Transport and Fate of Historic Mercury Pollution from Danbury, CT through the Still and Housatonic Rivers

by

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The Still River Runs Still
Words & Music by Tom Callinan, © Cannu Yusic, LTD.

REFRAIN:

Still waters run deep, deep waters run still;
But the Still is not stagnant, the Still is not dead. The Still is living Still!

The Still flows out of Putnam County, Southeast from Sanford's Pond,
It winds through downtown Danbury, turns North, meandering on.
For 17 miles, through countryside of several Connecticut towns,
It twists 'til it joins with the Housatonic, then heads South towards the Sound

REFRAIN:

In the early 1800's, as pretty as you please,
The clear, pure Still was bordered by stands of tall shade trees.
Christians baptizing in the Still River's waters oftentimes would meet
Fishermen, swimmers, bathers, and waders, escaping the summer's heat.

REFRAIN:

But the Industrial Revolution harnassed The Still for power.
Factories and hatteries rose on banks that had been deflowered.
Many a hatter was maddened by mercury, while rubbish, sewage, and waste,
In The Still spawned diseases where fish once thrived; The Still was a great disgrace

REFRAIN:

In 1900, The Still was a sewer, its waters polluted and foul,
Forgotten and long abused, no fish, no waterfowl.
After Danbury flooded in '55, they contained that squalid stream,
In a downtown, concrete channel, where The Still may still be seen

REFRAIN:

In the 1990's, the tide turned, when treatment at Lime Kiln,
Transformed that tainted tributary and clean water spilled into The Still.
While not yet pristine, newfound pickerel mean The Still is being restored.
And someday it may be stocked with fish, and that's never happened before.

REFRAIN:

Neglect and abuse nearly killed The Still River,
Toxic waste almost snuffed it out,
But people showed they still cared for The Still,
Which someday might spawn trout.
Great changes can come in one generation, if people have the will,
And when skeptics say we can't be successful, just point them to The Still.

Accessed from The Still River Alliance 2014
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Abstract:

An analysis is presented here of the transport of historic mercury pollution from the hatmaking industry in Danbury CT through the Still River, Housatonic River, and into Long Island Sound. Hg concentrations and mean accumulation rates from cores taken on either side of the Still River-Housatonic River junction are highest in both cores during the 1900, 1955, and 1970s periods of flooding in Southern Connecticut. An age comparison using Pb210 and Cs137 to previous work in the Still and Housatonic Rivers and Long Island Sound, as well as the point-source free record in Block Island corroborates the pattern of flood events driving mercury transport. The history of dam construction in the Housatonic River is used to create an estimate for the amount of mercury accumulating during periods of steady state transport.
1. Project Introduction

The goal of this study is to create a near-source time record of legacy mercury pollution in the Still and Housatonic Rivers. Goldoff (2002) found unusually high concentrations of mercury in surface samples in Danbury near the sites of late 19th century to early 20th century hatmaking factories. Cores from along the Still River, which runs North through downtown Danbury, contained average mercury concentrations several orders of magnitude above background values (Goldoff, 2002). Varekamp (2003) analyzed a series of sediment cores taken along a grid in Long Island Sound for mercury, finding concentration versus age profiles similar to those found by Goldoff (2002) in the Still River. This study theorizes that legacy mercury pollution originating in Danbury is carried North by the Still River to the Housatonic River, which deposits mercury-laden sediments in Long Island Sound, where they are in turn spread through tidal mixing first into Western Long Island Sound and then East to Central Long Island Sound. The history of dam construction in the Housatonic River precludes a simple steady-state transport model, so an inquiry is conducted into the relationship between mercury concentration measured in regional sediment cores and major flood events.
2. Mercury in the Environment

2.1 Introduction
The element mercury (Hg) has an atomic number of 80 and two stable oxidation states: 0 and 2+. The dominant species of mercury on earth are Hg(0) or elemental mercury, Hg(II) or oxidized mercury, Hg(P) or particulate mercury, which is also typically oxidized, MeHg or methyl-mercury, and DMMeHg, or dimethyl-mercury. The majority of mercury on earth is locked in insoluble Hg(II) salts such as Cinnabar (HgS), though in particularly mercuriferious outcrops such as those on Almaden, Spain, and Idrija, Slovenia, liquid mercury can form as silver liquid droplets on the surfaces of Hg-bearing rocks (Saupe, 1990; Gosar, 1996).

Elemental mercury, the species commonly known as “quicksilver”, is a dense, volatile liquid at STP, and easily amalgamates other metals such as gold and silver (Fig. 1). Because of these properties, humans have extracted mercury for a variety of ritual, pseudo-medicinal, mining, and industrial purposes since 1500 BCE (Cooke, et al. 2009; Streets, 2011). Identifying elevated concentrations of mercury in a given environment thus requires an understanding its long history as an environmental pollutant.

2.2 Major Historical Fluxes
The earliest known anthropogenic mercury flux to the environment is the use of vermilion (powdered HgS) in body paint by the Chavin Inca empire in Huancavelica, Peru (Cooke et al., 2009). Mercury mining in Europe began in Almaden, Spain by slaves and criminals during the Roman era. The
invention and proliferation of the patio silver amalgamation process in Mexico in 1554 greatly increased the mercury output of colonial outposts in Latin America (Nriagu et al., 1994). Between 1700 to 1850, pre-industrialization in Western Europe, the locus of global emissions was concentrated in the Mediterranean-Central Asian mercuriferous belt (Hylander, 2003) (Fig. 2).

2.3 Industrialization and Modern Record

Industrialization marked the beginning of a major increase in global atmospheric Hg emissions. Streets et al. (2011) estimate that 61% of the 350 Gg (Gigagram or 1000 tonnes) of all-time anthropogenic emissions were released after 1850. These new sources of Hg pollution included copper, zinc, and lead smelting, iron and steel manufacturing, caustic soda manufacturing in chlor-alkali plants, and combustion of coal, oil, and waste (Streets et al., 2011) (Fig. 3). Though other inexpensive processes have since been developed for extracting gold from ore, Artisanal Small Scale Gold Mining, in areas where legal mining operations have been abandoned and mercury is marginally abundant, is emerging as an increasingly important contributor to the modern global mercury budget, comprising >35% of total present-day emissions. (UNEP, 2013).

Background concentrations of mercury measured in a given locality reflect both legacy and modern Hg emissions. Elemental mercury has a residence time of several months to a year in the atmosphere, so the global record can be measured in remote locations such as Antarctic coastal ice.
cores (Vandal et al., 1993) (Fig 4). The EPA also maintains Hg monitoring stations across the United States through the National Atmospheric Deposition Program (Fig 5). As gaseous Hg(II) has a much shorter residence time than Hg(0), these records reflect local differences in climate and point source input as well as Hg(0) distributed globally. The systematics and processes that govern Hg cycling and deposition from the atmosphere will be discussed a following section.

2.4 Toxicology
Mercury has no known biological function. Bioavailability, bioaccumulation, and biomagnification are the three parameters that control the exposure pathway and risk mercury poses to ecosystems and individuals. Bioavailability refers to how easily a toxin is taken up by the tissue of an organism. A toxin is bioaccumulative if the rate at which the toxin is absorbed exceeds the rate at which it is flushed out. Biomagnification refers to whether the toxin will continue up the food chain as contaminated organisms are consumed by predators. In general, biomagnifying toxins are concentrated in larger predators, as they consume a greater number and a larger mass of contaminated individuals (Fig. 6).

Some forms of Hg are more bioavailable than others, and the pathway through which they enter the body affects bioavailability as well. In general, MeHg is the most bioavailable species, followed by inhaled elemental mercury and ingested Hg(II) salts, and lastly by ingested elemental mercury.
The EPA uses the Reference Concentration (RfC), to quantify the maximum amount of a toxin a person can inhale throughout their lifetime working an 8-hour day without experiencing deleterious effects. The Reference Dose (RfD) quantity refers to ingested exposure measured in weight concentrations per day per kg bodyweight.

Dimethyl- and Methyl-mercury are the most bioavailable and thus the most dangerous species of mercury. The RfD for methyl mercury is $1 \times 10^{-4}$ mg per kg bodyweight per-day. Dimethylmercury is one of the strongest neurotoxins and can be absorbed through the skin. (US EPA, 2012) Exposure to as much as .1 mL of liquid Dimethylmercury has proven fatal (OSHA, 2008). Because of this toxicity, Dimethylmercury is not biomagnifying, and does not pose a threat to as many humans not immediately exposed (Varekamp, pers com.). Methylmercury however, is primarily absorbed through digestion, and it is bioavailable, bioaccumulative, and biomagnifying. Consumption of large marine fish and shellfish is the primary exposure path of humans to methylmercury, and to non-occupational mercury poisoning in general. (US EPA, 2012) Saltwater fish typically have higher concentrations of methylmercury than freshwater fish because of bacterially-mediated reactions that occur in seawater, as discussed in a following section (Selin, 2010).

The RfD for inorganic mercury is 0.0003 mg/kg body weight per day (US EPA, 2012). Hg(II) is more soluble than Hg(0), and so poses a threat to
individuals drinking polluted water. The EPA limit for dissolved Hg in drinking water is 2 ppb (ASTDR, 1999).

The RfC for inhaled elemental mercury is \(3 \text{E-4 mg/cu.m}\). Inhaled elemental mercury vapor disrupts central nervous system function and can lead to tremors, emotional changes, neuromuscular changes, and reduced cognitive function. (US EPA, 2012).

The EPA has not established an RfD for ingested elemental mercury, though ingested elemental mercury can acutely disrupt digestive function, and chronic exposure can cause chronic central nervous system damage (US EPA, 2012). Famously, there is historical speculation as to whether Abraham Lincoln’s “Blue Pills” with mercury used to treat constipation caused his bouts of rage and irritability (Hirschhorn, 2001).

