Abstract.
Mercury (Hg) contamination is pervasive in aquatic ecosystems and its bioaccumulation may lead to severe health concerns for both wildlife and humans. In this study we quantify historical Hg fluxes to the profundal sediment of Seneca Lake, NY. Previous studies show that the highest surface sediment Hg concentrations occur here, near a major tributary, the Keuka Lake Outlet. This tributary hosted much of the early industry in the area. Analysis of a 137Cs and 210Pb-dated sediment box core indicates total Hg (HgT) fluxes were low (197 \( \mu \text{gm-2y-1} \)) in 1770 and peaked between 1890 and 1910 (583 \( \mu \text{gm-2y-1} \)) and gradually returned to regional background levels (127 \( \mu \text{gm-2y-1} \)) by 1977. This peak in HgT flux predates those observed in other local and regional lakes, suggesting that a point source rather than widespread atmospheric deposition is the reason for increased HgT flux to the sediment. Early industry, including tanneries, hatteries, paper mills, and a flourishing nursery market, as well as a growing population during the late 19th century are possible sources of the high Hg concentrations found in Seneca Lake sediment.

Introduction.
Mercury (Hg) is a toxic trace metal pervasive in aquatic ecosystems across the Northern Hemisphere (Fitzgerald and Clarkson, 1991). Its bioaccumulation may lead to severe health concerns for wildlife and humans (US EPA, 1997). Mercury, in its elemental form, has a relatively long atmospheric residence time of up to three years (Perry et al., 2004). Highly volatile, Hg can spread from the atmosphere to the hydrosphere and biosphere quickly, and is known to cause neurological problems in vertebrates. Due to its bioavailability, mercury bioaccumulates throughout the food chain, transferring methylated forms from contaminated waters into fish and then to higher mammals and humans. Since 2001, sixty-three New York State (NYS) lakes, reservoirs, and ponds have been added to the Department of Health’s fish consumption advisory list due to elevated levels of mercury (Callinan, 2001).

Natural (e.g., forest fires, volcanic eruptions) and anthropogenic (e.g., fossil fuel combustion, medical waste incineration, municipal waste combustion, metal smelting, coal combustion) processes may supply Hg to the environment (US EPA, 1997). At regional to global scales, the primary mechanism of Hg contamination is through atmospheric transport and subsequent deposition via dust, rain, snow (US EPA, 1997). At the local scale, Hg may enter aquatic ecosystems through direct point sources (Bookman et al., 2008).

Previous study of sediment box cores from four lakes in central NYS found that the source of Hg differed spatially and temporally (Bookman et al., 2008). Three of the four lakes investigated showed peaks in Hg deposition (0.9 ppm) during the 1970s as a result of a significant regional atmospheric source (Bookman et al., 2008). The fourth lake showed a peak in Hg deposition (0.16 ppm) during the 1990s, which may be associated with a new, local emission source. In order to assess the sources of Hg to the New York Finger Lakes, Abbott and Halfman (2009) analyzed the Hg concentration of surface dredge samples from Seneca Lake, the largest Finger Lake. The average concentration (0.127 ppm) in Seneca Lake is high compared to the other four NYS, suggesting both regional and local sources both contribute mercury. Based on a survey of dredge samples from Seneca Lake in 1975, Blackburn, Fogg and Cornwall (1979) identified two potential local point sources: the local coal-fired power plant in Dresden, NY and a defunct industry in the Keuka Lake Outlet watershed. To test this hypothesis and evaluate the relative importance of local versus regional sources of Hg to the Finger Lakes region over time, we analyzed the Hg content of a sediment box core from Seneca
Lake, at a high resolution (1 cm; 6-7 years). A better understanding of the long-term history of atmospheric Hg cycling and quantification of the importance of local and regional sources of Hg is critical for assessing the impact of anthropogenic Hg emissions and to develop effective emission control strategies.

