12-1-2012

Sediment Metal Concentrations as a Function of Land Use in the Charles River, Eastern Massachusetts

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Recommended Citation

Luce, Darryl L., "Sediment Metal Concentrations as a Function of Land Use in the Charles River, Eastern Massachusetts" (2012). *Graduate Doctoral Dissertations.* Paper 91.

SEDIMENT METAL CONCENTRATIONS AS A FUNCTION OF LAND USE IN THE CHARLES RIVER, EASTERN MASSACHUSETTS

A Dissertation Presented

by

DARRYL L. LUCE

Submitted to the Office of Graduate Studies,
University of Massachusetts Boston,
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2012

Environmental, Earth and Ocean Sciences Program

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ABSTRACT

SEDIMENT METAL CONCENTRATIONS AS A FUNCTION OF LAND USE IN THE CHARLES RIVER, EASTERN MASSACHUSETTS

December 2012

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Directed by Professors Gordon T. Wallace and Robert F. Chen

Two sediment cores and eleven grab samples collected from the Charles River were analyzed to determine changes to the concentration of metals in sediments due to anthropogenic changes in the watershed. The unique aspect of this research was that sediment cores from the same geologic setting, yet having widely different sources, were compared. The findings from that comparison were used to focus the investigation through the remainder of the Charles River. The radionuclides ^{210}Pb, ^{214}Pb, and ^{137}Cs established the year of deposition in the sediment cores. The concentrations of aluminum (Al), iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), chromium (Cr), cobalt (Co), lead (Pb), arsenic (As), cadmium (Cd), tin (Sn), scandium (Sc), strontium (Sr), silver (Ag), mercury (Hg) and total organic carbon (TOC) were determined in the sediment cores and surface samples.

The primary findings were that several metals in Charles River sediments exceeded regulatory standards for aquatic organisms and that storm water affected the concentrations of metals such as Cu, Hg, and Pb throughout much of the river. What appeared critical was the retention of metals within the upland areas of a watershed which was controlled by the amount of impervious surface. Storm water runoff from areas with greater amounts of impervious materials, coupled with the retention of sediments behind dams in the Charles River, increased the long-term availability of metals that may affect aquatic organisms. A simple model is presented that determines the concentration of Cu and Hg in sediments based on the percentage of impervious area and the concentration of TOC in the sediment. This model indicates that a potential key to reducing the concentrations of metals in sediments is to either reduce the amount of impervious surfaces in a watershed or decrease the supply of metals and TOC to sediments.

ACKNOWLEDGEMENTS

Work on this dissertation began in 1999 and would not have been possible without the patience and help of my family: Catherine, my wife, and our daughters Anastacia and Aurora. Catherine spent many hours reading and re-reading the text. My daughters can scarcely remember any part of their lives when I was not working on this dissertation. My advisors: Robert Chen, Curtis Olsen, Bill Robinson, and Daniel Brabander, were invaluable to finishing this work. Their patience and guidance are appreciated. Several students and University employees aided in the collection, processing and analysis of samples including Elva Wohlers who assisted in sample collection and helped process sediment cores, David Shull and Peter Edwards who collected a sediment core through diving, Tom Goodkind who fashioned a remote sampling device, and Melissa Ferraro, Franco Pala, Katrina Sukola, Li Li, Joe Smith and Greg Banks who were vital in assisting me in the analytical work. None of this would have been possible without the cooperation of the Environmental Protection Agency which supported portions of this effort. My constant companions in writing: first George, and then Lizzy, provided company and a friendly ear during the many long hours of writing. Lastly, I relied heavily on the advice and guidance of Professor Gordon Wallace. I regret not being able to consult him in the final labors of this work – he suggested this line of research and eagerly awaited our discussions of the data. I miss the challenge and guidance he provided.

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LIST OF ABBREVIATIONS

BPC – Biological, Physical and Chemical. A system devised by the U.S. Geological Survey to quantify changes in a stream based on a number of variables including aquatic community health, nutrients, dissolved oxygen, temperature and stream morphology, relative to urban intensity.

CAA – Federal Clean Air Act.

CWA – Federal Clean Water Act.

CF:CS – Constant Flux:Constant Sedimentation. A technique used to determine the dates of sediment deposition using radioisotopes.

CIC – Constant Initial Concentration. A variable rate dating model used to determine dates of sediment deposition using radioisotopes.

CIT – Commercial, Industrial and Transportation network area.

CRB – Charles River Basin.

CRS – Constant Rate of Sedimentation. A variable rate dating model used to determine dates of sediment deposition using radioisotopes.

CRWA – Charles River Watershed Association.

CSO – Combined Sewage Outfall. The co-mingling of sewage and storm water; during large storm events releases of raw sewage mixed with storm water to receiving waters are possible.

CVAA – Cold Vapor Atomic Adsorption. Used to determine the concentration of mercury.

DOM – Dissolved organic matter.

EPA – United States Environmental Protection Agency.

ERL – Effects Range Low.

ERM – Effects Range Median.

FDW – Fraction dry weight, which is a measure of the mass of the dry weight of sediment as a fraction of the total weight of sediment and water.

ICP-MS – Inductively Coupled Plasma-Mass Spectrometer.

K – Equilibrium constant.

MAR – Mass Accumulation Rate.

MWRA – Massachusetts Water Resources Authority.

NAWQA – National Water Quality Assessment.

NOAA – National Oceanic and Atmospheric Administration.

NPDES – National Pollution Discharge Elimination System.

pK_a – Equilibrium constant expressed in log scale.

POTW – Publically-owned Treatment Works. Sewage treatment facilities owned by communities that collect, treat and discharge treated waste to streams.

OM – Organic matter.

RCRA – Resource Conservation and Recovery Act of 1976.

TOC – Total organic carbon.

USGS – United States Geological Survey.

CHAPTER 1

INTRODUCTION

The alteration of metal concentrations in sediments due to anthropogenic discharges and changes in land use has been intensively studied (Coles et al. 2004; Chalmers et al. 2007). Metals have been shown to be particle reactive and thus incorporated into the sediments of lakes and streams (Olsen et al. 1982). This property may be used to estimate past water quality since the sediments being deposited may be assumed to be in equilibrium with the metals present in the water column (Turner et al. 1981; Olsen et al. 1982; Ren and Packman 2004). Metals in sediments have the potential for toxicity to aquatic organisms and may adversely alter water quality (Tessier and Campbell 1987; U.S. Environmental Protection Agency 1997; Simpson et al. 1998).