2.5 International Legislation

Though the health effects of occupational mercury exposure have been known since Roman times, the first mass-poisoning that lead to international legislation occurred in Minamata Bay, Kyushu, Japan in the late 1950s. Effluents from a chemical company using mercury as a catalyst to produce acetaldehyde entered the Bay’s ecosystem, biomagnifying in the large fish and shellfish that comprised the local diet. More than 2,200 people were diagnosed with mercury poisoning, and infants born in the area developed a cerebral palsy-like neurological disease (Harada, 1978). In 1965, a similar poisoning caused by an acetaldehyde company occurred in Niigata
province resulting in 700 cases of mercury poisoning (Harada, 1978). In response primarily to these episodes, the United Nations Conference on the Environment in Stockholm in 1972 created the United Nations Environmental Program (UNEP, 2013). In 2013, the UNEP published the Global Mercury Assessment and held the Minamata Mercury Convention, at which 140 countries, including the United States, China, and the European Union ratified an agreement to control mercury pollution across a range of industries and improve training for healthcare providers in identifying mercury pollution symptoms. In the United States specifically, the export of mercury was banned in 2008 under the Mercury Export Ban Act, which also included provisions for mercury management and long-term storage (UNEP, 2013).

2.6 Biogeochemical Cycling of Mercury

Global biogeochemical cycling of mercury is made up of primary sources--those that liberate mercury from the lithosphere, and secondary sources--those that re-cycle mercury between the oceanic, terrestrial, and atmospheric reservoirs. However, sophisticated multi-box modeling of mercury exchange consider three different exchange rates for armored, slow, and fast weathering soils, which complicates dividing the mercury cycle into long and short cycles analogous to those of the Carbon cycle (Amos et al., 2013) (Fig. 7). In this next section I will outline the primary and secondary exchange pathways between the lithosphere, ocean, terrestrial biosphere, and atmosphere pertinent to this study.
2.6.1 Emissions from the lithosphere

Volcanic heating processes—magma, hydrothermal fluids, and particle emissions—are the main primary sources of mercury release from the lithosphere. Volcanoes emit 90-500 Mg/a Hg, primarily as Hg(0) with a minority of Hg(II) in Hg-S complexes. (Pirrone et al., 2010). Slow weathering of mercury-rich rocks contribute some Hg(II) to the ocean and atmosphere, though it is small compared to the volcanic flux (Pirrone et al., 2010; Streets et al., 2011). Currently, Anthropogenic fluxes of contributing 2000 Mg/a primary emissions far outpace natural emissions of 500 Mg/a (Streets et al., 2011).

2.6.2 Hg in the atmosphere

Due to its volatility and inert nature, Hg(0) has a residence time of .5-1 year in the atmosphere (Selin, 2009). As a result of this long residence time, most gaseous elemental mercury will circulate globally until it is oxidized in a photo-dependent reaction to Hg(II). Though a minority is deposited directly as Hg(0). Early models suggested Ozone or OH radicals as the oxidizing agent of Hg(0), Donohue et al., 2006 demonstrated that Br is a more favorable oxidizer thermodynamically in this reaction.

Two processes remove Hg(II) from the atmosphere: wet deposition and dry deposition. These removal fluxes are quite efficient; Hg(II) as a residence time of days to weeks, at most (Shroeder, 1998; Selin, 2009). Wet deposition involves the dissolution of Hg(II) in clouds, and then scavenging by
rain or snow. Dry deposition involves settling of H(II) on the earth’s surface without precipitation.

Coal combustion, the largest anthropogenic flux of Hg to the atmosphere, produces Hg(II), Hg(P) and Hg(0). The Hg emitted through anthropogenic processes typically has a higher ratio of Hg²⁺/Hg(0) than Hg emitted through geogenic process does (Selin, 2009). This Hg will follow natural pathways of mercury cycling appropriate to the speciation, resulting in higher terrestrial and oceanic Hg(II) concentrations in areas near pollution point-sources.

2.6.3 Hg in the Terrestrial Biosphere
Hg(0) and Hg(II) deposited through dry processes are taken up by leaf stomata and fixed into the the pool of standing organic matter. Hg is released into the soil by the decomposition of leaf litter. Some of that mercury may again escape through respiration, though the majority will re-bind to sulfur groups and organic matter, or adsorb onto clay particles. Hg(0) adsorbed onto the leaf or land surface is secondarily-emitted into the atmosphere on a short time scale (Smith-Downey, 2011). Hg(II) deposited by the wet pathway and adsorbed to leaf surfaces is transported into the soil by throughfall, where it preferentially bonds to reduced sulfur groups and organic matter until remitted by respiration. (Smith-Downey et al., 2011) Hg residence times in soils depends on the substrate to which Hg has bonded or adsorbed, and the extent to which the soil is armored (Smith-Downey et al., 2011; Amos et al., 2013).
2.6.4 Hg in Aquatic environments

The redox potential of a water body, in addition its geometry and the size of its outflows and drainages, control its mercury cycling. Mercury enters aquatic systems both through wet and dry deposition and through a focusing term wherein runoff and groundwater bring in Hg adsorbed onto clays and bonded to organic matter. Mercury ultimately exits a waterbody bonded to outflowing organic matter, adsorbed onto outflowing clay particles, by dissolving and flowing through groundwater, or through photoreduction and volatilization at the water surface.

Within a water body, Hg(0) can be oxidized to Hg(II) by dissolved O2, and by anaerobic and aerobic bacteria such as Eschateria Coli, *Bacillus* and *Streptomycyes* (Smith et al., 1998). Once oxidized, Hg(II) can be converted to methyl and dimethyl mercury by sulfate-reducing bacteria or by dissolved organic carbons. Though sulfides in the water column have a high affinity for dissolved Hg(II), rates of Hg methylation have been observed to increase with elevated sulfide concentrations (Langer et al., 2001). Aerobic bacteria also drive a reciprocal breakdown methylmercury into CH4 and Hg(II), which typically occurs at the water oxic/anoxic interface. Methylmercury is also volatile, so MeHg that reaches water surface can evaporate from the lake.

As the creation of methyl mercury requires either low water pH, sulfate ions, or dissolved organic carbons, methylmercury concentrations are typically highest in anoxic seawater, and lowest in rivers and oligotrophic lakes (Selin et al., 2009) Long Island Sound is an archetypal example of how
anoxia from nutrient loading can exacerbate methylmercury pollution (Lamborg et al., 2004). This effect is mitigated somewhat by high concentrations of organic matter in LIS, which are a substrate for dissolved Hg(II), as well as the high affinity Hg(II) has for sulfides.

Figure 2.1 Experimentally derived mercury vapor pressure curve. From Huber et al., 2006.
Figure 2.2. Global historical records of primary Hg production with contributions from two major European mines. From Hylander et al., 2003.
Figure 2.3 Hg emission records by (a) source type and (b) region. From Streets et al., 2011
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Figure 2.5 Atmospheric Concentrations as Measured by the National Atmospheric Deposition Program. From Selin, 2009.
Figure 2.6 Bioaccumulation of Mercury. From Siegel, 1997.

Figure 2.7 Modeled modern Hg exchange between terrestrial, marine, and soil reservoirs. From Amos et al., 2013
3. Local setting

3.1 Hatmaking and Mercury in Danbury

Mercury has been involved in the hatmaking process for centuries as a matting agent to turn fur into felt (Greenwald, 1989). In pre-industrial times, Hats were made using predominantly hand tools: a tub of hot water and mercury nitrate to remove fur from pelts and mat it into felt, a plank bench, and stands on which to shape hoods and cones. The felting and shaping process took place in a back shop, whereas trimming and sizing took place in a front shop where no mercury was used.

However, at the onset of industrialization, the demand for hats increased significantly, and structural changes to the workplace fundamentally affected mercury exposure risk. The manufacture of fur hats consisted of three stages carried out in separate factories. The first stage involved fur-cutting plants, where the furs of rabbits, hares and other rodents were chemically treated with an orange-colored mercury nitrate "carroting solution" to form felt (Figure 3.1). (Beavers, the fur of choice in times prior, had fallen out of fashion with a near extinction of the animal in Europe. (Figler, 2009)) The felt was then taken to a back-shop where a machine shaped it on a cone and workers treated it with hot water until it shrunk to the desired shape (Figure 3.2). The hat body was then transferred to a front shop where it was trimmed and smoothed (Public Health Bulletin, 1941).

Hatmaking in Danbury started in 1780 with Zadoc Benedict opening a small 3 hat/day shop on Main Street. Changes in industrialization and mechanization affected both the demographics of the workers and their
mercury exposure risk. During Benedict’s time, hatting was a skilled labor done mostly by Yankee artisan men in small hat shops. Hatting was a highly respected profession, and hatters could move between hatting towns with a high degree of job security. Although the risks of “hatters shakes” (soon to be known as “Danbury shakes”) were known throughout the trade, workers had a high degree of autonomy over their workplace, and could control to an extent their degree of exposure (Greenwald, 1989). This labor-capital relationship changed with industrialization, and women and immigrants with less training and agency made up new workforce (Figure 3.3).

As demand for hats spiked in the early 19th century, Danbury grew in prominence as a hatting town, largely because the Still River flowing through its city center provided an accessible source of water. By 1887, 30 factories existed in Danbury manufacturing five million hats a year, and 80% of the town’s workers were in some way working in hatting industries by 1920. Danbury gained the motto “The Hat Capital of the World” and earned the slogan “Danbury Crowns Them All”.

In 1924, the Lee hatmaking company hired Dr. Constantine Fabian to create a non-mercuric caroting solution (Fabian, 1942). Although he succeeded, the new solution was not widely adopted by the industry. The advent of the Worker’s Compensation Act resulted in what union leader Dennis Caroll called in the Danbury Herald “a well-run and highly profitable racket” wherein workers would waive away their rights for compensation for mercury-related disease in exchange for employment, and the companies
would take the government compensation. (Carroll, 1941). A series of litigations came to a head in 1941 where the union had a hearing with Governor Hurley and the US public health service, and on “Mercury day, December 1st 1941” mercury caroting solution was banned in the industry. (Caroll, 1941). One historian, Richard Wedeen, is retrospectively skeptical of Caroll’s union triumphalism, suggesting instead that mercury was needed for the war effort for use in detonators (Weeden, 1989).