**Study Area.**
The 11 Finger Lakes of central New York occupy deep, narrow, north-south oriented glacially scoured basins (Schaffner and Oglesby, 1978). The largest by volume (15.54 km³), Seneca Lake has a surface area of 175 km², and is 57 km long, 5.2 km wide at its maximum and up to 188 m deep (Schaffner and Oglesby, 1978). The U-shaped lake has steep bedrock walls composed of Paleozoic sedimentary rocks (Schaffner and Oglesby, 1978). Soils of the region are Spodosols and Gleysols that developed in Quaternary glacial and glaciolacustrine deposits (USDA, 1958). Of Seneca Lake’s of 1181 km² watershed, 41% of the watershed is forested, 54% is devoted to agriculture, and the remainder, residential and urban (Schaffner and Oglesby, 1978).

The climate of Geneva, NY is typical of a midlatitude, temperate continental site, with cold, snowy winters and relatively mild, humid summers (Schaffner and Oglesby, 1978). Average temperatures range from 3.6°C in January to 26.5°C in July and the mean annual precipitation is 80 cm (Schaffner and Oglesby, 1978). Approximately 75% of the water reaching Seneca Lake comes from spring snowmelt (Michel and Kraemer, 1995). There are 16 major streams that enter the lake but only one outlet, located at the northeast corner of the lake (Fig. 1). Another Finger Lake, Keuka, drains into Seneca Lake via the Keuka Lake Outlet, and accounts for ~30% of Seneca Lake’s watershed. Seneca Lake is hydrologically open and the residence time is between 12-18 years (Michel and Kraemer, 1995).

Seneca is an oligo-mesotrophic, warm monomictic lake. Lake waters are well-mixed annually, alkaline (pH = 8.1), and characterized by high concentrations of Cl⁻ (139 mg/L), SO₄²⁻ (38 mg/L), alkalinity (106 mg/L, as CaCO₃), Na⁺ (79 mg/L), Ca²⁺ (42 mg/L), Mg²⁺ (11 mg/L), and K⁺ (2.7 mg/L) (Halfman et al., 2006). Waters remain well-oxygenated year round.

**Sampling.**
*Box Core Collection and Sampling.* A 36-cm long sediment core were collected from the profundal zone of Seneca Lake at 113 m water depth, north of the present day town of Dresden (42°46.296′N, 76°56.872′W) and between two streams, Kashong Creek and Keuka Lake Outlet using a modified Wildco box corer (Fig. 1). This site was selected because it had one of the highest concentrations of HgT at the sediment-interface in 1975 (Blackburn et al., 1979) and in 2008 (Abbott and Halfman, 2009). The core remained upright to preserve the sediment-water interface until sectioned. The core was extruded and sampled at a 1-cm interval at Hobart & William Smith Colleges (HWS). The outer smear was removed from each sediment increment with a stainless steel spatula, and samples were transferred into plastic containers. Samples were stored at 4°C until processing. Subsamples were sent to Rensselaer Polytechnic Institute for ²¹⁰Pb and ¹³⁷Cs analyses. The remainder of the sediment was frozen, freeze-dried and mechanically homogenized in plastic bags. Freeze-dried sediments were stored at room temperature.

**Analytical Methods.**
*Sediment Dating and Chronology.* Radiochemistry analyses of ¹³⁷Cs and ²¹⁰Pb at the Rensselaer Polytechnic Institute were conducted to develop an age chronology. ¹³⁷Cs 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. An age-depth model was constructed using a combination of $^{137}$Cs and $^{210}$Pb data. After identifying the Cs peaks, a regression line was fit mathematically to the $^{210}$Pb data. The slope of this line was used to calculate sediment accumulation rates and extrapolate ages for the core.

**Loss-on-Ignition.** Water, organic matter and carbonate content of dry sediment was determined on ~1 g using standard loss-on-ignition techniques (LOI) (Dean, 1974). Subsamples were first freeze-dried to determine the weight percent water content. The same subsamples were analyzed for weight percent total organic matter and carbonate content by LOI at 550°C and 1000°C, respectively. Mass measurements were made before and after freeze-drying and each heating using an electronic analytical balance. Dry density was calculated from water content, and fixed densities for the organic, carbonate and inorganic fractions.

