Environmental Assessment and Risk Analysis Element

Research Project Summary

NJDEP

Division of Science Research & Technology
Linking Science to New Jersey's Environmental Decision-Making

February, 2003

Assessment of Historical and Current Trends in Mercury Deposition to New Jersey Aquatic Systems through Analysis of Sediment/Soil Cores

Amy E. Kroenke[1], B.S.,
Edward L. Shuster[1], Ph.D.,
Richard F. Bopp[1], Ph.D. and
Mary Downes Gastrich[2], Ph.D.

Abstract

Atmospheric deposition is an important source of mercury to aquatic and terrestrial ecosystems and has global, regional, and local components. Deposition of mercury to waterbodies in New Jersey has resulted in elevated levels of mercury in fish across the state. Potentially significant sources of mercury to waterbodies in New Jersey include coal-burning power plants, municipal solid waste incineration, and metal smelting. Analysis of dated sediment cores has been a most useful tool for documenting historical changes in atmospheric mercury fluxes to waterbodies. This is the first study to analyze sediment cores to estimate the historic pattern of mercury to New Jersey aquatic systems. The objectives were to identify and characterize the extent of atmospheric mercury deposition to New Jersey aquatic systems and to identify indications of local sources of mercury contribution to these systems. Sediment core samples were taken from five lakes and one coastal marsh, dated based on radionuclide analyses, and analyzed for total mercury. The results indicated that mercury fluxes have generally decreased since an historic high rate in the late 1940s. Mercury fluxes were, however, still significantly elevated at most sites compared with estimates of mercury fluxes in remote areas in North America receiving background mercury deposition. However, the results in NJ lakes are comparable to recent mercury fluxes to the Great Lakes suggesting a large-scale regional influence. One site, Woodcliff Lake in northeastern NJ, had particularly elevated fluxes of mercury similar to Central Park Lake, NY and future efforts will be directed to determine if the mercury deposition to these waterbodies reflects a more localized area of elevated mercury deposition, and if so, to provide information on its likely sources.

Introduction

Recent studies have found elevated levels of mercury (Hg) in fish from near-pristine lakes in remote areas (Cope et al. 1990; Sorensen et al. 1990; Meili, 1991). Elevated Hg levels have also been found in fish sampled from many freshwater bodies including Central Park Lake in New York City (Kroenke et al. 1998), lakes in New Jersey (New Jersey Department of Environmental Protection, 1994) and pristine lakes in remote areas and in North America (Cope et al., 1990; Sorensen et al. 1990; Meili, 1991). Atmospheric deposition to watersheds as well as directly to waterbodies is an important source of mercury to aquatic and terrestrial ecosystems in general and to mercury concentrations in fish tissue in particular and may have global, regional and local components. Mercury deposition to waterbodies may also result from discharges to waterbodies and/or watersheds. There are many potential sources of atmospheric mercury including coal-burning power plants, municipal solid waste incineration, and medical waste incineration (Pirrone et al. 1998; New Jersey Department of Environmental Protection, 2001). This study is intended to allow comparisons of mercury deposition rates to sediments in New Jersey to deposition rates in other remote and regional sediments to allow determinations of the possible role of local-regional and New Jersey-specific contributions to mercury in New Jersey aquatic systems. In addition, this study is intended to provide a basis for assessing the effect of ongoing and future reductions in mercury releases on mercury entry into aquatic systems. The analysis of dated sediment cores has proven to be a most useful tool for documenting historical changes in atmospheric metal fluxes in Central Park Lake, New York City (Chillrud et al. 1999) and Wisconsin lakes (Engstrom & Swain, 1997; Engstrom et al. 1994; Rada et al. 1989).

Project Design and Methods

The research approach taken in this study is based on analyses of total mercury levels in sediment core sections. By combining mercury concentration data with results from radionuclide dating of the sediment cores, historical rates of mercury deposition to sediment (fluxes) were calculated for each site. The results were then compared to similar studies in both in-

dustrial and remote areas of North America, and among the New Jersey sites in this and related studies.