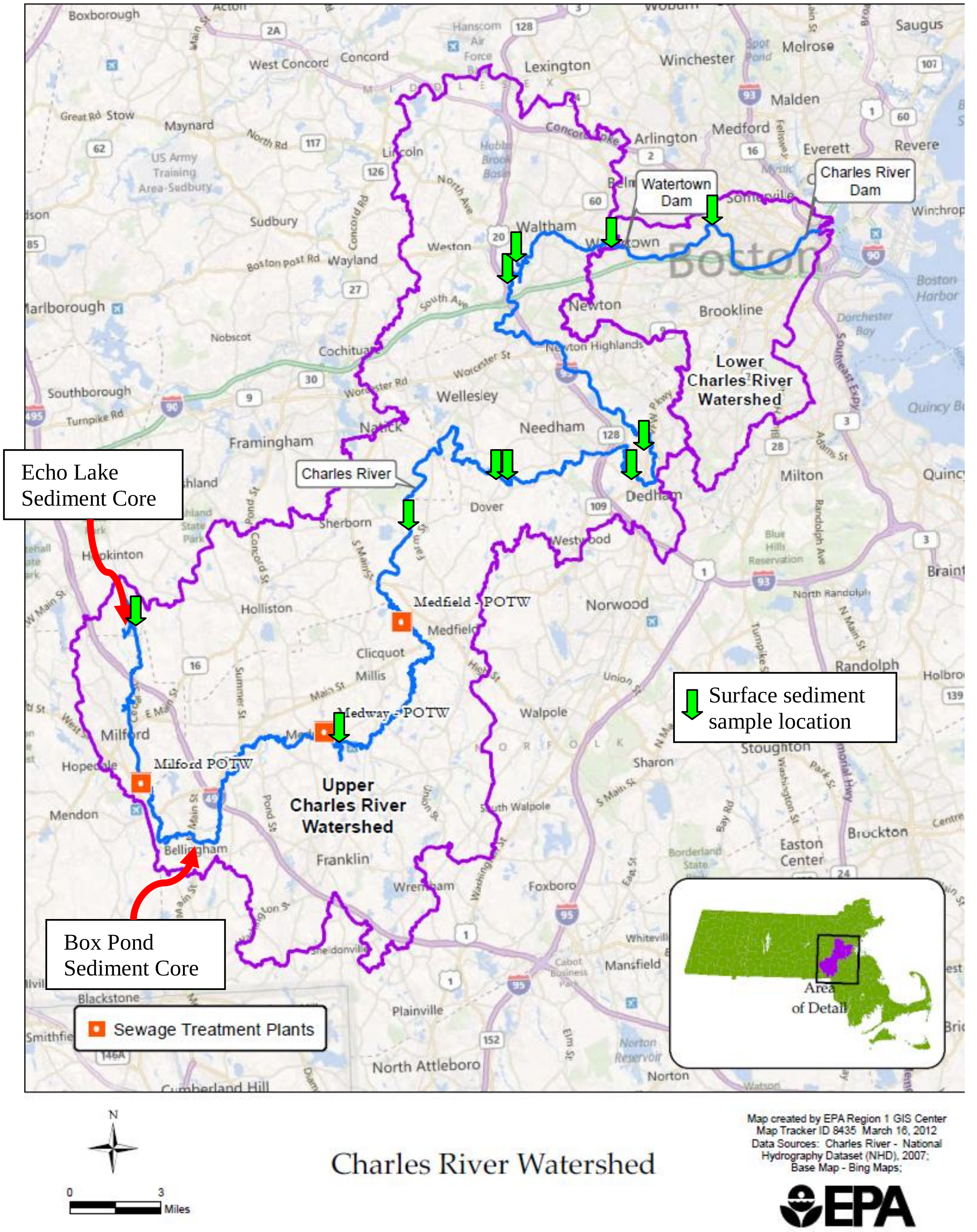
The general goal of this research is to determine how changes in land use change the concentration of metals in sediments along the Charles River in eastern Massachusetts. This goal was achieved by collecting and analyzing two sediment cores and eleven surface sediment samples.

The collected sediment cores were sectioned in discrete 5 mm thick, horizontal intervals. Gamma spectrometry, using the radionuclides ^{210}Pb, ^{214}Pb, and ^{137}Cs, established the year of deposition for each interval. Each interval was analyzed for: aluminum (Al), iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), chromium (Cr), cobalt (Co), lead (Pb), arsenic (As), cadmium (Cd), tin (Sn), scandium (Sc), strontium (Sr), silver (Ag), mercury (Hg) and total organic carbon (TOC). The analytical methods as well as quality control and quality assurance measures are described in Chapter 2.

The sediment core locations were selected to contrast land use in a narrow geographic area. Echo Lake, the headwaters of the Charles River, is the background location and had no alterations to its watershed until after 1970 when residential development began. Box Pond, 14 km downstream of Echo Lake, received industrial discharges and urban wastes for nearly 100 years.

Eleven surface sediment samples were collected from stations along the length of the Charles River and analyzed for Cu, Zn, Pb, Hg and TOC. The surface samples consisted of the upper 3 cm of sediment unless a distinct composition change was found. It was assumed that 3 cm would represent sediments deposited within the prior 10 years based on an average sedimentation rate of 3 mm yr^{-1} determined in both sediment cores.

The unique aspect of this dissertation is that no previous research has matched upstream to downstream sediment core locations for such a wide-range of metals, in a setting of consistent natural conditions, while providing a wide contrast in metal discharge history due solely to changing anthropogenic land use. This contrast allowed the determination of relationships between different land uses and the concentrations of various metals. These relationships also provided insight into the behavior of selected metals in the surface sediment samples. The location of the sediment cores and sediment surface samples are shown on Figure 1.1.



Map created by EPA Region 1 GIS Center
Map Tracker ID 8435 March 16, 2012
Data Sources: Charles River - National Hydrography Dataset (NHD), 2007;
Base Map - Bing Maps;

Figure 1.1. The Charles River watershed. The sediment sampling locations are shown along with important features.

Land use is the anthropogenic change in the physical character of the landscape. In the Charles River watershed those changes are generally the conversion of forest to industry, agriculture, transportation networks, and homes. Increasing land uses of these types have been demonstrated to have adverse effects on the environment (Coles et al. 2004; Chalmers et al. 2007).

Although land use introduces many substances into the environment, metals were selected for this research because they are commonly used in many anthropogenic applications , may be toxic to humans and the environment, and are readily sequestered in sediments (Luoma and Carter 1991). Sediments were examined because they contain the greatest reservoir of metals in contact with surface waters and therefore exert the greater long-term influence on water quality (Olsen et al. 1982).

Determining the effect that land use has on metal concentrations in sediment will provide a means of protecting human and environmental health and will enhance recreational uses. As concentrations of metals increase in sediments, aquatic life and human health may be affected. For instance, an increase in Cu and Hg was found to decrease the diversity of bacteria allowing for increased counts of single colonies creating an unstable population (Singleton and Guthrie 1977). Such an environment may produce poor water quality in the Charles River. In the Charles River basin it was found that some sediments may pose a threat to human health (Breault et al. 2000). Increased erosion may require that reservoirs be dredged to restore an impoundment to useful depths for recreation.

