indices assumed a uniform distribution. Ranked results provided median (no distribution assumed) and 95-percent upper and lower confidence intervals.

Principal findings and significance (year 1)

- The total annual load of dissolved Hg into Lahontan Reservoir was 54,680 g, with the Carson River, on average, contributing 30-percent. Dissolved Hg loads are highest during the Carson River spring discharge (425 g/d) in late May, with fluvial contributions spiking to 75-percent of the total during this period. Late summer dissolved Hg loads to the reservoir drop nearly an order of magnitude with river contributions making up only 1-percent of the total load.
- Fluvial contributions dominate loading of dissolved MeHg such that nearly 90 percent of the annual MeHg load (416 g) comes from the river. Contributions of MeHg from the river are 99 percent during periods of high river discharge with peak loads occurring in late May (5.72 g/d). Only in late August, when loading is two orders of magnitude less than the May peak, does the river contribution diminish to 30 percent.
- The highest phyto-Hg concentrations coincide with peak loading from the Carson River and the spring algal bloom in March and May. Late summer phyto-Hg concentrations are low for phytoplankton less than 35 μm despite linear growth. Large phytoplankton (>35 μm) show no Hg sorption during the massive late summer bloom of filamentous blue-green algae. Correlation analysis confirms that fluvial loads had the greatest impact on phyto-Hg concentrations.
- Efficiency of Hg sorption, as expressed as Hg per unit mass phytoplankton, decline throughout the summer months, suggesting that growth dilution may be, in part, responsible for blue-green algae's inability to concentrate Hg. Dilution is supported by increasingly negative BCF values throughout the summer season with large particles having more negative values than small particles.
- Phyto-MeHg concentrations and biomass specific MeHg concentrations in small
 phytoplankton were bimodal. A first peak occurred in the spring during high
 loading from the Carson River and a secondary, more substantial, peak occurred
 in the late summer when diffusion from benthic sediments may dominate the
 system.

- Phyto-MeHg concentrations and biomass-specific MeHg concentrations increase directly with phytoplankton growth and are more dependent on benthic loading.
- Given small phytoplankton are more efficient pathways of Hg sorption during the summer months, compared to larger phytoplankton, one might assume the same holds true for MeHg sorption. Therefore, it is hypothesized that the smaller, and more palatable phytoplankton become an important mechanism for the transfer of both inorganic and the more toxic organic mercury species to higher trophic levels
- Methylmercury becomes more concentrated in the algal population compared to
 water column concentrations during March, August, and September, but more
 diluted during May and June. The ability of cells to concentrate MeHg during
 peak algal blooms shows that MeHg is more transferable through the food web
 than inorganic mercury, which tends to become diluted in the algal masses when
 loading is small.
- The percent MeHg in small phytoplankton is low during the spring and early summer, with values near 2-percent, but increase dramatically during the late summer to 30 to 40-percent and compounds any assumption of a temporally constant fraction of bio-available mercury.
- Zooplankton results were not considered due to large uncertainty in results. Future work will need to minimize uncertainty in collection and measurement to address the relationship between phytoplankton mercury concentrations with respect to zooplankton growth and uptake.
- This study suggests that Hg sorption is driven by fluvial inputs to Lahontan Reservoir timed with the spring algal bloom. Fluvial inputs of MeHg are also important during the spring, but benthic loading appears more important during the late summer when MeHg concentrations accumulate in greater and greater percentages. Therefore, it is necessary to address the benthic community and the eventual transfer of MeHg from this community into the upper trophic levels in the reservoir.

Information transfer activities (year 1)

Paper:

Carroll, R.W.H., Memmott, J., Warwick, J., Fritsen, F.H., and J.C. Bonzongo. in review. Biotic sorption of mercury in Lahontan Reservoir phytoplankton: Implications of dynamic loading. *Science of the Total Environment*.

Conference (anticipated):

Carroll, R.W.H., Memmott, J., Warwick, J., Fritsen, F.H., and J.C. Bonzongo. in review. Biotic sorption of mercury in Lahontan Reservoir phytoplankton: Implications of dynamic loading. *American Geophysical Union (AGU) Fall meeting (December 2007), San Francisco.*

Student support (year 1)

Rosemary W.H. Carroll is a doctoral student at the University of Nevada, Reno and this project may serve as a component of her dissertation. John Warwick serves on her committee and acts as her primary advisor on Hg-related projects. Funding allowed Ms.

Carroll to manage her first project, direct laboratory staff and learn analytical techniques. Funds also helped support technical staff at DRI and several undergraduate students at the University of Nevada, Reno who aided Ms. Carroll in field preparation, data collection and laboratory analysis of phytoplankton and zooplankton.