**Grain Size.** Subsamples were treated with hydrogen peroxide and glacial acetic acid to remove the organic matter and carbonate fractions, respectively, and isolate the terrigenous component of the sediment using the methods of (Jackson, 1969). Samples were analyzed using a Coulter LS 230 Multivariable Laser Diffraction Particle Size Analyzer in duplicate. Grain size statistics were calculated using Folk and Ward’s (1975) equations.

**Mercury.** Total Hg concentration (HgT) of the box core was determined at the USGS Woods Hole Field Station using a direct mercury analyzer (DMA-80, Milestone Inc. Monroe, CT USA), which uses thermal decomposition, gold amalgamation and atomic absorption spectrometry and has a detection limit of 0.009 ng. Between 0.04 and 0.07 mg of each sample was analyzed in duplicate with one in six samples run in triplicate to calculate standard deviation. A calibration curve was generated using two reference materials: National Research Council of Canada Institute for National Measurement Standards MESS-3 (marine sediment, certified value = 91 ± 9 ng/g HgT [dry weight]) and US Commerce Department National Institute of Standards and Technology SRM 1515 Apple Leaves (certified value = 44 ± 4 ng/g HgT [dry weight]). Machine blanks were analyzed every 5-10 samples and reference samples were analyzed every 5-20 samples. Fluxes of HgT to the lake were calculated as the product of the $^{210}$Pb-derived sedimentation rates, sediment density, and dry weight HgT concentrations for each core interval and reported as mg m$^{-2}$ y$^{-1}$.

**Results.**

**Fig. 2.** $^{137}$Cs peak versus depth in box core S3. A worldwide peak in $^{137}$Cs occurs at 1963-64.

**Dating.** The $^{137}$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 (Fig. 2). Based on the $^{137}$Cs peaks, the net accumulation rate is approximately 0.2 cm y$^{-1}$ between 0 and 12 cm depth in the core.

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. The core exhibits an exponential decline in $^{210}$Pb with
depth, suggesting a near constant rate of sediment accumulation (Fig. 3). There is no indication of a surface mixed layer and both the $^{137}$Cs and $^{210}$Pb profiles (Figs. 2 and 3), which is consistent with a continuous accumulation. We assume a constant production rate in the watershed that gives rise to relative constant rate of sediment accumulation. Core chronology is based on $^{210}$Pb dating using the constant rate of supply model (Appleby and Oldfield, 1978). After identifying the Cs peaks, a regression line was fit mathematically to the $^{210}$Pb data. The slope of this line was used to calculate sediment accumulation rates and extrapolate ages. Based on both the $^{137}$Cs and $^{210}$Pb data, the net accumulation rate is approximately 0.18 cm y$^{-1}$ at the core top and is a little lower near the core base, 0.16 cm y$^{-1}$. These sediment accumulation rates were used to convert sediment core depths to ages. The core spans from 2008 to 1777 A.D.

Sediment Lithology. The entire core is comprised of finely laminated olive gray (5Y 3/2) and black (N1) clayey silt. The core shows a slight increase in organic matter upsection (Fig. 4). Overall, organic matter content is low, with an average of 4% (range= 3.0-5.7%). Carbonate content varies between 10.3 to 21.8% (average = 15.2%) and peaks in the early 1970s coincident with higher organic matter abundance.

The mean grain size of the sediment is 9.2 microns (medium silt), and ranges from 6.8 microns (fine silt) from the base of the core to 15.7 microns (coarse silt) near the top (Fig. 5). The trend in %sand mimics that of the mean grain size. The amount of sand increases upcore, from 2.7 to 18.8%, with an average of 7.1%.

HgT Concentrations. HgT concentrations ranged from 0.075 ppm in 1790 to a maximum of 0.414 ppm in 1890 and 1897 and an average of 0.24 ppm (Fig. 6). No correlation appears to exist between HgT concentration and wt. % organic matter, carbonate, or terrigenous grains and mean grain size or % sand. The onset of Hg contamination occurred in 1810 in Seneca Lake, whereas in nearby central-western NY lakes, the onset is dated at around 1910-1930, about a century later (Bookman et al., 2008).
Fig. 5. Grain size statistics with age. Mean grain size shows a coarsening upward trend. The % sand also increases upcore.