Prior to examining the results of this research it is important to outline the sources of metals, the variables that may alter their behavior, the potential effects of metals and sediments on human health and the environment, and other research that bears on this work.

1.1. Review of Sediment and Metal Behavior

Metals are delivered to water bodies from natural and man-made sources in both particulate and dissolved forms. Particle dynamics transfer the metals between the water column and the sediment based on a variety of physical and chemical processes (Turekian 1977; Olsen et al. 1982). The net effect is that the concentration of metals in each horizon of deposited sediments is related to the concentration of metals in the surface water at that time. Burial by subsequent layers of sediments preserves, to the extent allowed by bioturbation and diagenesis, the relative conditions at the time of deposition (Olsen et al. 1982; Stumm and Morgan 1996; Thimsen and Keil 1998).

The distribution and mobility of metals between surface water and sediments are complex functions of the interactions between a myriad of variables within broad factors such as climate, geology, geomorphology, biota, water chemistry, stream morphology, and the sediment load, none of which dominate consistently (Luoma and Carter 1991; Richardson and Kiffney 2000). The overall processes governing sedimentation in eastern North America have been relatively constant since the last ice age, approximately 18,000 years ago (Stearn et al. 1979).

1.1.1. Metal Sources

Metals found in sediments have several sources. Autochthonous metals occur in trace quantities in the minerals of rocks and soils, and are typically quite low in concentration. The Milford Granite underlies the watershed that contains both Echo Lake and Box Pond (Zen 1983). Common metals found in the mineral grains of granites include iron and manganese in various oxide and silicate minerals, and aluminum in feldspars. Trace mineralization containing other metals can occur within granite, and may include small vein fillings of galena (lead sulfide) and sphalerite (copper sulfide) as well as other trace elements. The weathering of geologic materials introduces metals to the river which become part of the sediment load as it is carried downstream to the ocean (Rudnick and Gao 2003).

Allochthonous metals, those derived from sources outside a watershed, are delivered through natural and anthropogenic means. There is a natural component of atmospheric fallout of several metals (Stumm and Morgan 1996). But the largest supply of allochthonous metals to a watershed is through industrial atmospheric emissions and fallout, as well as the abrasion of man-made metal objects (Galloway et al. 1982; Davis et al. 2001).

1.1.1.1. Atmospheric Deposition

Atmospheric deposition of natural and anthropogenically enriched aerosol particles can be significant sources of metals to a watershed (Galloway et al. 1982; Stumm and Morgan 1996). World-wide volcanism is a significant source of many heavy metals to the atmosphere such as Fe, Mn, Cu, Zn Sr, Pb, Hg and Cd among others (Schlesinger 1997; Schuster et al. 2002).

Anthropogenic sources of metals to the atmosphere include coal burning in power plants and trash incineration. The trace metal content of coal includes As, Cd, Cr, Co, Pb, Mn and Hg (Brownlow 1979; Szpunar 1992). Trash incineration was found to contain significant amounts of many metals including Pb and Sn (Chillrud et al. 1999).

Assessing the historic atmospheric deposition of individual metals requires special environments or the consideration of depositional factors. Peat bogs are a special depositional environment useful for determining the atmospheric flux of metals such as Pb, Hg, and Cd that sorb preferentially to organic matter (MacKenzie et al. 1998). Lake sediments also preserve depositional fluxes (Mahler et al. 2006). For instance, a study that examined lake sediments found that the atmospheric deposition of mercury in New England before 1850 ranged from 5 to 17 μg m^{-2} yr^{-1}, and although quite variable, now currently ranges from 21 to 83 μg m^{-2} yr^{-1} (Kamman and Engstrom 2002). Some modern trends are the result of long-term monitoring that have found atmospheric fluxes of metals, particularly lead, to increase from the 1920's and then peak and decline in the 1990's. In this instance, the trend for Pb deposition is due to regulatory measures imposed on atmospheric discharges, principally the phase-out of tetraethyl lead as a gasoline additive (MacKenzie et al. 1998; Chillrud et al. 1999).

The contemporary flux of metals to sediments from the atmosphere may be found through monitoring using a number of techniques which isolate wet and dry deposition as well as mimicking sedimentary environments. Atmospheric deposition of select metals in New England as shown in Table 1.1 (Golomb et al. 1997):

Table 1.1. Atmospheric Deposition of Metals into Massachusetts Bay: 1992 – 1993. Modifed from (Golomb et al. 1997).

Metal	**Total Deposition (μg m^{-2} yr^{-1})**	**Wet Deposition only (μg m^{-2} yr^{-1})**
Al	102,000	29,400
As	132	21
Cd	405	210
Co	58	12
Cr	2,700	1,500
Cu	3,500	700
Fe	140,000	36,000
Mn	4,420	975
Ni	7,200	3,000
Pb	2,700	855
Sb	160	64
Se	264	154
Zn	7,800	2,700

1.1.1.2. Historic Anthropogenic Direct Discharges

European colonization and the industrial revolution saw the wholesale use of rivers for both power generation and disposal of wastes (Haglund 2003). In the 19th and early 20th centuries textile mills discharged waste dyes and other “liquors” to many rivers along the New England coast. The dyes and “liquors” contained metals including Cd, Cr, Pb, Zn or Hg (U.S. Environmental Protection Agency 2004).

Metals are a key component of many industrial processes. Milford, Massachusetts, upstream of Box Pond, had historic industrial uses that included electrical component and paint manufacturers. During the 1960’s Cedar Pond, an impoundment of the Charles

River between Echo Lake and Box Pond, was reported to be various, unnatural colors due to discharges from the paint companies in Milford (Papuga 2004).

The metals discharged from the mills and industries in the 18th, 19th and early 20th centuries are retained in the sediments. Metals, unlike organic compounds, cannot be degraded over time to less toxic forms, but are conserved within the system (Stumm and Morgan 1996). Metals may be bound such that they are not bio-available, but conditions may change, allowing metal contaminants to become mobile within the environment and pose a hazard (Brezonik et al. 1991; Zoumis et al. 2001).

Contaminants that were discharged during the unregulated industrial era are stored in thick sediments behind dams (Breault et al. 2000). The general assumption that rivers today are cleaner than during the industrial past ignores the legacy of those metals in historic sediments. If these sediments are disturbed due to high flow events or through dredging, they may be exposed to the water column and serve as a significant source of metals and other contaminants to impoundments further down-stream (Simpson et al. 1998; Doyle et al. 2003).