Figure 1. Map of Sediment and Soil Core Sites
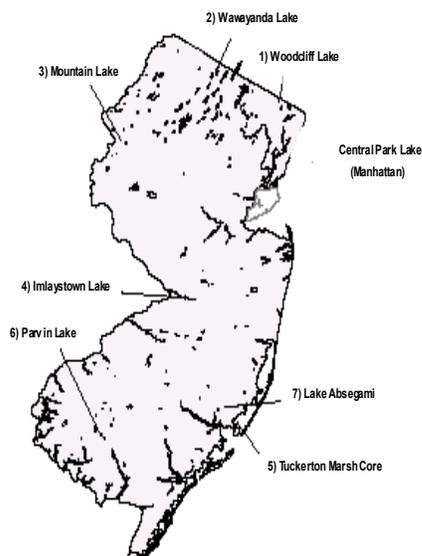
Lake sediment and soil cores were collected at six sites including five lakes (Woodcliff Lake, Wawayanda Lake, Mountain Lake, Imlaystown Lake, Parvin Lake) and one coastal marsh (Tuckerton marsh) from throughout the state of New Jersey (Figure 1) during 2000 and 2001. Because a well-dated core could not be obtained from Lake Absegami, these results were not used. Results from sediment cores in Central Park Lake, NY are discussed but were not part of this study. Criteria for selection of sites excluded lakes that were dammed after 1950, lakes with records of frequent dam blow-outs (e.g., breaks leading to massive water releases) and lakes suspected of having inputs of mercury from other than atmospheric sources. Lakes were included that had a good fishery and expected continuous sedimentation at rates of ca. 0.5 cm per year. Sediment cores with radionuclide profiles indicating continuous records of particle accumulation were used to reconstruct the history of atmospheric mercury fluxes. Soil cores were also collected near each lake that was cored. While soil cores do not provide any continuous record of particle accumulation and cannot be used to reconstruct the history of Hg deposition, they can provide an indication of the cumulative atmospheric Hg flux to a site. One advantage of soil cores is that they are much less likely to accumulate non-atmospheric sources of Hg (direct industrial inputs, e.g.) than lake cores.

Gravity or push cores were collected at the deepest section of Mountain and Wawayanda Lakes, in a sheltered cove in Parvin Lake, in a marshy area along the shore of Imlaystown Lake, and at the site of an archived, well-dated core in Woodcliff Lake in 2.5 inch outer diameter (O.D.) polybutyrate tubes and sectioned on site at 2 cm intervals (unless otherwise noted). In gravity coring, the tube is connected to a one-way valve and lowered by rope through the water column. Penetration of the sediment is aided by the addition of lead weights above the valve. In shallower water (less than about 10 feet), push coring is the preferred method. Metal pipe is connected to the

valve and the polybutyrate tube is pushed into the sediments. The marsh core (Tuckerton) was collected in a 4 inch O.D. polybutyrate tube with penetration aided by pounding. It was sectioned in the lab at ~1.2 cm intervals. Soil cores were collected by pounding a length of 2.5 inch O.D. polybutyrate core tubing into the ground. They were sectioned in the lab in 1 cm increments from 0-4 cm and 2 cm increments thereafter. All sediment and soil core sections were oven dried at 35°C under a flow of filtered air, ground using a mortar and pestle, and stored in pre combusted glass vials with teflon-lined screw caps or PVC-lined aluminum cans. Sections were analyzed by gamma spectrometry for ^{137}Cs (cesium), ^{210}Pb (lead), and ^{7}Be (beryllium) using an intrinsic germanium crystal and multi-channel analyzer (ORTEC GWL-120, 92X Spectrum Master, and Maestro software). Aliquots of the sections were sent to Brooks Rand, Ltd. for total Hg analysis under method BR-0002 (nitric/sulfuric acid reflux; stannous chloride reduction, gold amalgamation, and cold vapor atomic fluorescence detection).

Core dating information was obtained through radionuclide analysis of sediment core sections. The depth distribution of ^{137}Cs along the length of the sediment core provided information on the timing of sediment deposition. ^{137}Cs is associated with global fallout derived from atmospheric testing of nuclear weapons beginning in the early 1950s with a fall-out maximum in 1963 -1964. The activity of ^{210}Pb, a naturally occurring radionuclide derived from the decay of atmospheric radon decreases exponentially from the surface of the sediment with a half-life of 22.3 years. Be^{7}, a short-lived radionuclide, is confined to sediment samples containing a significant component of particles deposited within about a year prior to sample collection. In addition to sediment dating, sediment focusing factors were calculated in order to normalize mercury deposition estimates for sediment deposition rates. Depending on the topology and geology of the lake and its watershed, the rate of sediment transport to the lake can vary. For the purposes of this study, it was necessary to calculate the rate if mercury deposition over time (flux) was independent of the rate of sediment transport and deposition. Based on the concentration of mercury in the sediments normalized for the sediment deposition rate, the mercury flux (mg/m^2/yr) was determined over time for each waterbody.