Fig. 6. HgT concentrations and HgT fluxes with age in the core. The timing of changes in Hg are compared with events in the Seneca Lake watershed and Keuka Lake Outlet.


Discussion.

**Potential Sources of Mercury to Seneca Lake**

Seneca Lake’s peak HgT fluxes predate all other observed maximum peaks in the region (Fig. 7; Bookman et al., 2008; Pirrone et al., 1998; Lorey & Driscoll, 1999; Kamman & Engstrom, 2002; Perry et al., 2004). Seneca Lake’s maximum HgT flux of 584 μg m⁻² y⁻¹ is greater than most lakes except Lakes Ontario and Erie. All other lakes reach their maximum HgT flux post-World War II (WWII). The 20th century increase in Hg flux in these lakes almost certainly reflects the global rise in atmospheric Hg deposition caused by anthropogenic emissions. Fig. 8 depicts how Hg emissions peaked post-WWII as a result of burning fossil fuels, smelters, and waste incineration. Because these

**HgT Fluxes.**

The HgT concentration in surface sediments, dry matter content in surface sediments and sediment accumulation rate were used to calculate the net HgT input into the lake. HgT fluxes range from 196.8 and 113.7 μg m⁻² y⁻¹ in 1777 and 1996 respectively to a maximum of 583.7 μg m⁻² y⁻¹ in 1903 (Fig. 6). The average flux was 320.8 μg m⁻² y⁻¹. Relative peaks in mercury flux occurred
other regional lakes all follow a similar trend of HgT flux, we infer that the observed early peak in HgT in Seneca Lake was the result of direct discharge rather than atmospheric deposition. Pre-industrial increases in HgT accumulation in European peat records are generally ascribed to early Hg mining and metallurgy, while those from North America are attributed to gold and silver extraction (beginning with the Spanish conquest ca. 1500) and volcanism (Pirronne et al., 1998). None of these appear to play a role in the peak HgT influx to Seneca Lake (Fig. 8). Because we are not located near a volcano, we discounted that potential source. We compared the timing of gold and silver mining in North America (Ontario, Canada) to that of Seneca Lake and there is no overlap. This eliminates the possibility of the signal being related to the gold and silver mining whose air emissions of mercury peaked in the late 19th century. The absence of a widespread signal implies that the pre-industrial HgT influx to Seneca Lake was local rather than regional.

A look at the history of the Seneca Lake watershed reveals multiple potential industrial sources of Hg. During the 1800 and 1900s, mercury was useful in several industries: gold and silver mining, manufacture of agriculture, medical, chemical, glass making, and papermaking. Several of these were abundant in northern Seneca Lake during the last ~200 years. We explore these potential sources below.

Agriculture has played a significant role in the western NY economy for centuries. For most of the 1800s, orchards and nurseries at the northern end of Seneca Lake were the most abundant in the state and amongst the largest in the country (Grebinger and Grebinger, 1993). They reached their greatest prosperity and productivity during the late 1800s when the Timber Culture Act of 1873 was enacted and required homesteaders to plant 160 acres of their land. As the population in the Midwest doubled between 1860 and 1870, so did the fueled the nursery business in Geneva, NY (Grebinger and Grebinger, 1993). By 1870 Geneva was the national nursery center, with over 30 nurseries during the 1890s. New
York State Agricultural Experimental Station bulletins discuss mercury’s use as an effective pesticide for agriculture. In 1893 mercuric chloride was considered the most effective preventive of potato blight (Collier, 1893). It was later proved to also be an effective option for controlling seed born diseases and maggots in cruciferous crops (e.g., cabbage, broccoli, collards, cauliflower, brussel sprouts, kale) (Clayton, 1926). While its use was widespread in a variety of agricultural as well as domestic capacities, there is no evidence pointing to mercury as a prevalent solution with common enough usage in the Geneva, NY area to account for the mercury flux recorded in Seneca Lake. Discouraging the use of mercuric chloride was the high applications required to produce the desired results with the need for 10-15 lbs. applied per acre in dry form with an additional 2-6 lbs. required for every ton of fertilizer (Cunningham and Wessels, 1939). Organic mercury fungicides were manually applied to orchard trees in much of New York State to control fungus-borne diseases of the fruit during the 1930s-1960s, after the peak in HgT flux to Seneca Lake (Merwin et al., 1994).