1.1.1.3. Modern Anthropogenic Sources

Modern residential, commercial and industrial development concentrates, transports, and uses a broad spectrum of allochthonous metals. The weathering and wear of metal materials liberates those metals into a watershed (Van Metre and Mahler 2003; Taebi and Droste 2004). Metals associated with aerosols such as As, Cd, Co, Pb, Sn, Cu and Zn, have been characterized as road-specific heavy metals, originating from combustion in vehicles, oils and fuel, tires, brake linings and galvanized metal (Hopke et al. 1980; Hildemann et al. 1991). An investigation in a Maryland watershed found that common building materials such as brick, concrete, metal, unpainted wood and painted wood contained significant concentrations of Pb, Cu, Cd and Zn. Vehicle brakes have been found to be a significant source of copper and tire wear was a source of Zn (Davis et al. 2001). Table 1.2 summarizes the contribution of various sources of metals in a Maryland watershed.

Table 1.2. Contribution of metals to a Maryland watershed. From Davis, *et. al*., 2001.

		Sources					
	Total Flux	**Building Material**		**Atmospheric Deposition**		**Automobile**	
	(kg ha^{-1} yr^{-1})	**Siding**	**Roofing**	**Dry**	**Wet**	**Tires**	**Brakes**
Pb	0.069	79%	1%	10%	8%	1%	1%
Cu	0.038	22%	9%	14%	7%	1%	47%
Cd	0.0012	21%	5%	19%	41%	4%	10%
Zn	0.646	59%	7%	3%	2%	25%	3%

The research in the Maryland watershed found that doubling the housing density in the watershed doubled the pre-existing flux of Pb, Cu and Zn to sediments to 0.125, 0.0685 and 1.26 kg ha^{-1} yr^{-1}, respectively. Doubling the density of vehicle traffic in the Maryland watershed doubled the flux of Cu to 0.0566 kg ha^{-1} yr^{-1} and the flux of Zn increased from 0.646 to 0.837 kg ha^{-1} yr^{-1}. Doubling the atmospheric deposition increased the concentrations of Pb, Cu, Cd and Zn in storm water runoff by only small factors. The conclusion was that the majority of metal flux to sediments in the Maryland watershed was contributed directly by the materials brought into a watershed (Davis et al. 2001). Other research has found that metal roofing is a significant source of Cd and Zn, and that asphalt shingles are a source of Pb (Van Metre and Mahler 2003).

1.1.2. Processes that Affect Sediment Metal Concentrations

Anthropogenic modifications to a watershed and waterway change how metals are transported to, and sequestered in, sediments. A number of these processes must be considered to evaluate the data from this research. These changes include: impeding the flow within a stream by installing a dam, changing overland flow through storm water management, and adding anthropogenic wastes to a stream. These changes, among others, affect sediment chemistry through secondary means by altering the interactions at the sediment/surface water interface and changing the interaction of biota and metals.

1.1.2.1. Dams and Waterway Management

The first anthropogenic alteration to a river, and perhaps most profound, is the building of dams and the resulting impoundments. Prior to colonization, the Charles River had few impoundments or any deep water stretches (Haglund 2003). Beginning in the early 19th century dams were installed on many New England rivers, including the Charles River, to capture power for early industrialization (Cronon 1983). In the latter half of the 20th century, although the industrial use had ended, the dams and impoundments remained and the land surrounding the impoundments was developed. On the Charles River more than 20 dams still exist, and except for the drinking water reservoir at Echo Lake, these dams now serve only recreational purposes (McAdow 1992).

The early research on the effect of anthropogenic development on streams focused on the physical effects of dams. Dams alter the flow regime of a stream. The obvious result of a dam is an increase in the depth and volume of the impounded water body, and the slowing of the stream velocity. Once the stream enters the impoundment, its sediment load is deposited, including much of the fine-grained sediment. It was found that once the water passed over a dam it re-acquired its sediment load and accelerated erosion downstream (Dunne and Leopold 1978).

Dams create conditions that alter weathering and the substrate of a stream. The increased water volume increases the amount of saturated surface area within the watershed and increases the chemical weathering of the saturated geologic materials through redox processes liberating metals to the surface water in some instances. Behind a dam the stream deposits coarse material as it enters the pond while the organic-rich, fine-grained sediments settle in the broader, quieter stretch of the impoundment. In naturally flowing streams, fine-grained sediments are uncommon and are typically flushed downstream by spring flows eventually into the ocean (Dunne and Leopold 1978). Dams change this, retaining fine-grained sediments that are richer in total organic carbon (TOC) and increase the surface area of sediment which can alter water and sediment chemistry (Dunne and Leopold 1978). The amount of TOC is increased in this sediment which allows for greater adsorption of metals and organic contaminants (Neihof and Loeb 1974; Thimsen and Keil 1998).

Dams also affect surface water quality through physical and photochemical changes. In their natural state, streams run through narrow channels and are shaded through much of their watershed. Dams and development change that by removing trees and creating broad expanses of open water (Coles et al. 2010). The large expanse of water open to the sun warms the surface water reducing its ability to hold oxygen. The increased sunlight contributes to the oxidation of organic matter which also reduces oxygen and produces CO_2 and PO_4 concurrently (Zafiriou et al. 1984; Stumm and Morgan 1996).

Photochemical reduction of metals can result in the dissolution of Fe-organic colloidal matter complexes which produces Fe (II) and other reduced species of metals. Dissolved organic matter (DOM) and other forms of organic matter (OM) are important in photochemistry because they contain chromophores that absorb light and mediate other reactions in the water column and, in shallow water, at the sediment surface as well. Photochemical transformations of metals are dependent on many factors and are capable of altering the composition of surface waters and sediments with respect to metals (Zafiriou et al. 1984; He et al. 2012). The net effect of this additional sunlight is to alter the mobility of metals from the sediments during daylight hours.

An example of photochemistry altering metal mobility is the cycling of Hg in the environment. In a reduced environment sulfate reducing bacteria are understood to remove Hg from sediments through methylation (Stumm and Morgan 1996). Methylmercury is toxic and bioaccumulates in food chains (Wallace et al. 2004). However, in clear surface waters Hg has been shown to be extremely susceptible to photo-demethylation (Lennherr and St. Louis 2009). Demethylation decreases toxicity and mobility, but redistributes Hg to other sediments.

The increase in water depth and volume behind a dam may cause temperature stratification, a condition not common in a natural stream. Thermal stratification of the water column can be an important influence on redox processes and biota in the water column and sediments in deeper water bodies (Kalff 2002). Thermally stratified intervals are typically depleted of oxygen and are not permanent, existing only during the summer months (Kalff 2002). The importance of stratification is the variation of oxygenated water in contact with the sediments throughout the year. During the summer a thermally stratified water body will have oxygen-depleted waters and sediments beneath a thermocline whose environment becomes reducing. Typically, in the autumn, the thermocline will disappear during “overturn.”

During the overturn the entire water column and a small portion of the upper sediments will become oxygenated causing a significant change of redox. The significance of the redox shift is that metals are sensitive to redox and these changes mobilize, sequester, and transform metal species in the sediment that may affect the water column (Warren and Haack 2001; Meylan et al. 2003).

