MERCURY AND METHYLMERCURY RELATIONSHIPS IN CONTAMINATED STREAMS IN THE SOUTHEASTERN USA

G.R Southworth[1], M.A. Bogle[1], and R.R. Turner[2]

Abstract:

Field and laboratory studies have demonstrated that concentrations of methylmercury in freshwater systems are influenced by the concentrations of precursor inorganic mercury. Because the production of methylmercury from inorganic mercury is influenced by a large number of chemical and ecological factors, extrapolation of observed relationships between precursor mercury and methlymercury in specific aquatic systems to other systems generally fail. However, in chemically and ecologically similar lakes and streams, generalizations concerning the relationship between inorganic mercury and methylmercury in water may be more universal. We measured total mercury and methylmercury in filtered and unfiltered water samples from 28 sites in 13 freshwater streams in Tennessee, Kentucky, Virginia, and North Carolina. All sites were sampled under warm weather baseflow conditions. Seven of the streams had a previous or ongoing history of mercury contamination from point sources, while three others were suspected to be contaminated based on concentrations of mercury in fish. Three were presumed to be influenced primarily by atmospheric and geologic sources of mercury. Total mercury concentrations varied more among the 28 sites than did methylmercury concentrations, and regression of methylmercury versus total mercury did not yield evidence of a strong relationship. However, when data from contaminated sites receiving discharges from Dept. of Energy facilities in Oak Ridge, TN were excluded, there was a much stronger relationship. We hypothesize that some chemical characteristic of these streams associated with the industrial discharges lessens the net methylation rate of inorganic mercury.

1 Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN,
corresponding author e-mail - SouthworthGR@ornl.gov
2 RT Geosciences Inc., Squamish, British Columbia, Canada

Introduction:

Field and laboratory studies have demonstrated that concentrations of methylmercury in freshwater systems are influenced by the concentrations of precursor inorganic mercury. (Kelly et al. 1995; Parks et al. 1989). Because the production of methylmercury from inorganic mercury is influenced by a large number of chemical and ecological factors, extrapolation of observed relationships between precursor mercury and methlymercury in specific aquatic systems to other systems generally fail. However, in chemical and ecologically similar lakes and streams, generalizations concerning the relationship between inorganic mercury and methylmercury in water may be more universal. The objective of this study was to investigate the relationship between aqueous total mercury concentrations and methylmercury concentrations in chemically similar warm water streams contaminated by point source mercury inputs or influenced by industrial discharges suspected of contributing mercury. A secondary objective was to further understand the apparent low bioavailability of mercury in a stream highly contaminated by mercury inputs from past losses of mercury at a headwater industrial site.

Methods:

We measured total mercury and methylmercury in filtered and unfiltered water samples from 28 sites in 13 freshwater streams in Tennessee, Kentucky, Virginia, and North Carolina. All sites were sampled under warm weather baseflow conditions. Seven of the streams had a previous or ongoing history of mercury contamination from point sources, while three others were suspected to be contaminated based on concentrations of mercury in fish. Three were presumed to be influenced primarily by atmospheric and geologic sources of mercury. Samples for dissolved mercury and methylmercury were filtered immediately in the field. Water samples were placed on ice immediately upon collection and shipped by overnight carrier to be analyzed at Frontier Geosciences in Seattle, WA using EPA method 1631 for total mercury

(EPA 1999) and aqueous phase ethylation/cryogenic gas chromatography and cold vapor atomic fluorescence spectroscopy (Bloom 1989) for methylmercury.

Results and discussion:

Total mercury concentrations varied more among the 28 sites than did methylmercury concentrations, and regression of methylmercury versus total mercury did not yield evidence of a strong relationship (Fig. 1). However, when data from contaminated sites receiving discharges from Dept. of Energy facilities in Oak Ridge, TN were excluded, there was a much stronger relationship. Data from sites investigated by other researchers (Bonzongo et al. 1996; Kelly et al. 1995; Watras et al 1995; Watras, Morrison, and Bloom 1995) generally fell within the range of the plot for 'all other streams'. It appears that reduction in aqueous total mercury concentrations in contaminated warm water streams should result in a decrease in methylmercury concentrations. We could not find any other sites, including the highly contaminated Carson River system (Bonzongo et al. 1996), where the methylmercury:total mercury relationship appeared similar to that observed in East Fork Poplar Creek (EFPC) and White Oak Creek.