Mercury was a common “kill-all” solution. Mercuric chloride, as a corrosive sublimate was commonly used
as rat poison. It was also valued for its medicinal purposes. Besides its use in thermometers, drinking amounts around or above a half-pound of mercury was considered a cure for constipation and thus a preventive of “Iliac Passion,” or gastrointestinal agony (Willich and Mease, 1803). These processes would not be able to account for the high HgT concentrations in the lake.

Geneva was a bustling city during the 1800s. Water transport via the Finger Lakes and canals was slow, but much cheaper than over-land transportation making the shipping of both raw materials and finished goods in the Finger Lakes region over long distances more economically feasible. As a result, glass manufacturing companies began to flourish in the 1800s. The Ontario Glass Manufacturing Company and the Geneva Glass Works both operated on a small northern bay. In 1823, more window glass was made in this region than in any other town in America (Miscellaneous Register, 1823). Glass manufacturing remained a relatively important industry into the early to mid-1900s.

Blackburn, Cornwall and Fogg (1979) suggested that early industry along the Keuka Lake Outlet, a major tributary to Seneca Lake, might be responsible for the high HgT levels in the lake. Keuka Lake’s water exits via a 13.8-km long outlet to Seneca Lake. The elevation drop along the outlet is ~82.2 m with a number of waterfalls, making it an ideal location for the many mills that sprang up since 1790, when the first mill was erected (Dumas, 1989). Numerous gristmills, sawmills, tanneries, paper mills, batteries, and chemical factories were built along the outlet to take advantage of the waterpower of the outlet and later the convenient road and railroad access. Blackburn, Cornwall and Fogg (1979)’s analysis of dredge samples from the Keuka Lake Outlet indicated especially high concentrations of HgT associated with three abandoned mills, Milo and Cascade (Fig. 9). Milo Mill was a distillery until 1870s when it was converted into a paper mill that was successful until 1910, when it burned down (Dumas, 1989). Originally a grist and sawmill (1827-1866), the Cascade Mill site was converted to a paper mill in 1866 and it operated until 1900 (Dumas, 1989). Of the potential direct sources of Hg to Seneca Lake, the industrial boom along the Keuka Outlet including tanneries, paper mills, and batteries are the most likely cause of the elevated mercury fluxes during this time period. The timing of the HgT flux to the lake coincides with the greatest number of paper mills along the creek (Fig. 6). Paper mills along the Keuka Outlet may have used mercury-containing chemicals. Historically, paper mills used mercury as a biocide to prevent bacterial growth in the pulp and finished paper product (Watras and Hucklebee, 1992), so it is possible that this is the main source of mercury to the outlet and lake as the timing of the growth of the industry mimics the trend in Hg accumulation in the lake.

Variations in HgT Flux to Seneca Lake
The commencement and cessation of paper production along the outlet may be responsible for the gradual rise and fall of HgT in the lake. Concurrent with these mills was the deforestation of the region. Upon the arrival of Europeans in the late 1790s and early 1800s, the land was cleared for agriculture (Galpin, 1941; Schaffner and Oglesby, 1978). By 1880, ~73% of the Finger Lakes region had been clear-cut and replaced by farmland (DeLaubenfels, 1966; Siles, 1978). Deforestation destabilizes soils and results in a major increase in the contribution of terrestrial material. As a result, erosion rates were higher, and could explain the near simultaneous increase in HgT influx with the number of paper mills in operation. Although paper production had ceased in the watershed by 1910 (Dumas, 1989) and deforestation slowed and reforestation began (Siles, 1978), Hg still entered the lake.