Results

Results showed that peak calculated mercury fluxes in the NJ sites between the 1930s and 1960s at all of the sites (Table 1; Figure 2). At five of the six sites, mercury fluxes were significantly elevated with respect to previous estimates of mercury fluxes in North America but were comparable to mercury levels in the Great Lakes sediments. This suggests a large-scale regional influence. At the Tuckerton site, the initial sedimentation rate model that was applied yielded a second peak in mercury fluxes in recent (2001) sediments. An alternate model produced recent trends more consistent with those observed at the other sites. Decadal data from Parvin Lake were not reported because mixing in the upper sections of the core limited the temporal resolution, however the Hg flux integrated over the past half century was similar to that observed at Tuckerton (Table 1). At one site, Woodcliff Lake in northeastern New Jersey, mercury fluxes were about 5 -100 times higher than at the other sites (Table 1; Figure 2). In another study, similarly elevated mercury fluxes observed in Central Park Lake, New York City (Kroneke et al. 1998) were related to local at-

mospheric inputs derived from municipal solid waste and coal combustion. This suggests the possibility that this area is subject to more local atmospheric inputs possibly including combustion of municipal and solid waste and coal combustion by power plants. However, because mercury levels in the soil sample adjacent to this lake were significantly lower than the sediments, it is also possible that direct (i.e., non-atmospheric) inputs of mercury may also be significant.

of mercury at all five NJ sites decreased considerably from levels observed three to four decades ago. The model of sediment flux in the Tuckerton Marsh core, employed in the initial analysis (Table 1; Figure 1), suggests that after a decline in mercury flux at that site, a gradual increase began in the 1970s and has continued. However, an alternative model of sediment flux at this site, equally consistent with radionuclide dating information, results in a pattern of mercury flux with

Table 1. Temporal Trends in Mercury Flux Rate ($\mu g/m^2/yr$)

Decade	Woodcliff Lake	Wawayanda Lake	Mountain Lake	Imlaystown Lake	Tuckerton Marsh[a]	Parvin Lake		Central Park Lake[b]
1990s	400	18	20	45	210			700
1980s	570	18	30	65	190			1200
1970s	1900	20	50	85	160			1500
1960s	3000	20	55	110	230			2000
1950s	2900	30	75	90	250			1800
1940s		30	65	90	300			1000
Average (past 50 yrs)	1750	25	50	80	225	231[c]		1400

[a] Fluxes are normalized to xsPb-210 based focusing factors. Dating for Tuckerton based on a mass sedimentation rate (MSR) model. The model used two sedimentation rates to match the 1954, 1963, and 2001 time horizons.

These time constraints can also be met with a linearly decreasing sedimentation rate model. This alternate model yields Hg fluxes that decreased since the 1970s, similar to the other sites.
[b] Fluxes from Kroenke et al. (2002).
[c] Cs-137 used for normalization; unable to calculate temporal trends due to mixing in the core.

After Woodcliff Lake, the next highest mercury fluxes (lower by about an order of magnitude) was seen at Tuckerton marsh site followed by Imlaystown Lake, Mountain Lake, and Wawayanda Lake. Although there was a general decline in mercury deposition fluxes from the peak period of the 1940s–1960s at all of the sites, there is some evidence of an increase in mercury fluxes over the last two decades at the Tuckerton marsh site.

Discussions And Conclusions

Results of this study were compared to the United States Geological Survey National Water Quality Assessment Program (Long et al. 2003) where sediment cores were taken from three northeastern NJ lakes in 1997 and were dated using ^{137}Cs and analyzed for trace metals. Orange Reservoir, located in an urban watershed, contained the highest mercury concentrations with peak mercury levels found in sediments from 1995 among sediments dating back to the 1930s (United States Geological Survey, in draft). A steady increase in mercury concentrations was seen in this reservoir between 1950 - 1995. The mercury concentration levels in the Orange Reservoir were comparable to those found in Woodcliff Lake in this study but with a peak in the 1960s, and subsequent decline with a slight increase in the 1970s that leveled off through the present. Mercury flux estimates were not available from the Long et al. (2003) study for comparison with Woodcliff Lake mercury flux estimates.