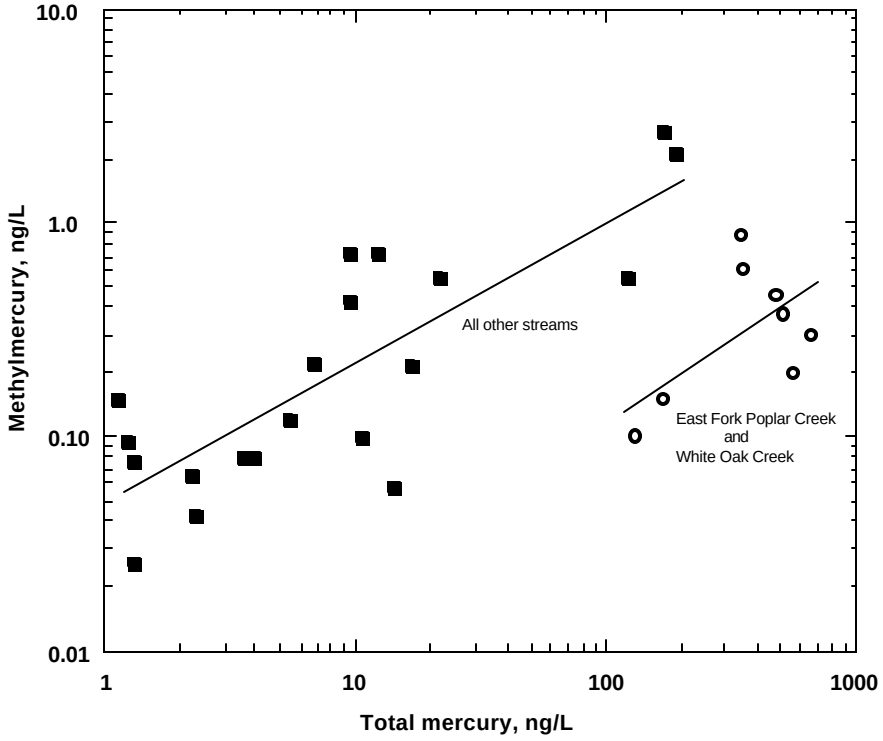

Fig 1. Concentration of total mercury versus concentration of methylmercury at 28 sites in 13 freshwater streams. Each point is mean of 1 to 5 samples (varies with site)

Data from East Fork Poplar Creek showed an unusual pattern over time and distance from the headwater source (Fig. 2). In recent sampling (1997 - 1999), total mercury decreased with distance downstream from the source, but methylmercury concentrations increased substantially with distance downstream. Additional inputs of water from tributaries and point source discharges increase the flow of EFPC roughly 3 fold over that reach. Six years earlier, the downstream profiles of total mercury and methylmercury were strikingly different. Total mercury concentration at the headwater site was much higher, and the downstream profile decreased much more rapidly (Fig. 2b). Methylmercury decreased with distance similarly to total mercury in the upper 5 km of stream, but increased with distance farther downstream. Major changes in upper