Hatmaking itself however, was on the decline in Danbury by this time period. In the end fashion, not mercury, drove the demise of the industry. No Danbury hat crowned the head of John F. Kennedy at his 1961 inaugural address. By 1965, the Stetson Hat Company had closed up shop.
Figure 3.1 The “blowing” process which separates coarse hair from fur. From “Danbury Leads the World in Hatting” by J Moss Ives. Accessed online at Connecticuthistory.org
Figure 3.2. Workers shape a hat. From “Danbury Leads the World in Hatting” by J Moss Ives. Accessed online at Connecticuthistory.org

Figure 3.3. Women comprised a sizeable proportion of workers during the industrial hatmaking period. From “Danbury Leads the World in Hatting” by J Moss Ives. Accessed online at Connecticuthistory.org
3.2 Physical Description of the Still River

The Still River is 22 miles long, and flows west from its headwaters in Eastern New York State through the town of Danbury, where it turns North and joins the South-flowing Housatonic river. The Still River is sluggish, with a mean flow of 384 cubic feet per second measured at the Robertsville, CT USGS stream gauge. The Still River meanders for much of its length, and its Northern reach includes many oxbows. It has a relatively small drainage area of 85 square miles.

The Still River also has a history of use as an urban sewer. In 1885, over a third of all 2800 families in Danbury dumped sewage into areas that drained into the Still River (Danbury.org/stillriver). Urbanization of the Danbury landscape involved replacing the forest, wetland, and soils with concrete, cut lawns, and asphalt. These changes resulted in increased channelization in the floodplain, carrying additional pesticides and fertilizers into the river. For this time period, the Still River did not support higher order aquatic life such as fish (Danbury.org/stillriver).

Since 1970, ongoing reclamation efforts have dramatically improved the health of the Still River, and fish have returned to its waters (Danbury.org/stillriver). In 1995, the city of Danbury created the Still River Restoration Project which involved alterations to the floodplain to reduce channelization, a “Greenway” hiking trail, and advertised paddle events. The Still River Alliance currently stewards the Still River, and hosts regular educational and recreational events (Danbury.org/stillriver).
3.3 Path of the Still River
The Still River has its origin in small tributaries and two small ponds in Eastern New York State near the village of Mill Plain. It flows East-West through following route 6 into East Danbury, where it travels beneath Mill Plain road, pours into Lake Kenosia, and discharges through Mill Plain swamp to join Miry Brook behind the Danbury Mall Fairgrounds and crossing route 7 into downtown Danbury.

At White Street, the river flows through a concrete flood control channel built in the 1960s to control flooding at the railroad trestle. The river continues through the artificial channel for 1 mile until discharging at Caspar street, where it flows under Triangle street until joined by Sympaug Creek. At the confluence of the Still and Sympaug, the river changes direction from West to North. The Still flows through Commerce Park, the site of the “Still River Greenway Project”, where it is joined by Limekiln Brook before crossing Route Six.

At route six, the Still River meanders along a flat reach Northward for 16 kilometers, paralleling route 7. In Brookfield it passes through a straight bedrock gorge East of Candlewood lake into New Milford. There, the Still River flows through Harry Brook Park and then joins the South-flowing Housatonic in Lover’s Leap State Park.

3.4 Geology of the Still River Valley
The Still River is underlain primarily by the Inwood Marble. The Inwood Marble can be both calcitic or dolomitic, and contains variable amounts of
tremolite, phlogopite, and other silicates distributed in layers. In general, the
Inwood Marble is very erodible, though its variable mineralogy accounts for
differences in comparative resistance at different points. (Thomson, 1970)

During its Northward reach, the Still River occupies a half-mile wide
valley, excepting a 1 mile gorge through Brookfield. Glacial sediment
comprises the majority of material in the Still River valley. These include an
upper and lower till representing two different glaciations and ice contact
drifts. Glaciolacustrine sediments can be found along the whole length of the
valley (Thomson, 1970). Eolian silt and weathered bedrock are found in more
limited amounts in the valley, and some floodplain deposits have been
located in areas close to the river banks. A CT DEEP flood insurance map
indicates that flood areas are constrained primarily within the valley (Fig 3.4).

The Still River’s sluggish flow and limited flooding along the Western
banks can be attributed to the valley’s unusual width and Northward gradient.
The latest worker to describe these features was Thomson (1970) of the
USGS. His hypothesis for the glacial and pre-glacial history of these features
is as follows:

Thomson argues that the Still River’s Northward drainage is a pre-
glacial feature, and the Still River originated as a small tributary of the
Housatonic. On the basis of the heights of bedrock terraces and bedrock
contours, the Still either originated near Lanesville and lengthened toward
Danbury, or the Southern part of the still was a tributary of the Saugatuck. In
both hypotheses, the Still River valley was carved by the Still River itself, and
not the Housatonic, as too meters of glacial overdeepening would have been necessary to overcome the bedrock gradient. The width of the valley is attributable to the erodibility of the underlying Inwood Marble.

The last glacial retreat accounts for the River's current path. During the most recent glaciation, glacial lake Danbury formed as a pond between the ice front and Connecticut's Western highlands. Outlets opened as the ice retreated, filling what now comprises the Still River Valley. Though glaciation removed large quantities of marble from the Still River valley, a high bedrock surface around Danbury prevented the Still waters from escaping to the South or West, as in pre-glacial times. Thus, while the last glaciation determined the path of the current Still River, its bedrock contours and pre-glacial morphology ultimately control its Northward gradient and valley width, which are two important parameters for sediment transport.
Figure 3.4 CT DEEP Flood Zone Map for New Milford, CT. (2010)
3.5 The Housatonic River

The Housatonic River has its headwaters in Pittsfield, Western Massachusetts. It has a total length of ~ 240 km with a drainage area of 5,100 km$^2$ located West of the drainage area of the Connecticut River. It flows mainly South-Southeast in a meandering pattern with numerous oxbows. It meets the Still River in New Milford, CT ~120 km along its southward reach, and drains into Long Island Sound in Stratford, CT (Zierzow, 2002; Housatonic Valley Association, 2012).

The Housatonic has a fall of 1430 feet over its length, resulting in an overall vigorous flow rate (Housatonic Valley Association, 2012). The Housatonic River has been dammed for power on small scales since colonial times. Beginning in 1870, the company that would become Northeast Utilities constructed three hydroelectric dams along the Housatonic River south of New Milford, resulting in three in-stream lakes. The Shepaug dam in Southbury (built in 1955) formed Lake Lillinolah, the Stevenson Dam (built in 1919) created Lake Zoar in Monroe, and the Derby dam (built in 1870) formed Lake Housatonic between Derby and Shelton (Zierzow, 2002; Housatonic Valley Association, 2012). Lake Lillinolah has an area of 1900 acres, Lake Zoar has an area of 976 acres, and Lake Housatonic has an area of 975 acres (Housatonic Valley Association, 2012). The construction of these dams is a key parameter controlling the transport of sediment and Hg to Long Island Sound.
4. Problem at Hand – Hg in Western /Southern Connecticut

4.1 Mercury in Western Connecticut and Long Island Sound

Mercury pollution across Western / Southern Connecticut and Long Island Sound show evidence of both point- and far-field atmospheric sources of mercury. The Hg concentrations of 150-200ppb measured in soil and wetland samples on remote mountain areas such as Mount Riga in NW Connecticut indicate the omnipresence of Hg deposition from the atmosphere (Kreulen, 1999). Mercury pollution in southern New England is most likely impacted by this atmospheric deposition process. An array of local Hg sources have been recognized that may have impacted the Connecticut natural environment as well (Fig 4.1). It is a challenge to distinguish the effects of point source pollution from atmospheric deposition with sediment focusing when all these processes occur simultaneously. This is especially true for Long Island Sound, where the Hg is delivered from a variety of sources (Varekamp et al, 2003; Balcom, 2006).

It has been proposed that a local reference site for atmospheric Hg deposition is needed, and the ponds, lakes and marshes of Block Island may serve such a purpose (Neurath et al., in review). I will use the data from that study as the benchmark site for atmospheric deposition only, be it with the usual sediment focusing.
Figure 4.1. Sample locations considered in this study.
Three types of point sources of Hg pollution are known in the Connecticut region:

I. Waste water treatment plants (WWTP)

II. Legacy Hg from the hatmaking industry in western Connecticut

III. Legacy Hg from a mercury boiling power plant near Hartford, active during the first half of the 20th century (significance still under study)

Mercury from these sources is transported into LIS through the Housatonic and Connecticut Rivers. The Housatonic River transports legacy Hg from the 1820s-1941s hatmaking industry in Danbury, CT and surroundings via the Still River, a North-flowing tributary of the Housatonic River. The Connecticut River transports the legacy Hg pollution from the power plant. These mercury contributions are mixed through tidal stirring in LIS and ultimately the Hg-rich sediments are deposited on the bottom of the Sound. The leading question behind Hg studies in Southern / Western Connecticut is as follows: in how far has the whole sediment bed of LIS been impacted by these point source contributions? This question can be addressed by looking for fingerprints of the various pollution sources, such as the association with cysts for WWTP Hg characteristic chemical associations for Housatonic River sediment, and possibly using Hg isotope ratios to trace sources (Varekamp et al., 2000; Varekamp et al., 2003; Balcom et al., 2006).
4.2 Long Island Sound Hg Record

The investigation of point sources of anthropogenic Hg in Southern Connecticut began with the discovery of Hg contamination profiles in Long Island Sound by Varekamp, 2000. These profiles indicated that Hg in LIS had increased by a factor of 5-6 over the last few centuries, but decreased by up to 30% since 1970 (Varekamp, 2000). Pb-210 dating of cores in Western Long Island sound revealed the onset of mercury pollution in the mid 1800s, with peaks in Hg concentration around 1900 and 1955 (Varekamp, 2003).

A series of cores taken on a grid in LIS revealed a gradient ranging from <50 ppb Hg in Eastern LIS to >600 ppb in Western Long Island Sound (Fig 4.2). (Varekamp, 2003) This gradient was hypothesized to be a result of changes of sediment lithology and grain size, with coarser sediment on the more energetic east side of LIS. The vigorous tidal mixing in LIS may have spread point source Hg along much of WLIS and possibly even into ELIS.