The chemistry of sediments may also be affected by the changes in water levels due to dams. Research performed in a lake similar to Echo Lake found that seasonal flooding re-suspended sediments into an upper, aerobic layer that resulted in an increase in metal concentrations in the surface water. Lowering of the water level in summer caused stagnant areas of water which created anoxic conditions. The overall effect of these interactions is to cause metals to be mobilized at different times of the year, creating varying conditions of toxicity dependent on climate and hydrological conditions (Van Griethuysen et al. 2005).

An additional effect of sedimentation is that approximately 85% of the dams in the United States will near the end of their operational lives and will be filled with sediment by 2020 (Doyle et al. 2003). By the late 1990's it was estimated that more than 11% of the volume of the Charles River Basin, approximately 250,000 m^3, was filled with highly contaminated sediments (Breault et al. 2000). As recreational lakes become filled with sediments, the residents want the impoundments dredged to restore a useful depth for fishing, boating and swimming. Also, there is an increasing trend of removing dams to enhance water quality and the environment by restoring fish runs and a free-flowing stream (Doyle et al. 2003). Management and disposal of contaminated sediments is expensive and can cost more than \$1,000/m^3 (U.S. Environmental Protection Agency 1993).

1.1.2.2. Storm Water Management

Storm water management is a modern concept. In an unaltered landscape the weathering, erosion and transfer of metals from the rock and soils to waterways and sediments is a slow process (Karouna-Renier and Sparling 2001). Anthropogenic land uses changes the flow of water and the flux of metals to bodies of water.

Storm water may be divided into construction and post-construction phases. During construction, large amounts of earth are moved and erosion can transmit large amounts of fine-grained material to waterways (Dunne and Leopold 1978). A long-term investigation that monitored 42 lakes in Connecticut beginning in the late 1930's and lasting into the early 1990's, found that land clearing during the construction phase removed acidic forest soils and exposed metal-rich sub-soils that were then easily eroded (Siver et al. 1996). Such erosion may not increase the concentration of metals, but will increase the rate of sediment deposition containing autochthonous metals in lakes and streams (Dunne and Leopold 1978; DiToro 2001).

In the post-construction watershed, large areas of low-permeability or impervious surfaces such as roadways, parking lots, roofs, and landscaped areas, greatly increase the amount of water discharged to waterways (Dunne and Leopold 1978). The impermeable surfaces leach metals and organic substances, collect metals that are abraded from other objects, and collect metals from atmospheric fallout (Boutiette and Duerring 1993; Van Metre and Mahler 2003). The resulting runoff adds pollutants, including metals, to rivers and streams in greater quantities than natural runoff (Van Metre and Mahler 2004).

Post-construction storm water runoff has physical and chemical effects in water bodies. Although the same volume of rain may fall, a natural watershed will infiltrate and discharge that water over a greater period of time. In a natural setting, precipitation may take years or decades to enter a waterway. As impervious area increases in a watershed it will collect and discharge rain more quickly which decreases infiltration through soils and increases the size of the downstream flow during storms thus increasing erosion (Dunne and Leopold 1978). The increase in flow also has the potential to re-suspend and remobilize contaminated sediments in the stream creating the potential for mobilizing contaminants and allowing those sediments to be spread into formerly uncontaminated areas (Dunne and Leopold 1978; Simpson et al. 1998).

The chemical changes in surface water begin with temperature increases. Runoff from impervious surfaces may be warmer than the unaltered stream, but the greatest change in temperature is due to the diminished infiltration. The natural watershed infiltrated precipitation and allowed it to slowly seep in the ground taking years to arrive at a stream (Drever 1997). This base flow is in equilibrium with the average annual temperature, which in New England ranges from 9ºC to 11ºC (Dunne and Leopold 1978). With increased impermeable area, less precipitation infiltrates, less base flow is therefore available, and the temperatures of the stream are more dependent on the temperature when the rainfall event occurred, which is usually in the range of 15ºC to 20ºC (Dunne and Leopold 1978). Base flow cools a stream in summer and warms it in winter. The base flow of an altered stream is not only diminished in volume, it will run colder in the winter months and hotter in the summer months (Dunne and Leopold 1978).

Increased water temperatures decrease water viscosity causing higher settling velocities of particles and higher re-suspension rates of sediments (Dunne and Leopold 1978). High temperatures also result in a decrease in oxygen solubility. A decrease in oxygen alters the metabolism of microbes that use organic carbon and makes anaerobic conditions more likely which will alter metal mobility (Lovley 1991).

Post-construction storm water also introduces many metals that would otherwise have been attenuated by sorption onto natural substrates, but instead are conveyed to water bodies (U.S. Environmental Protection Agency 1993; Yuan et al. 2001; Van Metre and Mahler 2003). For instance, rooftops have been found to increase the flow of Hg in a watershed (Van Metre and Mahler 2003). Also described in Section 1.1.1.3., roadways may contribute Cu and Zn to storm water, through the wear of automobile brakes and tires (Davis et al. 2001). Engineering controls may be installed to sequester metals and other pollutants, but a significant fraction of metals are discharged to water bodies (Goonetilleke et al. 2005).

1.1.2.3. Changes in Surface Water Metal Chemistry

The critical reactions and the conditions for metal deposition to the sediments are established in the surface water. There are three basic variables that control the composition of surface water and the behavior of metals: pH, Eh, and the solution composition (Stumm and Morgan 1996).

In stream water pH values can vary considerably and exert considerable influence on metal chemistry. The mobility of Hg was found to be governed by a number of factors, but pH generally controlled the binding of Hg with other ligands (He et al. 2012).

In aerobic environments, such as surface sediments and stream water, Eh, the electro-potential state of the constituents of a medium, also termed “redox,” does not greatly affect metal mobility (Kalff 2002). The two general states are aerobic environments where oxygen respiration dominates, and anaerobic environments where respiration may use Fe, sulfur, nitrogen species and other organic or inorganic materials. Redox can have a significant effect on metal speciation in anaerobic environments such as in thermally-stratified or stagnant, oxygen-depleted waters and sediments (Turner et al. 1981; Brandenberger et al. 2004). In these environments metals may be sequestered and any toxic effects muted (Tessier and Campbell 1987; National Oceanic and Atmospheric Administration 1999). In addition to thermal stratification, anaerobic conditions may be generated by density stratification when salt-rich storm water from road salting enters a pond during the winter months.

The solution composition of surface water systems are affected by direct discharges of metals and other anthropogenic wastes, organic carbon, climate, geology, biota, sediments, sunlight, hydrodynamic forces and the morphology of a water body - to name a few. Additional complexity is imparted by the properties of water, the presence of solutes and particles in water, and the water/air and water/sediment interfaces. The difficulty in describing the impacts and relationships is that these processes are interconnected with no dominant associations.