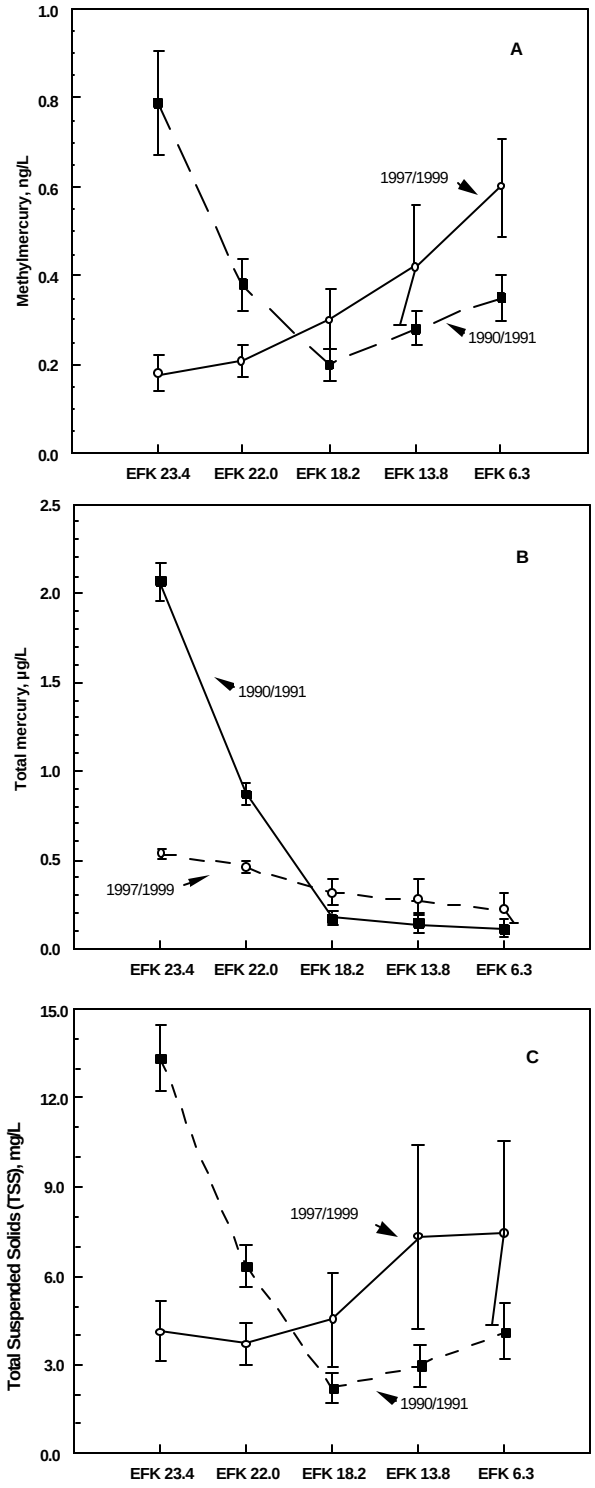

Fig. 2 Mean baseflow concentrations (± SE) of total mercury, methylmercury, and total suspended solids in EFPC, 1990 -1991 (N=7) and 1997 - 1999 (N=5).

EFPC occurred between the 1990/1991 and 1997/1999 periods. Remedial actions reduced point source mercury inputs, and an additional 4 - 5 mgd (out of a total flow of 7 - 8 mgd at the uppermost site) was added to restore base flow to the historical norm. In 1990/1991, stream flow discharged from a lined pond just upstream from EFK 23.4. The pond served unintentionally as a reactor for the production of

methylmercury, and as a temporary repository for mercury-contaminated sediments, which accumulated in the pond during storm events and gradually washed out during intervening baseflow periods, raising the total mercury concentration in the outlet above that in the inlet flow. The pond was partially bypassed by a temporary siphon array in 1996, and completely bypassed starting in 1998. The data in Fig. 2 indicate that methylmercury concentrations in upper EFPC were responsive to changes in total mercury concentrations. In 1990/1991, downstream decreases in total mercury concentration were accompanied by commensurate decreases in methylmercury concentration over a distance of 5 km. The decrease in total mercury concentration at EFK 23.4 that occurred between 1990/1991 and 1997/1999 was also accompanied by a similar decrease in methylmercury concentration. However, in both data sets, eventually downstream dilution of the stream flow was associated with an increase in the concentration of methylmercury relative to the concentration of total mercury in the water column. Thus, it appears that the availability of inorganic mercury for methylation in EFPC increases with distance downstream from the source. The chemical characteristics of the EFPC headwaters differ considerably from most other streams, being enriched in trace metals (cadmium, zinc, nickel, copper, uranium), nutrients (nitrate and phosphate), and sulfate, as well as other chemicals associated with process water use and discharges from waste treatment processes. We hypothesize that some chemical characteristic of the stream associated with the industrial discharges lessens the net methylation rate of inorganic mercury near the headwaters, and that downstream dilution and sequestration of the responsible agent(s) allows net methylation to increase in the lower reaches of the stream.

Acknowledgements:

We thank M.J. Peterson and S. E. Lindberg for helpful review comments. This work was sponsored by the Oak Ridge Y-12 Plant, Health, Safety, and Environment Division. The Y-12 Plant is managed by Lockheed Martin Energy Systems, Inc., under contract DE-AC05-840R21400 with the U.S. Dept. of Energy. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

References:

Bloom, N.S. :1989 'Determination of Picogram Levels of Methylmercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapor Atomic Fluorescence', *Can. J. Fish. Aquat. Sci*.. **46**, 1131 - 1140 **.**

Bonzongo, J.J., Heim, K.J, Y. Chen, W.B. Lyons, J.J. Warwick, G.C. Miller, and P.J. Lechler. 1996. Mercury pathways in the Carson River - Lahonton Reservoir system, Nevada, USA. Environ. Tox. Chem. 15: 677 - 683.

Environmental Protection Agency (EPA). 1995: Method 1631: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. EPA-821-R-95-027 Office of Water, U.S.EPA, Washington, D.C.

Kelly, C.A., J.W.M. Rudd, V.L. St. Louis, and A. Heyes :1995, 'Is Total Mercury a Good Predictor of Methylmercury Concentration in Aquatic Systems', *Water, Air, and Soil Pollut.*. **80**, 715 - 724.

Parks, J.W., A. Lutz, and J.A. Sutton. :1989 'Water column Methylmercury in the Wabigoon/English River - Lake System: Factors Controlling Concentrations, Speciation, and Net Production,' *Can. J. Fish. Aquat. Sci*., **46**, 2184 - 2201.

Watras, C.J., K.A. Morrison, J.S. Host and N.S. Bloom. (1995). Concentration of Mercury Species in Relation to Other Site-Specific Factors in Surface Waters of Northern Wisconsin Lakes. Limnol. Oceanogr. 40, 556-565.

Watras, C.J., K.A. Morrison, and N.S. Bloom. :1995, 'Mercury in Remote Rocky Mountain Lakes of Glacier National Park, Montana, in Comparison with other Temperate North American Regions' *Can. J. Fish. Aquat. Sci,*. **52**, 1220 - 1228.