Figure 4.2 Hg Concentration Gradient in Long Island Sound. (Varekamp, 2003).
4.3 River Inputs to Long Island Sound

4.3.1 The Still River

Goldoff (2002) investigated the relationship between the Danbury Hatmaking industry and the legacy Hg in the Still River. Surface samples taken from around the building foundations of the Mallory “back shops” in downtown Danbury had concentrations between 30 and 67 ppm Hg, and surface samples from the Still River Basin ranged between 654 ppb to 14 ppm Hg. Goldoff (2002) also took two cores of small coves of the Still River adjacent to Erikson Road, which also returned extremely high Hg concentrations. Core SRNER C-1 had a broad Hg* peak over 100 ppm between 1875 to 1955 (Fig 4.3). Core SRNER C-2 peaked first in 1875 at 90 ppm, and again in 1955 at ~88 ppm (Fig 4.4). Goldoff (2002) took a third core in a catchment along Del Mar Drive, which returned a similarly contaminated two-peak Hg profile with a 112 ppm spike at ~1960 and a 1975 peak of ~54 ppm (Fig 4.5). The SRNER C-2 core was dated using Pb-210 and Cs-137 radio-chronology. Ages for the other two cores were extrapolated by comparing their peaks in the Hg record to those of SRNER C-2, and then assigning dates to those peaks accordingly.
Figure 4.3. Hg* concentration in the first Erickson Road core. From Goldoff, 2002.
Figure 4.4. Hg* Concentration in the second Erickson Road core. From Goldoff, 2002.

Figure 4.5. Hg* Concentration in the Del Mar Drive Core. From Goldoff, 2002.
4.3.2 The Housatonic River

The lower reaches of the Housatonic River contain several small (600-700 m) islands 9 km proceeding its delta in LIS. From North to South, cores have been taken and analyzed from marshy sediments on Fowler Island, Long Island, Pope’s Island, and Knell’s Island. The Long Island core profile peaks in 1900 and at 1955, as does the Pope’s Island core. The Knell’s Island core does not show the 1900s peak, though the 1955 peak is easily identifiable. Of these, the Knell’s Island core is most rigorously dated, with clear Cs-137 peaks and a Pb210 model that is depleted during the 1955 flood event.

Figure 4.6 Hg⁺ Concentration from Knell’s Island. From Varekamp, 2003.
Figure 4.7. Hg* Concentration in Long Island. From Varekamp, pers com, 2014
4.3.3 The CT River

Chapman Pond, a freshwater body along the Connecticut River ~23 km from LIS also showed a similar age-contamination profile with mercury onset in the 1840s, and peaks in the early 1900s and mid-1960s (Varekamp, 2003) (Fig 4.9). As this pollution is across a drainage divide from the Housatonic records, this record reflects a separate point source. A spill in the HELCO power plant in the mid 20th century is likely implicated in cores from Wethersfield Cove, a cut off meander farther upstream in the Connecticut River (Varekamp, 2011).
4.3.4 Jarvis Creek

Jarvis Creek is a small brook that drains into LIS nearly halfway between the Housatonic River Delta and the CT River delta. This study considers two cores, JC-6 and JC-12, taken in a catchment ~.25 kilometers North of where Jarvis Creek meets LIS. The JC-6 core was analyzed for mercury, and contains the local LIS record of coastal Hg accumulation removed from known point sources. The JC-6 profile shows a spike in 1900, a small dip between 1930-1940, a second peak in 1955 followed by a plateau through 1980 and a decrease from 1980 until present (Fig. 4.10).
4.3.5 Climatic influences

Of the cores considered in this study, Zierzow (2002) studied the trace metal record of Cu, Zn, Cr, Cd, Co, Ni, and Pb in cores from Pope Island, Fowler Island, Knell's Island, and LIS and WLIS cores. Of these, only the Knell's Island core contained a near-"classical" contamination record with background metal concentrations until 1900, a peak between 1960-1970, and a decline until present. Metal values fluctuated greatly in the other Housatonic cores, and Zierzow identified re-worked sediments in low-gradient sections of the river during periods of high flow, specifically during the 1938 hurricane, the 1955 flood, and the 1970s period of high rainfall. The climatic history of
this time period in Southern Connecticut is shown in Figure 4.11. Changes in non-Hg metal contamination indicate the considerable influence that changes in flow regime, rather than point source input, has in pollutant transport to LIS.

Figure 4.11. Major precipitation events in Connecticut. From Varekamp et al., 2003.

5. Methods

5.1 Fieldwork and sample processing

Five grab samples were taken from the Dean Road neighborhood in Brookfield, CT (41°28'22.00"N, 73°24'6.00"W) along a cut off meander of the Still River known to residents to be covered in Still River floodwater regularly. The dean Road neighborhood was chosen for sampling because of its proximity to the SRNER C-1 core and community concern regarding an
anecdotally high incidence of neurological disorder in the neighborhood (Varekamp, pers com). Surface samples were collected using an aluminum spade which was cleaned between samples.

A 37 cm push core was taken 2 feet of water in a catchment along the Still River just below the steep part of the Still River where it exits Harry Brooke Park, south of the Housatonic-Still River junction (41°32'34.00"N, 73°24'48.00"W). A second 50 cm push-core was taken in 5-6 feet of water in Lake Lillinolah in the Housatonic River. Both these cores were short because the corer reached a sandy layer through which it could not penetrate. These cores were capped beneath the water surface, and secured upright during transport to Wesleyan for core extrusion. Extrusion at Wesleyan consisted of mounting the cores on a cylindrical extruder, and sectioning off 1 cm intervals onto clean styrofoam plates whose weights had been recorded. These samples were left to dry overnight and weighed dry. After each sample was weighed wet and dry, ~20 g of each sample were homogenized in a hood using a mortar and pestle. The mortars and pestles used include agate, stainless steel, and ceramic varieties. Non-homogenized samples were stored in plastic cups, and homogenized samples were stored in plastic vials.

Two additional grab samples were taken from two terraces of a floodplain along the Still River from underneath the “no entry” bridge to Harry Brooke Park. These grab samples were dried, weighed, and homogenized using the same procedure as the Dean Road samples.
Multiple visits and consultations with historians at the Danbury Historical Society and UConn Dodd Research Center were carried out to investigate archival materials regarding the mercury purchases of hatting companies in the Danbury area and the industrial and labor history behind ban of mercury nitrate in the hatting industry.

5.2 Laboratory analysis

5.2.1 Mercury Analysis through thermal decomposition

Homogenized samples were analyzed for mercury concentrations using a Milestone DMA-80 mercury analyzer. The DMA-80 employs a thermal decomposition atomic absorption (AA) spectrometry in order to measure the nanograms of mercury in a given sample, and then calculates the Hg concentration in the sample using weights entered by the user (Fig. 5.1) This method is detailed by US EPA Method 7473, and a brief description of its operating principles is as follows:

First, sample material is poured into heat resistant non-reactive Nickel crucibles, weighed, and then placed on a rotating magazine. A pneumatic arm lifts up a sample to be analyzed, and then inserts it into the first of four heating chambers. In the first chamber, a quartz combustion furnace, O2 gas is burned in order to dry samples at 300 degrees C for 10 seconds check method on machine, and is then thermally decomposed at 850 degrees C for three minutes. The continuous flow of Oxygen transports the decomposition products to the catalytic furnace, where all mercury is reduced to elemental mercury, and halogens, sulfides, nitrogen oxides are trapped. The O2 gas
directs the remaining decomposition products to a gold amalgamator which selectively traps mercury particles. The amalgamator is then heated and the mercury gas is purged to two absorbance cells. The absorbance cells are of two different lengths, allowing for determination of a wide range of Hg amounts using two different calibration curves. A mercury lamp at one end of the absorbance cells emits light at 253.7 nm, and a spectrometer measures the amount of absorbance, which is proportional to the amount of mercury in the cells according to De Beer’s law.

Figure 5.1. Schematic of DMA-80 from Milestone SRL, 2013.
5.2.2 DMA Quality control

Three to four blank crucibles were analyzed before the beginning of each session of DMA-80 use. A blank crucible was also run in between each sample. 1-2 reference standards, also separated by blanks were analyzed at the beginning of each session and in between every 3-4 samples. The two reference standards used were NIST San Joaquin (1400 ppb Hg) and NIST PACS2 (3040 ppb Hg) (Fig 5.2).

5.2.3 Sample Correction

All Hg concentrations generated by the DMA-80 in the following procedure. First, the amount of Hg on the blank boat proceeding each sample was subtracted from the amount of Hg in the sample, in order to correct for residual mercury in the O-ring through which the pneumatic arm inserts each sample. These values were typically below 1 ng. Next, the standards were plotted by order in which they were run, in order to determine whether the measurements drifted over time. No such correction was necessary in this sample. Third, the measured standard values were compared to their consensus values. After discounting outliers, the Hg concentration of all measured standards were on average 2% below their consensus values. The Hg concentrations for all samples were thus multiplied by a 1.02 correction factor. Using this correction factor, the PACS2 standards were on average 8.6 percent different than their consensus values, and the San Joaquin Standards were on average 3.7 percent different than their consensus values.
5.2.4 XRF Analysis

Samples SRL 1-1 through 1-21 and SRL 2-1 through 2-25 were analyzed for trace element concentrations using the Pioneer S4 XRF at Wesleyan. The principles of X-Ray Fluorescence analysis are as follows.

Samples are bombarded with a primary X-Ray beam which causes electrons from the K- and L- shells, which are inner shells are not involved in chemical bonding. The vacancy left by atoms ejected from the inner shells are filled by electrons from outer shells. This change in energy from a high to a low valence state is released as X-Ray radiation. As each element has a
characteristic energy shell configuration, this change in energy can be used to identify different elements (Fig 5.3).

Figure 5.3 Schematic of X-Ray fluorescence. From Bruker, 2008

The S4 pioneer uses a Wavelength Dispersive X-Ray Fluorescence (WDXRF) analysis to identify major and trace elements. First, X-Rays are sent through a filter wheel which to ensure emitted rays are of wavelengths characteristic for common trace elements. Once X-Rays are re-emitted from the sample they are sent through a collimator to remove background signals, such as those from the sample cup. From there, X-Rays pass into a vacuum chamber and sent through a collimator changer. Collimated rays are then diffracted by analyzer crystals before being sent to a scintillation counter detector (for heavy elements) or a proportional counter (for light elements) (Fig 5.4). Diffracting the photons before detection allows for precise, high resolution
Pellets for use in the XRF machine were created through the following procedure:

1) Crushing homogenized sediment with a binder with a clean, dry ceramic mortar and pestle
2) Pouring crushed sediment into a sample cup and inserting the sample into a stainless steel die
3) Compressing the die using a hydrologic laboratory press for 4.5 minutes at 15,000-20,000 pounds of pressure.