Estimates of mercury fluxes to the waterbodies in this study can vary by two orders of magnitude depending on choices related to sedimentation rates, focusing factors, and background Hg levels. However, it is clear that atmospheric fluxes

the continuous recent decline observed at the other sites. In addition, atmospheric fluxes of mercury to aquatic systems at sites throughout the state are higher than fluxes reported for remote areas of North America. At Imlaystown Lake, Tuckerton Marsh and Parvin Lake, mercury fluxes are similar to those reported for the Great Lakes and about ten times the remote background flux. Somewhat lower fluxes were calculated for the northcentral and northwestern NJ sites (Wawayanda Lake and Mountain Lake). The similarity of these levels to those found in the Great Lakes suggest the influence of large-scale regional mercury deposition. The highest mercury fluxes were found for sediments in Woodcliff Lake in northeastern NJ which had mercury fluxes comparable to those found in Central Park Lake at about an order of magnitude higher than at any other NJ sites. The greatly elevated, but comparable levels from these two waterbodies located in the same general area suggests the influence of local sources of mercury deposition. While the results from Woodcliff Lake are generally consistent with atmospheric source of deposition, a contribution to the lake from direct inputs cannot be ruled out at this time.

 Future efforts should characterize the sources of mercury to Woodcliff Lake to confirm the existence of local sources of mercury deposition that may be impacting the northeast portion of New Jersey. This should include a comparison of sediment core data from Woodcliff Lake to similar data from neighboring lakes. Sediment core samples should also be analyzed for other trace metals including Pb (lead), Zn (zinc), Sn (selenium), Sb (antimony), Cd (cadmium), V (vanadium), and Cr (chromium) to investigate source-specific patterns of elemental deposition, which may be useful in identifying specific emissions sources.

Figure 2. Mercury fluxes at NJ sites (µg/m²/y) (normalized to Pb-210 focusing factor). Note: The flux data are plotted on a logarithmic scale.
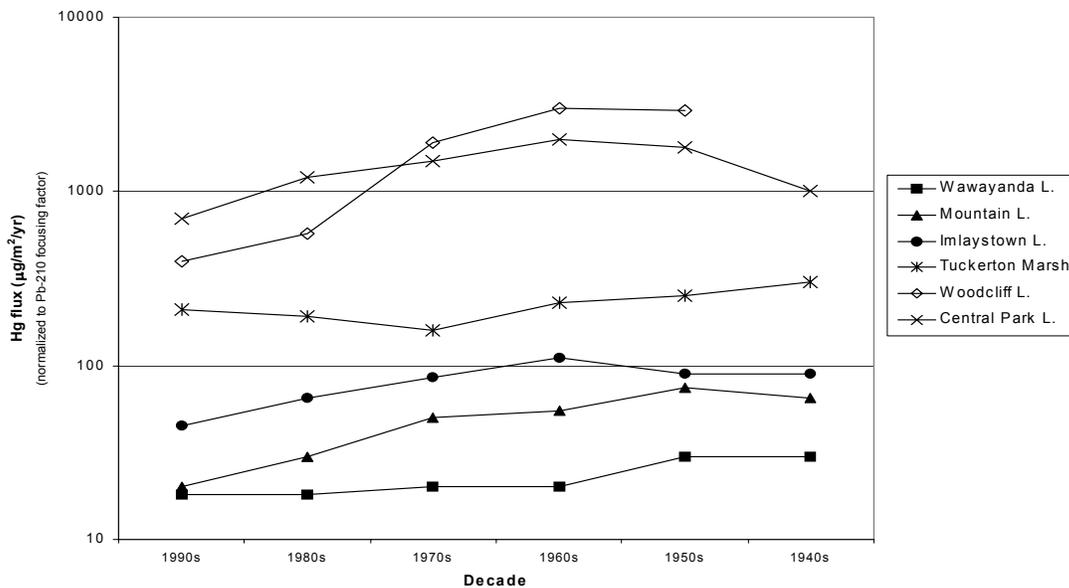
Bibliography

Chillrud, S.N., R.F. Bopp, H.J. Simpson, J.M. Ross, E.L. Schuster, D.A. Chaky, D.C. Walsh, C. C. Choy, L.Tolley and A. Yarme. 1999. Twentieth century atmospheric metal fluxes into Central Park Lake, New York City. *Environmental Science & Technology*. Vol. 33, No. 5: 657-662.