These small-scale peaks in HgT that occurred between 1810 and present do not appear to correlate with changes in the number of mills on the outlet or other important industry in watershed or changes in land use (Fig. 5). We propose that climate-related events might play a role in some of these small-scale peaks in HgT that occurred in, approximately, 1863, 1917, 1937 1950, 1972, and 2002. To evaluate this hypothesis, we compared the HgT flux record to that of a local tree-ring record of Palmer Drought Severity Index (PDSI) (Fig. 10). PDSI is used to evaluate wet and dry
periods, specifically how moisture conditions depart from normal. Cook and Krusic (2004) reconstructed summer (June-August) PSDI values using variations in tree ring widths. PSDI values range from -6.0 (extreme drought) to +6.0 (extreme wet conditions). Some more recent peaks can be compared to written meteorological records. For example, in 1972, Hurricane Agnes caused intense flooding and erosion along the Keuka Outlet (Blackburn, Cornwall, and Fogg, 1979). We suspect similar heavy rainfall events and floods events might have played a role in transporting the Hg-contaminated sediment to Seneca Lake. Many of the known wet summer periods based on the PSDI record correlate to peaks in HgT (Fig. 10). The relatively wet period of the early 1800s, early 1900s and 1930-50s likely enhanced flushing of the watershed and led to increased Hg fluxes from the Keuka Lake Outlet to the lake. The reservoir of Hg-laden sediment in the Keuka Outlet may provide a source of Hg contamination for the lake for decades to come, even as reduction in atmospheric Hg flux continues.

**Conclusions**

1. Comparison of HgT accumulation rates in the Seneca Lake sediment core with the Hg emissions from silver and gold mining in North America and anthropogenic Hg emissions from burning fossil fuels, waste incinerators, and smelters in the Great Lakes region and all of North America suggests that atmospheric deposition was not the major source of Hg entering the lake. The timing of the HgT in Seneca Lake occurs after the mining boom and before major industrial boom after World War II. The most important contribution to the northern region of Seneca Lake likely originated from local point sources.

2. Sediment from former paper mills in the watershed and especially in the Keuka Lake Outlet is contaminated with Hg even today and is the most likely source of Hg to Seneca Lake.

3. Much of the contaminated sediment transport in Seneca Lake occurs during heavy rainfall events and floods, creating peaks in HgT.

4. The drop of about 50% in HgT accumulation rates between the 1910s and 1970s is largely the result of a combination of four factors: 1) fewer active mills along Keuka Lake Outlet, 2) reduced atmospheric Hg emissions in the Great Lakes region, 3) reforestation in the watershed post 1910, and, to a lesser extent, 4) climatic factors.

**Acknowledgements**

Thanks to Michael Bothner at the USGS Woods Hole Field Station for the use of his lab. We thank John Nichols, John Abbott, Meghan Brown, Meredith Eppers, Cameron Avelis, and Gwendolyn Wheatley for field assistance. Richard Bopp at Rensslear Polytechnical Institute performed radionuclide analyses. We thank the Geneva and Yates County Historical Societies and Sara Greenleaf at Hobart & William Smith Colleges’ library for their guidance and access to their archives, the Prouty-Chew Museum staff for extending their archive access hours as well as the NY State Agricultural Experimental Station for use of their libraries and archived bulletins. This study received financial support from a grant from New York State for radionuclide and lithological analyses. Additional funding from the Kloman Fellowship Fund (Hobart & William Smith Colleges) defrayed
the cost of traveling to Woods Hole, MA to conduct Hg analyses at the USGS.

References
Clayton, E.E. 1926. NYS Agricultural Experimental Station, Bull. No. 537, 1-29.
Collier, P. 1893. NYS Agricultural Experimental Station, Bull. No. 49, 1-16.
Miscellaneous Register v. 2, 1823. Geneva, N.Y.


Willich, A. F. M. and Mease, J. 1803. The domestic encyclopaedia, or, A dictionary of facts, and useful knowledge: comprehending a concise view of the latest discoveries, inventions, and improvements, chiefly applicable to rural and domestic economy: together with descriptions of the most interesting objects of nature and art, the history of men and animals, in a state of health or disease, and practical hints respecting the arts and manufactures, both familiar and commercial. W.Y. Birch, and A. Small, Philadelphia.