Pellets were then stored in separate hard plastic containers. Samples being run in the XRF were inserted into steel loading cups with a film to prevent dust from entering the machine.

The Bruker GEO-QUANT calibration program was used to determine trace element concentrations for Sc, TiO2, Cr, MnO, Fe2O3, Co, Ni, Cu, Zn,
Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Sn, Cs, Ba, La, Ce, Pb, Th, and U. The Standards used with this calibration were Bruker Soil DC73324 brown, and Bruker Granite DC73301, grey. A calibration procedure was carried out using known correction values from multiple analyses of the XRF standards. The XRF trace element analysis returned highly accurate and precise measurements of trace elements in both the Still River and Housatonic Cores, with all soil and granite standards matching the consensus values with R^2 values >99.5% (Fig. 5.5).

![Soil XRF Standards](image)

**Figure 5.5a.** Correlation between measured Bruker Soil Standards and consensus values
5.2.5 Loss on Ignition

The loss on ignition laboratory procedure allows for the determination of the weight % of organic matter in a sample. Samples 1-20 of core SRL-1 were weighed in ceramic crucibles and then placed in an oven which heated to 1200 degrees C for 30 minutes. After 30 minutes, the samples were placed to cool for at least 10 minutes before weighing to account for heat convection altering the measured weight of samples. While in samples containing large amounts of carbonate, the LOI procedure requires heating in a sequence of steps, these samples were derived largely from glacial deposits lacking significant carbonate concentrations. Thus, the difference in the heated versus not heated samples equaled the amount of organic matter evaded.
5.2.6 Selective Thermal Evasion
The Selective Thermal Evasion process as described by Azzaria et al., 1991 allows for the determination of the speciation of mercury in a given sample. As each species has a slightly different boiling point, heating a sample to just above those points in a stepwise fashion and then analyzing it for mercury allows for the determination of the wt % for each species. These samples, SRB 1 and 2, SRL 1-9 and 1-17, and SRL 2-33, were homogenized and then heated to 130 degrees C as instructed by Windmoller et al., 1995 to determine the concentration of elemental mercury versus other species.

5.2.7 Pb210 and Cs137 Radiometric Dating
Activities of the radioactive isotopes Pb210 and 137Cs were measured on seven SRL-1 samples with the gamma-ray counter at Yale University. Prior to analysis, samples were sealed in plastic vials for two weeks to gain secular equilibrium between the various isotopes of interest.

One of the main principles of Pb-210 radiochronology is that of secular equilibrium. Secular equilibrium refers to a decay sequence in which the half life of the parent isotope is much longer than the half-life of its daughters. The Pb-210 production and decay series is as follows:

\[
\begin{align*}
238U & \rightarrow 226Ra \rightarrow 222Rn \rightarrow 210Pb \rightarrow 210Po \rightarrow 206Pb \\
4.51\times10^9y & \quad 1602y \quad 3.82d \quad 22.26y \quad 138.4d
\end{align*}
\]
In this example, 226-Radium is in secular equilibrium with its parent U238, but more importantly, in closed environments with its direct daughter, 222-Rn. (Appleby et al., 1978). The 222-Radon nuclide is an inert gas which will evade from crustal rocks into ground waters and then may evade into the atmosphere. As a result, some Rn builds up in the atmosphere but will decay within weeks to 210Pb, which is particle reactive and quickly removed from the atmosphere. As 226-Ra is close to secular equilibrium with 222-Rn only a small fraction escapes from rocks, and this crustal flux of 222-Rn gas is almost a constant Pb210* has a half-life of 22.26 years, and so is used to date sediments buried within 150 years of the present time. (Appleby, 1984; Lubis, 2006) (Fig 5.6). Since 222-Rn has such a short half-life, depositional records of Pb-210 vary according to local climate and geology (Graustein, 1987)

Figure 5.6. Schematic of 22Rn evasion from crust and decay into Pb210. From Pittauerova, 2009
In aquatic environments, there is both a depositional flux (sediment) and an atmospheric in situ flux to the sediments of 210-Pb. The 210-Pb falling directly onto the water surface is scavenged in the water column and deposited on the sediment water interface. Sediment derived from the watershed with its own excess 210-Pb is deposited as well. The sum of these fluxes of 210-Pb is called the “unsupported” or excess 210-Pb. The component of 210-Pb that is a result of in situ decay of 226-Radium is called the “supported” Pb-210. In some aquatic environments, an additional sediment focusing term may occur where Pb-210 from surface sediment is concentrated in a given depositional area.

In order to use 210-Pb as a geochronometer, the “supported” Pb-210 activities must first be discounted from the total Pb-210 activities. In practice, this is accomplished by subtracting the amount of measured 226-Radium in sediments from the measured amount of 210-Pb. Formally stated, the concentrations of Pb210 in a given sediment sample is:

\[ CPb = CPb(0)e^{\lambda t} + CRa(1-e^{\lambda t}) \]  
(Appleby, 1978)

This study employs two models of interpreting 210-Pb activities in order to create a chronology: the Constant Initial Concentration (CIC) model and the Constant Rate of Supply (CRS) model.
5.2.8 The CIC model

The CIC model rests upon two assumptions:

1) Every sedimentary layer has the same initial Pb210* concentration when it was deposited
2) Pb210 is not remobilized by post depositional processes

(Krishnaswami et al. 1971)

Given these assumptions, the CIC model is akin to “burying a clock”. Given a known initial concentration of Pb210 and with the Pb210 activity known in a given sample, the time, t, can be calculated through re arranging the basic decay formula:

\[ C = C(0) e^{-kt} \]

Where k is the radioactive decay constant for Pb210 (\( k = \ln(2/T_{1/2}) \)).

5.2.9 The CRS model

The constant rate of supply model assumes a constant flux of Pb-210 at the sediment-water interface and no post-depositional mobilization, but can explicitly account for changes in sedimentation rate throughout the core. The CRS model considers the cumulative amounts of ex-210Pb at a given sample depth relative to the total amount accumulated in the core of 210Pb.

According to Krishnaswamy et al. (1971), the cumulative residual excess of 210Pb below sediments of age t varies according to the following formula:
\[ A_i = A(0) e^{-kt} \]

Where \( A_i \) is the cumulative inventory at depth \( i \), \( A(0) \) is the core’s total \( 210 \text{ Pb}^* \) inventory, \( k \) is the radioactive decay constant and \( t \) is the number of years above or below the slice depth, dependent on whether inventories were cumulated from top to bottom or the reverse. Age of sediments of a given depth are thus calculated using:

\[ \left( \frac{1}{k} \right) \ln \left( \frac{\text{cumulative inventory at bottom of slice, } i}{\text{core inventory}} \right) \]

### 5.2.10 Cesium-137 dating

The 137-Cs nuclide is an anthropogenic isotope originating from nuclear weapons testing and generated during nuclear meltdowns of powerplants (Clark, 1988). It has a half-life of about 30 years. The 137-Cs has a residence time of 2.5–5 years in the atmosphere, so its fallout is measurable worldwide, with some variation due to local climate and precipitation (Alvardo, 2014). Most 137Cs comes from the atmospheric nuclear tests, and the global onset of 137-Cs pollution is dated to 1953. The 1963 Nuclear Test Ban Treaty outlawed atmospheric nuclear testing, and the release of environmental 137Cs decreased rapidly after that (Alvardo, 2014). A typical Cs137* profile thus has background concentrations until 1953, a spike until 1963, and a steady decrease until flat present day values.
5.2.11 Bulk Dry Density

The bulk dry density or BDD (gr/cm³ dry) of sediment is estimated in order to be able to calculate inventories of isotopes or pollutants from cores. The BDD was calculated from the measured water contents and an estimated density of the solid rock in the sediment. The following relationship was developed to obtain BDD from these two parameters:

\[
BDD = \rho_r \left[ (WF - 1) / (WF - WF \cdot \rho_r) \right].
\]

Where \(\rho_r\) is the dry rock density and WF is the water fraction by weight (amount of water/wet mud weight). Dry rock density was measured by compressing 1-2 grams of dry, homogenized, finely ground sediment at 3000 pounds in a 6.4 mm stainless steel die for forty minutes. Four pellets were made from dry sediment samples in SRL-1. These values were plotted against measured % OM concentrations, and a linear relationship between them \((r^2 = .98)\) was obtained (Fig. 5.7). The linear equation was used to calculate bulk dry densities for each sample based on its WF and OM contents. For SRL-1 samples deep in the core for which no LOI was calculated, an average %OM was used from the bottom three slices of the core.
Figure 5.7 Relationship between % OM and dry rock density.

6. Results

The Dean Road and Still River Bank grab samples were analyzed for Hg concentrations. SRL-1 and SRL-2 were both analyzed for Hg and trace element concentrations. Pb210 and 137Cs radiochronolgy was performed on SRL-1. Selective Thermal Evasion was attempted on 6 samples originating from SRB 1 and 2 and SRL 1 and 2.
6.1 SRL-1 Mercury vs. Depth

Core SRL-1 was analyzed for Hg and other metallic pollutants and the results are portrayed here initially as concentration versus depth. The SRL-1 Hg versus depth plot shows pre-industrial concentrations ranging from 22-98 ppb of mercury between 36.5 cm and 18.5 cm. Mercury concentrations increase at 17.5 cm, and remain steady until a large peak between samples 12.5 and 8.5 cm, with a maximum value of 10.5 cm of 1588 ppb. Mercury concentrations fall to ~580 ppb between 8.5 and 6.5 cm, and then spike upwards reaching a core’s maximum Hg concentration of 2969 ppb.
Hg concentration drops to 2821 ppb at 1.5 to .5 cm, though this may be a result of homogenization in the top three centimeters.

6.2 SRL-2 Hg vs Depth

![SRL-2 Hg Concentration vs. Depth](image)

Figure 6.2 Hg Concentration in SRL-2 versus depth.