Cope, W.G., J. G. Wiener, and R.G. Rada. 1990. Mercury accumulation in yellow perch in Wisconsin seepage lakes: relation to lake characteristics. *Environ. Toxicol. & Chem*. 9, p. 931-940.

Engstrom, D.R. & E.B. Swain. 1997. Recent declines in atmospheric mercury deposition in the Upper Midwest. *Environ. Sci. Technol*. 31, p. 960-967.

Engstrom, D.R., E.B. Swain, T.A. Henning, M.E. Brigham and P.L. Brezonik. 1994. Atmospheric mercury deposition to lakes and watersheds: A quantitative reconstruction from multiple sediment cores. In: *Environmental Chemistry of Lakes and Reservoirs*, pp. 33-66. (Baker, L.A., Ed.). Washington, D.C., American Chemical Society.

Kroenke, A.E., D.A. Chaky, R.F. Bopp, S.N. Chillrud, E.L. Shuster, and F.D. Estabrooks. 2002. Mercury Depositon in Sediments of the New York/New Jersey Harbor Area (in preparation).

Kroenke, A.E., R.F. Bopp, D.A. Chaky, S. Chillrud, Ed. Shuster, F.D. Estabrooks, and J. Swart. 1998. Atmospheric deposition and fluxes of mercury in remote and urban areas of the Hudson River Basin. EOS, Transactions of the American Geophysical Union, 79 (17) Spring Meeting Supplement, S86.

Long, G., M. Ayers, E. Callendar, and P.C. Van Metre. 2003. Trends in chemical concentration in sediment cores from three lakes in New Jersey and one lake on Long Island, New York. U.S. Geological Survey Water Resources Investigation Report 02-4272.

Meili, M. 1991. Mercury in boreal forest lake ecosystems. Dissertation. *ACTA Universitatis Upsalienses.* No. 336., Sweden.

New Jersey Department of Environmental Protection. 2001. New Jersey Mercury Task Force. Volume I: Executive Summary and Recommendations. NJDEP Report, December 2001.

New Jersey Department of Environmental Protection. 1994. Preliminary Assessment of Total Mercury Concentrations in fishes from rivers, lakes and reservoirs of New Jersey. A Report prepared for the NJDEP by the Division of Environmental Research, The Academy of Natural Sciences of Philadelphia, Philadelphia, PA.

Pirrone, N., I. Allegraini, G.J. Keeler, J.O. Nriagu, R. Rossmann, and J.A. Robbins. 1998. Historical atmospheric mercury emissions and depositions in North America compared to mercury accumulations in sedimentary records. *Atmospheric Environment.* 32: 929-940.

Rada R.G., J.G. Wiener, M.R. Winfrey & D.E. Powell. 1989. Recent increases in atmospheric deposition of mercury to North-Central Wisconsin lakes inferred from sediment analyses. *Arch. Environ. Contam. Toxicol.* 18, p. 175-181.

Sorenson, J.A., G.E. Glass, K.W. Schmidt, J.K. Huber, and G.R. Rap, Jr. 1990. Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediment, plankton, and fish of eight northern Minnesota Lakes. *Environ. Sci. Technol*. Vol. 24, pg. 1716-1731.

United States Geological Survey. National Water Quality Assessment Program (Report In draft), http://water.usgs.gov.

Wang, J. 1993. Sediment accretion rates and atmospheric heavy metal contamination recorded in high salt marshes adjacent to Long Island Sound, New York. MS Thesis. State University of New York, Stony Brook.

Funding

Prepared By

[1]Amy E. Kroenke, B.S., Edward L. Shuster, Ph.D., Richard F. Bopp, Ph.D. Rensselaer Polytechnic Institute, Department of Earth and Environmental Sciences, 110 Eighth Street, Troy, NY, 12180.

[2]Mary Downes Gastrich, Ph.D., Research Scientist and Project Manager, New Jersey Department of Environmental Protection, Division of Science, Research and Technology.