Direct discharges to waterways are the most direct means to alter water chemistry. Direct discharges to waterways include sewage, industrial wastes, and direct atmospheric fallout from local and regional industrial sources. In much of New England sewage disposal is through individual septic systems. Septic systems inject water contaminated with metals and organic materials that alter groundwater chemistry and ultimately surface water chemistry when the flow enters water bodies. The overall alkalinity in lakes has been found to increase over time due to septic systems and lawn care chemicals (Siver et al. 1996).

Other means of sewage disposal collect, treat, and then discharge significant amounts of household and industrial wastes into rivers through centralized sewage treatment plants. The Charles River has three sewage treatment plants in the upper portion of the watershed that discharge to the river in Milford, Medway and Medfield, Massachusetts. The communities in the lower Charles River watershed discharge their wastes to the Deer Island facility in Boston and ultimately, Massachusetts Bay (Massachusetts Water Resources Authority 2005).

The direct discharge of industrial wastes has been examined in several cases that document the rate of accumulation of select metals discharged from specific industrial uses (Kolak et al. 1998; Chi et al. 2009; Outridge et al. 2010). In most cases though, these rates were extreme examples from singular sources such as deposition from a metal smelter. Typically, baseline conditions for individual metals such as Hg or Cu in an altered environment are not described in great detail. In the Charles River no legal industrial discharges occur except through pre-treatment programs designed to protect the river water quality (Massachusetts Water Resources Authority 2005).

Water quality in any stream is influenced by climate which has anthropogenic changes embedded as well. Rainwater consists of natural dusts and various compounds injected by interaction with water bodies, volcanoes, and plants as well as aeolian erosion. Rainwater is naturally, slightly acidic. Pure water at 25° C in equilibrium with atmospheric CO_2 will have a pH of 5.6 (Stumm and Morgan 1996). Anthropogenic modifications, such as burning petroleum, injecting nitrogen oxides and sulfur oxides into the atmosphere and generating additional acids results in precipitation in New England that may be as acidic as pH 4.3 (Drever 1997). Acid precipitation exacerbates weathering of geologic materials and changes water column and sediment chemistry affecting how metals, both natural and anthropogenic, are sequestered or released from the sediments to the water column (Flanagan et al. 1999). Acid precipitation alters even the most remote and undisturbed watersheds (Brimblecombe and Dawson 1984).

Stream water chemistry is a factor in whether metals will be swept downstream or incorporated into sediments. In aerobic waters at a pH of 6, geochemical models predict the majority of metals will either be "free" in aquo-complexes or exist as hydroxides (Turner et al. 1981; Stumm and Morgan 1996). The predominant hydroxides formed, as well as the amorphous oxyhydroxides, are those of Fe, Al and Mn. Surface waters are typically under-saturated with respect to mineral phases and the direct precipitation with anions to form chlorides, fluorides, carbonates or sulfates is not the typical fate of trace metals. In fresh water, divalent species of Cd, Co, Cu, Fe, Pb, and Zn as well as the monovalent Ag are shown by geochemical modeling to form "free" metals. But in the natural environment, trace metals do not exist as "free" metals in surface water, they are either hydrated or, more likely, adsorbed by particulates (Stumm and Morgan 1996). Reactive particulate phases present in the water column include DOM, aluminum oxides (clays), sulfides, and hydroxides of Fe, Al and Mn (Warren and Haack 2001).

Organic matter in general, including DOM, has been found to be the primary transport agent of many substances in water. DOM and OM affect photochemistry and adsorb contaminants, but more importantly serve as an energy source for microorganisms that result in the release of adsorbed metals to the dissolved phase and enhancement of their mobility in the environment (Goonetilleke et al. 2005). The microbial activity fostered by DOM and OM further alters pH, the redox chemistry of sediments and the water column, and the solution composition (Schiff and Anderson 1986; Stumm and Morgan 1996; Warren and Haack 2001).

1.1.2.4. Changes in Sediment Metal Chemistry

The formation of sediments is a function of the chemistry and physical character of surface water. Metals are highly particle reactive and readily sorb to colloids and other suspended materials in the water column (Olsen et al. 1982). Dissolved metals form stable complexes that include hydroxides, oxides, sulfides, chlorides and carbonates as well as organic complexes (Stumm and Morgan 1996). Deposition of particles in the water column occurs when the mass of a particle is sufficient to allow gravity to pull the particle to the bottom and the flow velocity is sufficiently low (Olsen et al. 1982). Because metals are particle-reactive they become closely associated with sediments that collect in the stream bottom and are representative of surface water metal concentrations at the time of deposition (Turekian 1977; Olsen et al. 1982; Chalmers et al. 2007). Succeeding deposition buries the deposited particle with the sorbed metals unless re-suspension, bioturbation or diagenesis mobilizes or further alters the metal or particle (DiToro 2001).

Once buried, sediments are not inert to the environment and are subject to a number of processes that affect the mobility and toxicity of sediment-bound metals. The primary controls on sediment chemistry are similar to the surface water including organic matter and redox, but may also include other conditions such as those created by grain size and pore water.

The grain size of sediments depends on the velocity of the water in the depositional environment. Sand and gravel sediments are present in high energy environments such as fast-flowing streams, while fine-grained sediments exist in quiet pockets of streams as well as in lakes and behind dams (Linsley et al. 1975; DiToro 2001). Grain size affects how sediments interact with the overlying surface water by either diffusive flow or by advection (Ren and Packman 2004).

The interaction of surface water and sediments is through pore water that occupies the void spaces between the sediment grains. Porosity, the connection of the void spaces in the sediment matrix, determines the rates of the interaction and whether diffusive flow or advection dominate (Berner 1980). The void space between the grains in sediment and can range from 30 – 90% of the volume of sediments (DiToro 2001).

Sediment grain size is important primarily due to the presence of organic matter and the increased surface area of the finer sediment particles and hence the potential increase in binding of metals and other contaminants (Thimsen and Keil 1998). In some instances sediment grain size was observed to have little effect on Cu and Pb sediment concentrations, but did exert some influence on Zn concentrations (Feng et al. 2004).

Organic matter diagenesis in the sediments may have the greatest influence on sediment chemistry. The concentration of organic material in lakes and streams is in the percent range while metals and nutrients are orders-of-magnitude lower in concentration. The oxidation of organic matter and reduction of metals and nitrate species in anaerobic environments has been found to reduce acidity and increase alkalinity which may decrease metal mobility (Schiff and Anderson 1986; Lovley 1991; Siver et al. 1996).