The Hg profile of core SRL-2 is very different from that of SRL-1: the bottom of this core has higher Hg values than the top, and displays a strong oscillatory pattern with concentrations ranging from 170 ppb at 8.5 cm to 1401 ppb at 39.5 cm. The bottom 37 cm of the core includes four sharp peaks in Hg concentrations, the biggest two of which are between 39.5 cm and 38.5 (difference of 935 ppb) and between SRL 2-25 and 2-24 (difference of 861 ppb).
Between 22.5 cm and 4.5 cm, there is a 405 ppb increase, and then an oscillatory decrease passing through the core’s Hg minimum value of 170. At 3.5 cm, the Hg concentrations begin a steady increase up to 519 ppb at the top of the core.

The depth of this core was controlled by presence of a thick, sandy layer 50 cm into the stream bed. The presence of this layer, which likely represents a large flooding event, may account for not reaching pre-industrial Hg concentrations in this core.

6.3 Grab samples

6.3.1 Dean Road Samples

![Hg in Dean Road Grab Samples](chart.png)

Figure 6.3 Hg concentration in Dean Road grab samples.

The Dean Road grab samples returned values between 17-105 ppb. The variations in concentrations are an artifact of grain size: the samples that returned more mercury within this range (DR-2 and DR-3) were both from catchments with finer marsh sediment, whereas the other samples came the
sandier river bed.

6.3.2 Still River Bank Samples

The two grab samples from the bank of the Still River floodplain terraces returned Hg concentrations higher than any other samples measured in this study. SRB-1, the sample closest to the river on the lower terrace returned 6965 ppb Hg. SRB-2, the sample on the terrace below returned an Hg concentration of 6447 ppb.
6.4 XRF Results

Presentation of XRF results will focus primarily on Cu, Zn, and Pb, as they are similar industrial-age pollutants to Hg. %FeO2 in ratios with other elements as a normalizing factor for variations in grain size. The elements Cr, Ni, V, and Co are omitted from results because homogenization in stainless steel pestles may have caused additional inputs of those metals. Results for As, Mo, Sn, Sb, Cs, and U are also omitted due to known calibration errors in the Wesleyan Pioneer S4.

6.4.1 Metal pollutants in SRL-1

Figure 6.5 Cu, Zn, and Pb concentrations in SRL-1 as measured by XRF

XRF Trace element analysis was completed on samples SRL 1-1 through SRL 1-21. Cu, Zn, and Pb concentrations are all correlated with one
another, with onset beginning at 12.5 cm, a peak value at 10.5 cm followed by a shallow ~10 ppm valley between 10.5 cm and 5.5 cm, and a second peak at 6.5 cm followed by constant values until the top of the core. The first peak value of Cu however is actually somewhat offset from first Pb and Zn peaks, beginning at 11.5 cm and realigning with the other metals at the second peak. The background values for Cu, Pb, and Zn are 18 ppm, 17 ppm, and 90 ppm, respectively. The first peak maxima for Cu, Pb, and Zn are 26 ppm, 31 ppm, and 113 ppm. The upper flat values are 45 ppm, 35 ppm, and 144 ppm for CU, Pb, and Zn.

6.4.2 Metal pollutants in SRL-2

![SRL-2 Metal Pollutants vs Depth](image)

Figure 6.6 Cu, Zn, and Pb concentrations in SRL-2 as measured by XRF
XRF trace element analysis was completed on samples SRL 2-1 through SRL 2-25. Similar to the metal pollutant profiles of SRL-1, the Cu, Zn, and Pb vs depth curves are all strongly correlated with one another, with Zn showing the highest amplitude fluctuations. The Zn concentrations are the highest on average, followed by Pb with Cu just slightly below. All three metals peak first at 24.5 cm, drop to a valley at 22.5 cm, reach a peak at 18.5 cm, drop slightly between 18.5 and 14.5, decrease sharply at 13.5 cm, peak a third time between 11.5 and 12.5 cm, decrease until 7.5 cm, peak a fourth time at 6.5 cm, decrease until 4.5 – 5.5 cm, and then steadily increase to the top of the core. Again, the Pb and Cu profiles are somewhat offset from one another, with Pb reaching its second maxima 1 cm after Cu, and reaching its second valley 1 cm after Cu. The ranges of Cu, Zn, and Pb are 13-33 ppm, 78-147 ppm, and 19-36 ppm, respectively.

6.5 Selective Thermal Evasion
The data from the selective thermal evasion procedure were highly inconclusive and statistically insignificant. SRB-2 and SRL 1-17 lost mercury after heating, while SRB-1, SRL 1-9, and SRL 2-33 each gained additional mercury after being heated. The results are shown below in Table 6.1.
<table>
<thead>
<tr>
<th>Name</th>
<th>PPM</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRB-1</td>
<td>6.842</td>
<td>-0.138</td>
</tr>
<tr>
<td>SRB-1-140C</td>
<td>7.786</td>
<td></td>
</tr>
<tr>
<td>SRB-2</td>
<td>6.357</td>
<td>0.1467</td>
</tr>
<tr>
<td>SRB-2-140C</td>
<td>5.424</td>
<td></td>
</tr>
<tr>
<td>SRL 1-9</td>
<td>0.575</td>
<td>-0.1099</td>
</tr>
<tr>
<td>SRL 1-9-140C</td>
<td>0.638</td>
<td></td>
</tr>
<tr>
<td>SRL 1-17</td>
<td>0.2981</td>
<td>0.3937</td>
</tr>
<tr>
<td>SRL 1-17-140C</td>
<td>0.1807</td>
<td></td>
</tr>
<tr>
<td>SRL 2-33</td>
<td>0.8335</td>
<td>-0.6347</td>
</tr>
<tr>
<td>SRL 2-33-140C</td>
<td>1.362</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1. Results from selective thermal evasion procedure.
6.6 Age model

The data from the gamma counter yielded Pb210* and 137Cs* activities that were used to outline the age model of SRL-1. The plot of LN Pb210* vs depth is generally linear with a negative trend, as is expected given a constant input of Pb210 at the sediment-water interface and a constant rate of decay (Fig 6.6). However, there are a few exceptions to this trend. The point at 3.5 cm is higher than the Pb210* value of the .5 cm. This is an artifact of homogenization during the extraction process, wherein the top 3 cm of the core were mixed. The other exception to this trend is the point at 5.5 cm, which is 1.05 LN mBq/g lower than what is estimated by the linear model.

The plot of LN activity 137Cs* vs depth is also generally linear with a negative trend (Fig. 6.7). Like the Pb210* record, the point at 1-4 is higher than 1-1. As these points are close to the top of the core it is most likely that the peak represents homogenization of the top three centimeters rather than additional input of 137Cs. Though one would expect to find a peak of Cs137* in 1964 representing the peak of nuclear arms testing, there is no clear peak in these samples. However, the onset of Cs137* above is apparent in sample SRL 1-7, so it was used as marker point for 1954, the height of nuclear arms testing.
Figure 6.7 Pb210* and Cs137* activities in SRL-1
Both CRS and CIC models were applied to the available samples. Their results, along with supplemental geochemical markers such as the onset of 137Cs at 6.5 cm and the first spike in copper pollution, known regionally to be in 1850 (Zierzow, 2002) at 12.5 cm, were plotted on the y axis against depth. A 2nd order polynomial regression gave the ages used in the final age model, with an R^2 of .93 (Fig 6.8).

The CIC data points were calculated using data points for SRL 1-1, 1-4, 1-5, 1-6, 1-7, 1-9 and 1-12. Samples taken below 1-12 were omitted, as they returned insignificant concentrations of Pb210. In order to correct for the homogenization, the LN of the Pb210* activities were plotted versus depth,
and a linear regression was used to estimate the amount in each slice. As the CIC model is dependent on an accurate measurement of the initial Pb210 concentration at the time of sediment burial, a model-measurement validation procedure was used. The procedure involved calculating a percent difference between the cumulative Pb210* inventories in the upper three slices with the values for those samples as determined by the model, and then adjusting the initial value in the model until the percent difference in the summed inventories dropped below 5%.

The Pb210* activities used in the CRS model were obtained by interpolating using averages between measured Pb210* activities. As the CRS model uses the difference between summed inventories, a correction for changes in sedimentation is built into the model. Slice inventories were calculated by multiplying the bulk dry density in (g/cm^3) by the slice thickness (1 cm) by the activity (in mBq). Whereas the CIC method used the “mid depth” of each slice, the CRS method calculated ages by subtracting the cumulative inventory up to a midpoint from the midpoint below it, yielding values at the tops and bottoms of each slice.

Error ranges for the SRL-1 age model were created by repeating the mixed CRS-CIC-geochemical marker modeling process using Pb210* activities from the high and low ends of the ranges given by the gamma counter. In general, the error of the model is smallest near the top of the core, where activities of Pb210* are highest, and largest at the bottom of the core, where lower activities of Pb210* are used to extrapolate dates (Fig 6.9)
most likely location of error is at SRL 1-6, where the linear regression-derived activity of Pb210*, 11.067 mBq/g, was much higher than the measured value of 3.862 mBq/g.

Figure 6.9. Age Depth model for SRL-1.
6.7 Validating Age Model -- Cumulative Pb210* and Cs137 Inventories

Both 137Cesium radiochrometry and CIC and CRS Pb210* dating stipulate that post-depositional processes do not remobilize the radioactive elements of interest from the sediment core. In order to test whether this assumption holds for the SRL-1 core, its cumulative Pb210* and Cs137* inventories are compared to regional inventories in Table 6.2. For Cs137*, no clear peak was identifiable in the samples, and the cumulative inventory is .5072 dpm/cm², orders of magnitude lower than expected regional inventory of 32 dpm/g (Graustein et al., 1987). The Pb210* cumulative inventory is below this expected value as well. A possible explanation for this is that this
core received proportionally less Pb210* from the sediment-water interface at the outset.

Table 6.2 Cs and Pb210* inventories

<table>
<thead>
<tr>
<th>Core Name</th>
<th>Cs inventory dpm/cm^2</th>
<th>Pb210* inventory</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP-1</td>
<td>8.000</td>
<td>55.69</td>
</tr>
<tr>
<td>WBFM-1</td>
<td>56.24</td>
<td>57.63</td>
</tr>
<tr>
<td>JC6</td>
<td>10.87</td>
<td>42.25</td>
</tr>
<tr>
<td>JC12</td>
<td>23.16</td>
<td>36.79</td>
</tr>
<tr>
<td>SRL-1</td>
<td>0.5072</td>
<td>7.660</td>
</tr>
<tr>
<td>SRNER C-2</td>
<td>15.70</td>
<td>73</td>
</tr>
<tr>
<td>KI-10C-Pb</td>
<td>10.28</td>
<td>76.93</td>
</tr>
</tbody>
</table>

6.8 Mean Accumulation Rate - SRL-1

Given the age model, a mean accumulation rate of Hg in the SRL was calculated by multiplying the Hg concentrations by the bulk dry density of the sediment and the sample slice thicknesses, and then dividing that amount by the amount of years in each sediment slice. This calculation yielded an accumulation profile that strongly resembles that of the Hg concentration profile. (Fig. 10)
Figure 6.11. Mean Annual Accumulation Hg in SRL-1.
7. Discussion

With an understanding of the change in Hg concentrations with depth in SRL-1 and SRL-2, and with an age model for SRL-1, these cores can be put into a regional context. First, however, an overview of two key parameters is necessary in order to make proper comparisons between cores and evaluate changes in transport regime. The first parameter is the amount of mercury carried in sediments versus the concentration due to atmospheric deposition. The difference between measured Hg concentrations in sediment and known atmospheric deposition is denoted Hg*. The second key parameter is grain size variation, which can denote both changes in water velocity and account for changes in measured Hg concentrations. Geochemical proxies are be used to measure these parameters, and so each are discussed below.

7.1 %Fe as a Proxy for Grain Size

Varekamp (2000) determined an empirical relationship of Fe concentrations to grain size.(Fig 7.1). Quartz and Feldspar, the common minerals comprising lithic fragments, do not contain iron. This grainsize-Fe relationship is significant to this study, as Hg preferentially adsorbs onto Fe-
bearing clays. Thus, higher concentrations of both Hg and Fe2O3 are expected in fine grained sediment.

Figure 7.1a Relationship between Hg in sediment with % Fe. From Varekamp et al., 2000.

Figure 7.1b Relationship between Hg and grain size. From Varekamp et al., 2000.

7.2 Distinguishing Hg atm from Hg*

There are two methods to create a measurement of Hg*. The first is to subtract the average background concentrations from pre-industrial times in a
dated core. However, this method does not account for increased wet atmospheric deposition during times of increased precipitation, or for modern changes in atmospheric deposition. In this study, the core records from Block Island provide a record of strictly atmospheric deposition of Hg, as they are remote from known point sources. In practice, the ratio of Hg/Pb210* is used to compare cores values and identify point-sources of Hg pollution. Pb210* is removed from the atmosphere through wet and dry depositional processes similar to those of Hg. Therefore, if cumulative Hg/Pb210* inventory of a given core is higher than those of a local reference core, than it can be inferred that the sample is enriched in Hg from depositional processes.

7.3 Point Sources Versus Far-Field Sources

The regional contribution of Hg atm is known over time through the Block Island marsh cores, FP-1 and WBFM-1 (Fig 7.2). A comparison between these records and regional sediment cores reveals evidence for point-source Hg pollution.
Figure 7.2. Block Island Hg profiles for cores FP-1 and WBFM-1

Figure 7.3. SRL-1 Hg concentration versus age.
The Hg concentration of SRL-1 outstrips the atmospheric deposition starting in 1820 with the Hg onset peak (Fig 7.3), with SRL-1 values of 255 ppb, and Block Island core values of 30-40 ppb. After 1820, at no point do the Block Island Hg concentrations overtake the SRL-1 values. Additionally, the cumulative Hg*/Pb210* inventory of SRL-1 is 41800 ng/dpm, versus 331 in FP-1 and 195 in WBFM-1, indicating that sediment focusing was not responsible for the difference in Hg concentrations.

The shape of the Block Island Hg profiles suggest that the regional Hg record is not a result of increased atmospheric deposition. The Block Island cores show steady from global industrial Hg onset in 1870 to a peak value at 1960 of 322 ppb, but do not exhibit clear peaks and valleys corresponding to the flood events in 1900, 1938, and 1955 floods. At least one of these flood peaks is evidenced in all sediment cores taken in the Still River, the Housatonic River, and in Long Island Sound. A detailed comparison between Hg* inventories of all regional cores is shown in Table 7.1.
<table>
<thead>
<tr>
<th>Core name</th>
<th>date onset</th>
<th>date of spike 1</th>
<th>date of spike 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LIS Cores</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1GGC1</td>
<td>1820</td>
<td>1900</td>
<td>1955</td>
</tr>
<tr>
<td>B1C2</td>
<td>-</td>
<td>1955</td>
<td>--</td>
</tr>
<tr>
<td>JC-6</td>
<td>1850</td>
<td>1900</td>
<td>1955</td>
</tr>
<tr>
<td><strong>Housatonic Cores</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Long Island</td>
<td>1800</td>
<td>1900</td>
<td>1955</td>
</tr>
<tr>
<td>Pope's Island</td>
<td>1800</td>
<td>1900</td>
<td>1950</td>
</tr>
<tr>
<td><strong>Still River Cores</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRL-1</td>
<td>1817</td>
<td>1913</td>
<td>1967-2013</td>
</tr>
<tr>
<td>SRNER C-1</td>
<td>1820</td>
<td>1875-1955</td>
<td>1875-1955</td>
</tr>
<tr>
<td>SRNER C-2</td>
<td>1850</td>
<td>1875</td>
<td>1955</td>
</tr>
<tr>
<td>SRN C-1</td>
<td>1850</td>
<td>1875</td>
<td>1955</td>
</tr>
<tr>
<td><strong>Block Island</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WBFM-1</td>
<td>NR</td>
<td>1960</td>
<td>1975</td>
</tr>
<tr>
<td>FP-1</td>
<td>1850</td>
<td>--</td>
<td>1960-1970</td>
</tr>
<tr>
<td><strong>Chapman pond</strong></td>
<td>1780</td>
<td>1900</td>
<td>1960</td>
</tr>
</tbody>
</table>
7.4 SRL-1 Age Profile

The SRL-1 mercury versus age core exhibits the two-peak Hg pollution profile characteristic of other cores in the region. The grain-size normalized plot (Figure 7.4) reveals that this profile is not an artifact of changes in grain size. Onset of Hg pollution occurs around 1810 and peaks at the 1900 “wash out” peak identified by Zierzow (2002). Historically, the 1900s peak is consistent with the height of the hatting industry, and the timing of the following low is consistent with the 1941 ban of mercury nitrate for use in hatting. However, these highs and lows also correspond closely to the 1903 hurricane and the 1938 hurricane and flood. Considering the high density of Hg and that only a small fraction is transported as particulate or dissolved forms (Balcom, 2006) these changes in concentration are reflective of the flood record, as opposed to changes in Hg output in Danbury.
Considering Hg concentration profile for SRL-1 on its own, the 1955 flood peak is not recognizable in this core. However, several other lines of geochemical evidence suggest that the sample just above the bottom of the 1900s peak represents the 1955 flood. This point, SRL 1-6, is dated by the age model to be in 1967. However, the upper error bar for the age model at this point is +11.4 years. Additionally, SRL 1-6 is anomalously low on the LN Pb210* vs depth plot, suggesting that this layer represents an influx of older sediment. Finally, the %Fe2O3 drops at this point, suggesting an input of coarser flood deposits. (Figure 7.5)
Still, this interpretation of SRL 1-6 as the 1955 flood peak must be reconciled with the continued increase in mercury concentration in following samples. A possible explanation is that the 1960s and 1970s also represent a period of enhanced atmospheric Hg washout and flood transport, as is prominent in the SRNER C-1 core. The difference in sampling resolution between SRNER C-1 and SRL-1 likely explains the invisibility of this “missing valley.” Whereas SRL-1 has a mean sedimentation rate of .84 mm/year, the sedimentation rate of SRNER C-1 is much faster, at 6 mm/yr. So, even though the SRL-1 core was analyzed for Mercury at every 1 cm versus every 5 cm in SRNER C-1, there is on average 11.7 years per sample analyzed for
mercury in SRL-1 versus an average of 8.3 years per sample analyzed for mercury in SRNER C-1.

The top three points on the graph are artifacts of homogenization in the core. However, given their high concentrations, and the fact that the Erikson Road cores and Del Mar Drive cores decrease after 1970, some other explanation for those high concentrations is necessary. One such explanation could be that artificial changes made to the Still River shoreline during the Still River Greenway reclamation project remobilized mercury from older sediments. A rigorous survey of riverbanks affected by the project would be necessary to test this hypothesis.

7.5 Still River Hg Inventories

The cumulative Hg* inventory of the Erikson Road and Del Mar Drive Still River cores are considerably higher than those from SRL-1 (Table 7.2). The most reasonable explanation for this disparity is that the geometry of the SRL-1 catchment was one where less fine grained material was trapped. Whereas the SRNER and SRN cores were both taken in catchments with very narrow inlets, SRL-1 was taken in a sidearm of the Still River, where water flows more vigorously and carries coarser sediment. This hypothesis is corroborated by the Hg*/Fe ratios, as well the relative depletion of Pb210* in SRL-1 (Table 7.2).
Table 7.2. Mercury Inventories for Regional Cores

<table>
<thead>
<tr>
<th>Core name</th>
<th>ng Hg*/cm^2</th>
<th>mg Fe/cm^2</th>
<th>inventory ratio Hg*/Fe</th>
<th>Hg*/Pb210 *ng/dpm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LIS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average LIS cores</td>
<td>8815</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>WLIS-75 B1GGC1</td>
<td>21342</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>JC 6</td>
<td>1540.4</td>
<td>NR</td>
<td>NR</td>
<td>36.4</td>
</tr>
<tr>
<td><strong>Housatonic River</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1C2 (HR Delta short core)</td>
<td>9208</td>
<td>830</td>
<td>11.1</td>
<td>NR</td>
</tr>
<tr>
<td>B1GGC1 (HR delta long core)</td>
<td>10580</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>KI1</td>
<td>5,253</td>
<td>159</td>
<td>33.0</td>
<td>68.28</td>
</tr>
<tr>
<td>Long Island</td>
<td>4569</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>Pope’s Island (PI 1)</td>
<td>64462</td>
<td>84</td>
<td>657</td>
<td>NR</td>
</tr>
<tr>
<td>Fowler’s Island (FI 1)</td>
<td>32274</td>
<td>71</td>
<td>672</td>
<td>NR</td>
</tr>
<tr>
<td><strong>Still River</strong></td>
<td></td>
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</tr>
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<td>SRL-1</td>
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<td>NR</td>
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<td><strong>Block Island</strong></td>
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<td>Value2</td>
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<td>--------</td>
<td>--------</td>
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<td>WBFM-1*</td>
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<td>751.2</td>
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<td>NR</td>
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<td>Connecticut River</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chapman Pond</td>
<td></td>
<td>8,209</td>
<td>1,290</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Table 7.2 Continued
7.6 Housatonic Core Profile

As the Shepaug dam that created lake Lililnolah was partially completed at the time of the August 1955 flood, the thick, sandy layer that prevented the core from penetrating deeper into the riverbed likely represents flood deposits trapped from that event. Using this interpretation, and the grain size normalization available for the top 25 cm of the core on which XRF analysis was completed, it is possible to identify also the 1970s wet period using the Hg concentration record. At 24.5 cm, there is a peak in Hg*/Fe ratio followed by a valley and an overall trend of reduction in Hg concentrations. (Figure 7.6) This decline is consistent with both SRNER cores and the SRN core as well.