Although pH controls sorption in many situations, organic matter coatings on nearly all materials in sediments can minimize the effects of pH (Warren and Haack 2001). Mineral surfaces, regardless of pK_a acquire a slight negative charge from the small quantities of absorbed organic matter that exist on the exterior of the mineral (Neihof and Loeb 1974). Organic complexes, and humic acids in particular, become the most important and pervasive of metal-ligands in most fresh waters. The important factors governing metal-humic complexes are the stability constant of the metal and the major ion concentrations which further affect competition (Mantoura et al. 1978). The effect is that the addition of organic matter can sequester metals into the sediments and the diagenetic changes to the sediments can lead to release of metals. Organic matter has been shown to be a better indicator of bioavailability of metals to biota over other factors such as grain-size, depth and chloride content (Peeters et al. 2000).

Redox changes in organic-rich sediments have varying degrees of influence on the behavior of metals. It has been observed that where oxygen penetrates ≤ 1 cm into sediments, several metals may diffuse into the water column after release from Mn-hydroxides (Morford and Emerson 1999). The same research found that Cd was initially released to pore-waters during organic matter diagenesis but then quickly sequestered into acid volatile sulfides (Morford and Emerson 1999).

The interaction of metals between sediment, pore water, and surface water can occur between the various species of hydrated metals, solid phases of organic matter, hydrous oxides of Fe, Al, and Mn, as well as sulfides and other less common complexes (Stumm and Morgan 1996). For any metal the concentration in sediment dwarfs that of the over-lying water on a per unit volume basis, frequently being greater than two orders of magnitude in concentration (Filgueiras et al. 2004). The controlling variables cited for the water column: pH, redox, and the concentrations of the species, are still operative and an important consideration in geochemical models between surface water, pore water, and sediments (DiToro 2001).

Whereas, aerobic environments form various hydroxides from Fe, Mn and Al that complex other metal species, under anaerobic conditions metal complexes are more varied and the potential for “free” metals is greater. For instance, in the case of sulfate reduction in sediments, or on particles in surface waters under reducing conditions, the sequestration of various metals will lie in the order of their solubility constants. The first sulfide complex to form will be HgS ($-\log(K_s) = 38.5$), next will be CuS ($-\log(K_s) = 22.19$), followed by PbS, CdS, ZnS and NiS, respectively. It can be expected that Hg and Cu will out-compete Pb and the other elements for binding sites with sulfides (Chapra 1997). Similar competition occurs with other ligands under varying conditions.

What may be inferred from the discussion of surface and sediment chemistry is that the interaction of metals with sediments and water is not governed solely by sorption coefficients nor easily modeled. Many factors, such as the availability of oxygen, the amount of organic matter, and other physical and chemical changes to a river may affect the amount of metal sequestered in sediment.

1.1.2.5. Biota

Anthropogenic alterations may also alter biota with consequences to metal concentrations in sediments. Biota includes macroscopic plants and animals, both terrestrial and aquatic, and microbial organisms. Anthropogenic changes to the biota impart effects that would otherwise not occur in natural waters and thereby change the concentration of metals in sediment.

Removing trees and other terrestrial plant communities will raise the temperature of surface water, deplete oxygen thus generating an anaerobic environment, and cause the photo-reduction of metals making them more bio-available and potentially toxic (Sposito 1989; Coles et al. 2010). The profusion of nuisance aquatic vegetation may necessitate dredging, which liberates historic metals to the environment, or chemical treatments with copper sulfate and other inorganic compounds (Commonwealth of Massachusetts 1953; Doyle et al. 2003). Introduced exotic invasive plants have grown so successfully in some areas so as to render a water body eutrophic and change the availability of oxygen and therefore the concentrations of metals in sediment (Stumm and Morgan 1996; Kalff 2002).

Physical influences exerted by animals include the transfer of metals through mechanical means, such as re-suspension and bioturbation (Simpson et al. 1998). Aquatic animals can change the sediment porosity and alter diffusion and advection through bioturbation, creating burrows and moving deeper sediments to the surface, mixing and homogenizing the upper layers of the sediment (DiToro 2001). Biota may also affect sediments by the addition of organic matter, either through growth, or as waste products. Introduced organic matter, produced by biota, is an important and a significant variable to consider with respect to metals. The organic matter may affect the porosity of the sediment, the ability of the sediment to adsorb metals, and the redox conditions (DiToro 2001).

Microbial processes, which drive redox conditions and alter the pH of waters, are among the more important and complex associations in the environment (Chapelle 1993). Micro-organisms in the sediment alter the chemistry of the sediments through metabolism, reducing and mobilizing many metals (Cooper et al. 2005). For instance, micro-organisms transform Hg from elemental to methyl forms making it more mobile in the environment and thus reduce its concentration in sediments (Stumm and Morgan 1996; DiToro 2001).

Microbial activity consumes organic carbon, oxygen, and other reducible species in infiltrating waters in ground water and can create conditions favorable to liberating metals from soils and rock (Chapelle 1993). Typical ground water evolution, after infiltration from the surface, results in less oxygenated, more reduced ground water capable of dissolving minerals within the aquifer matrix as micro-organisms consume the more easily oxidized materials first (Chapelle 1993; Schürch et al. 2004).

1.2. The Effect of Metals on Aquatic Life

The toxicity of metals in sediments is well-known (Luoma and Carter 1991). Based on the association of particles, metals and sediments, EPA issued a National Assessment of Sediment Conditions that evaluated 21,096 stations nation-wide (U.S. Environmental

Protection Agency 1997). The assessment used various metrics to develop tier rankings that classified the effects of sediments on aquatic life. The rankings and their definitions were:

- Tier 1 - Sediments contaminated to such an extent as to be associated with probable adverse impacts.
- Tier 2 – Impacts from sediment contaminants are likely but expected infrequently.
- Tier 3 - Finds no indication of impacts from contaminants in sediments.

The EPA assessment examined organic and metal contaminants. Among the Tier 1 stations the dominant contaminants were polychlorinated biphenyls (PCBs) (29%), Hg (10%), and organic compounds other than PCBs. Within the Tier 1 stations, metals, except Hg, were the least dominant class of contaminants (approximately 5%). However, metals were the dominant contaminant among Tier 2 stations (59%). There were 2,648 sampling stations in rivers and streams in New England, of these:

- 27% of samples were Tier 1.
- 59% were Tier 2.
- 14% were Tier 3.

Table 1.3. Top eight metal contaminants in New England sediments. Summarized from 2,648 stations as reported by EPA, 1997.

Metal Contaminant	**# of Tier 1 Stations**	**# of Tier 2 Stations**	**Total #**
Cu	0	625	625
Pb	0	623	623
Cr	59	438	497
Ni	0	491	491
Hg	176	312	488
As	14	373	387
Zn	0	376	376
Cd	0	339	339

Table 1.3 demonstrates that in New England, metals are a ubiquitous, low-level contaminant in sediments affecting nearly 25% of the sampled streams in New England. It is expected that Hg and As would pose Tier 1 impacts; however, Cu and Zn are also demonstrated to have potential impacts as Tier 2 contaminants.