![SRL-2 Hg normalized to grain size](image)

Figure 7.6 SRL-2 Hg Profile normalized to grain size.
7.7 Hg in Long Island Sound

The Hg* profiles downstream in Long Island Sound delta and in Western Long Island Sound reflect those of the Housatonic River. The B1GGC1 long exhibits a two-peak profile in 1900 and 1955, as does the WLIS 75GGC1 long core (Figs 7.7 and 7.8). The strength of this point source signal is demonstrated by the WLIS record. The WLIS 75GGC1 is distant from the B1GGC1 core in the Housatonic Delta, and is fed sediment through E-W tidal mixing in the sound. The persistence of the Hg* signal in WLIS demonstrates that the concentration of Hg* was high enough to remain visible in the record even with some dispersion from the tidal forces.
Figure 7.7. Hg* record from the Housatonic River Delta. From Varekamp et al, 2014.

Figure 7.8. Hg* Record from WLIS. From Varekamp et al, 2014.
The Hg* of Jarvis creek is notable as it remote from known point sources (Fig 7.9). Yet, the JC6 record shows evidence of point source pollution: it has a cumulative Hg* inventory less than that Chapman Pond or of any of the Housatonic River cores, but double that of the Block Island cores. Additionally, it’s Hg*/Pb210* ratio is more than double that of the Block Island, precluding explanation from sediment focusing. Given that Jarvis Creek is in between the Housatonic and Connecticut River watersheds and that tidal mixing is E-W in the sound, its Hg* record likely reflects more the Connecticut River point source than that of the Housatonic.

Figure 7.9 Hg record from Jarvis Creek. From Varekamp, pers comm
7.8 Grain size normalized XRF

The profile of all three grainsize-normalized Zn, Pb, and Cu vs depth records share a similar shape both to each other and to the non-normalized records. The major difference between the normalized and non-normalized profiles is that the amplitude of the peaks and valleys in the normalized versions are much smaller (Figs 7.10 and 7.11)

Figure 7.10. Metal Pollutants Normalized to grain size SRL-1
Figure 7.11 Metal pollutants normalized to grain size SRL-2
The Knell's Island normalized curve from Zierzow (2002) provides a fertile regional comparison. (Figure 7.12) The Pb, Cu, and Zn from Knell’s Island all have their onsets at 1830. The Knell’s Island Cu record increases exponentially until 1960, at which point it drops exponentially. The Knell’s Island Pb record increases starting in 1830, though its rate of increase rises greatly at 1900 with the onset of leaded gasoline. From there, Pb concentrations rise until 1950, drop until the 1970s, increase slightly until 1980 and then decrease until present. From its onset, Knell’s Island Zinc concentrations increase steadily until 1870, and is largely constant with a few valleys at 1910 and 1970, and a decrease until present. The SRL-1 record shares the time of onset for all metal pollutants, as well as the characteristic Pb maxima at 1900. However, whereas 1950 a peak for pollutants in the Knell’s Island core, it is a valley for SRL-1 metal pollutants. In addition, the metal pollutants in SRL-1 are all shown to increase after 1970. This anomaly is similar to that of the modern Hg* peak in SRL-1 versus the modern Hg* valley in KI1. It is likely then, that the difference between these records also shows the interference in transport from the Houastonic River dams.
7.9 Calculating Hg flux through Lake Lillinolah

Dams along the Housatonic River act as sediment traps during periods of steady state transport. Thus, since the creation of the Shepaug dam in 1955, nearly all Hg delivered from the Still River to the Housatonic River has been collecting in Lake Lillinolah apart from the portion transported by flood events. Thus, it is possible to create an order of magnitude estimate for both the total amount of mercury trapped in Lake Lillinonah and the flux of mercury from the Still River that reached the Housatonic since 1955 using the Hg inventory from SRL-2:

Total amount of Mercury = inventory of SRL-2 in ng/cm^2 * lake area = total mass of Hg in Lake Lillinolah
25578 ng/cm^2 * 6.261*10^10 cm^2 lake area = ~ 1601.439 kg Hg in Lake Lillinolah

Dividing this amount by 58 years yields an average flux of ~27 kg/year of Hg trapped in Lake Lillinolah. However, this amount cannot be used as a flux into Long Island Sound, as the Stevenson Dam was built in 1919 and the Derby dam was built in 1870. Knowing these dates and the fluxes of Hg, it is possible to create an estimate of how much is trapped behind each of the dams by multiplying the flux rate by the span of years for which each dam was the most northwardly dam.

The Stevenson Dam was the most northwardly dam between 1919 to 1955:
36 years * 27 kg Hg /year = ~970 kg Hg trapped currently in Lake Zoar

The Housatonic Dam was the most northwardly dam between 1870 and 1919:
49 years * 27 kg Hg/year = ~1300 kg Hg trapped currently in Lake Housatonic

### 7.10 Creating an LIS Hg Budget and Flood Record

Balcolm et al., 2004, calculated an annual Hg^* input to LIS of 1030 moles, or 206.61 kg Hg^* by summing steady-state fluxes from the riverine, atmospheric, and effluent Hg^* inputs to the sound. Given the Hg^* inventories from cores distributed across Long Island Sound, it is possible further
constrain this balance by estimating the total mass of Hg* by multiplying those inventories by the surface area of the Sound. This estimation was calculated through the following procedure:

1. Separating Long Island Sound into polygons based on bathymetry, and then estimating the area of those polygons using ArcMap 10.1.
2. Averaging the ng Hg*/cm^2 cumulative inventory between cores that fall within the same polygon
3. Multiplying the averaged inventories by the area of the polygon in which they fall.
4. Summing the ng Hg* in all polygons.

Fig. 7.13 Polygons used in LIS.
This “back of the envelope” calculation returned a value of total 150,000 kg of Hg in Long Island Sound sediments.

7.11 Flood Versus Steady State Transport from the Housatonic River

The Balcom et al. 2004 study measured sediment fluxes through the major riverine inputs to LIS during periods of steady-state transport. However, given the damming history of the Housatonic River, it is likely that the majority of Hg transported to the sound occurred during periods of flooding. Thus, in order to get an accurate measurement for the true input from the Housatonic river, a sediment and particulate trap similar to those used by Balcom et al would need to be in place during a flood event. Using that calculated flood-transport flux, a fertile comparison could be made to the steady-state flux calculated above from the amount of sediment trapped behind Lake Lillinolah.

8. Conclusions

The SRL-1 record exhibits a “dilute version” of Hg* pollution events found in the cores by Goldoff et al., 2002. The Erikson Road and Del Mar Drive cores represent an “inflated” pollution record reflecting accumulation of large amounts of fine-grained matter contaminated with Hg, whereas the SRL-1 record is relatively poor in fine-grained sediment. Hg* transport from Danbury into the Still and Housatonic River watersheds may be dominated by transport during flood events, most notably during the 1900 period identified by Zierzow (2002), the 1936-1938 hurricanes, the 1955 floods, and the 1970s
wet period. The top of the SRL-1 core contains a peak of both Hg* and Zn, Cu, and Pb not found in other cores either closer to Danbury or downstream in the Housatonic or in Long Island Sound.

The dams installed in the Housatonic River in 1878, 1919, and 1955 control the transport of metals to LIS by retaining a fraction of fine grained polluted sediment during periods of steady state flow. Likely approximately 1600, 970, and 1300 kg Hg are trapped behind the Shepaug, Stevenson, and Derby dams, respectively. This mercury record should be considered if changes to the dams are proposed, and careful monitoring of the water for anoxia-inducing nutrient loads should be undertaken so as to protect methylmercury accumulation in fish. Pertinent future work includes a precise determination of the flux of mercury from the Housatonic into Long Island Sound during flooding events, and coring and dating of the sediment record behind each of the three dams.
9.0 References


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## 10. Appendix

### Appendix 1 Hg in SRL-1

<table>
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<tr>
<th>Name [best samples]</th>
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<th>Bulk dry density g/cm^3</th>
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<th>MAR Hg ng/cm^2*yr</th>
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Appendix 2 Hg in SRL-2

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## Appendix 3 SRL 2 XRF Data

Items in red contain systematic error.
Objects in red contain systematic error.
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### Appendix 7 Sedimentation Rate SRL-1

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Appendix 8 Supporting Data for Age Model Error Bars

**low end ages**

\[ y = 0.1819x^2 - 11.74x + 2016.8 \]

\[ R^2 = 0.8539 \]

**LN pb210* low estimate**

\[ y = -0.2097x + 3.2957 \]

\[ R^2 = 0.6358 \]
Age Model High End Estimate

\[ y = -0.3023x^2 - 5.0518x + 2014.8 \]
\[ R^2 = 0.8519 \]

Series1
Poly. (Series1)

LN Pb210* High estimate

\[ y = -0.1762x + 3.6735 \]
\[ R^2 = 0.707 \]

Series1
Linear (Series1)