Regulatory agencies have not been able to establish numeric sediment standards because toxicity has been found to be unrelated to concentration (Tessier and Campbell 1987; Luoma 1989). Currently, sediment toxicity is assessed by a stepped process. Sediment metal concentrations are evaluated against numerical standards that are based on prior testing of other sediments which also had toxicity sampling performed (National Oceanic and Atmospheric Administration 1999). Several values have been established and applied as conditions warrant (U.S. Department of Commerce 2012). The Equilibrium Partitioning methods developed guideline values called Effects Range Low (ERL) and Effects Range Median (ERM) which were established by collecting large amounts of data and comparing those results to toxicity test results (Ingersoll et al. 1996). The National Oceanic and Atmospheric Administration (NOAA) incorporated the ERL and ERM values as part of their Sediment Quality Guidelines designed to help assess and rank sediment contamination throughout the nation in various waters, marine and freshwater. ERL values are defined as those concentrations below which adverse effects to aquatic organisms is not likely to be observed, whereas ERM values are concentrations above which adverse effects are frequently observed (National Oceanic and Atmospheric Administration 1999). The values established for the metals in this research are shown in Table 1.4.

Table 1.4. Freshwater sediment regulatory guidelines for the metals in this research.

Metal	ERL (μg/g dry weight)	ERM (μg/g dry weight)
As	13	50
Cd	0.70	3.9
Cr	39	270
Cu	41	190
Mn	730	1700
Pb	55	99
Zn	110	550
Hg*	180	1060

ERL and ERM concentrations from Ingersoll, *et. al*., 1996.

* The values supplied for Hg are not from Ingersoll (none are provided), but are TECs and PECs, Threshold Effects Concentration and Probable Effects Concentration, for Hg as provided by NOAA (U.S. Department of Commerce 2012).

Recognizing the factors governing toxicity for many contaminants, the ERL and ERM values were developed not as regulatory standards, but as trip wires to conduct empirical studies to determine if sediment can pose an ecological hazard and should be examined further. NOAA and other users of these values acknowledge the vagaries of toxicity and that an adverse effect may occur with concentrations below the ERL and that no effects may be seen with concentrations above the ERM.

The toxicity of metals is governed by forces other than concentration. Metals transfer between solid phase and aqueous phase in aquatic environments with varying bioavailability (Brezonik et al. 1991). The measures of metal bioavailability may be the result of many factors such as other ions and complexes present (Turner et al. 1981), the life cycle of the organism, the nature of the substrate (Brezonik et al. 1991; Luoma and Carter 1991), and diffusion and advection processes (Van Leeuwen 1999).

Measures of the diversity of aquatic invertebrate species has also been used to determine if metals in sediments affect the environment (Clements 1991; Coles et al. 2004). Anthropogenic land use, particularly urbanization, has been found to be a consistent factor in a loss of abundance in species found in streams (Clements 1991; Peeters et al. 2000; Coles et al. 2004; Chalmers et al. 2007). This measure includes the number of species as well as the number of individuals within each group of species. The spectrum of species typically shifts to organisms that can tolerate common anthropogenically-enriched contaminants (Peeters et al. 2000). Even the early stages of urbanization have been found to be hazardous to aquatic life (Coles et al. 2004). The primary cause of the loss of species in some instances has been found to be the trace metals present in urban storm water runoff (Luoma and Carter 1991; Peeters et al. 2000; Coles et al. 2004). Another consistent finding is the inverse relationship between benthic diversity and impermeable land cover in a watershed (Robson et al. 2006).

The USGS examined the effects of urbanization by measuring the effects on aquatic invertebrates in watersheds in New England including data points in the Charles River. The percentage of altered land was compared to biological, physical, and chemical (BPC) changes in the streams (Chalmers et al. 2007; Coles et al. 2010). The investigations found that residential land use begins negatively impacting stream quality, as indicated by benthic organisms, at urban densities of less than 5% land cover. With increasing urbanization, corresponding decreases in species richness occurred until a value of approximately 35% urbanization. It was found that development beyond 35% had only minimal effect and the greatest changes in water quality and the BPC measures occur early in the urbanization of a watershed before a problem can be recognized (Coles et al. 2004).

Coles calculated several metrics of urban land use from road density, impervious area, forested land, and several socio-economic factors. Spearman rank correlation demonstrated that road density had the strongest adverse correlation with site scores. There were negative correlations with the number of Toxic Release Inventory sites, the density of impoundments and the amount of disturbance of stream buffer zones. The number of point discharges did not have a significant correlation with lower BPC scores. It was determined that road salting, metal contaminants introduced in runoff or available in sediments, and surface water temperatures that were anthropogenically altered may have adversely affected aquatic life (Coles et al. 2004). The study found a strong relationship between metal chemistry and road density ($R^2 = 0.912$) (Coles et al. 2004).

Other studies have pointed to the loss of biological diversity in streams and the impermeable area within a watershed along with the causal factors being identified as dissolved metals, in particular cadmium, chromium, copper, lead and zinc (Robson et al. 2006). The decline in environmental quality in all residential areas, with respect to surface temperature, rainfall runoff (quantity), and biodiversity was inversely related to green space cover and in particular, tree cover (Pauleit et al. 2005). Tree cover was found to indicate less disturbed ground and therefore better water quality and biodiversity (Coles et al. 2010).

1.3. Charles River Investigations

The Charles River has been the focus of previous specific research by the U.S. Environmental Protection Agency and the U.S. Geological Survey, dating from early efforts to control the river's hydrology beginning in 1968 (Barron 1976). In 1995 EPA established the *Clean Charles 2005* program and began additional monitoring (U.S. Environmental Protection Agency 2005). Other research on the Charles River has been primarily on the lower sections of the river that experience higher public use such as the Charles River Basin (Breault et al. 2000). In the upper sections of the watershed, some water quality sampling has been performed by the US Geological Survey (USGS) that included collection of a sediment core and other parameters at a location downstream of the study area of this research (Van Metre et al. 2004).

However, there is little information regarding water quality and sediment quality with respect to metals on the upper portions of the Charles River. An EPA study in 1997 examined surface water, sediments and potential toxicity to test organisms at nine stations, two of which are the sediment core locations of this research; the general finding was that although no toxicity was exhibited, a number of metals such as copper and mercury did exceed limits set as guidelines for potential toxicity at several sampling sites (U.S. Environmental Protection Agency 1997).

1.4. Environmental Regulation

Communities establish zoning regulations to direct how land is developed. Zoning regulations control the density of development and construction standards. Environmental regulations at the federal, state and local level are further controls to protect resources.

The first environmental regulations included the 1899 Rivers and Harbors Act, the 1948 Water Pollution Control Act and the 1956 Federal Water Pollution Control Act. These Acts primarily supplied funding and technical assistance to state and local governments to address pollution concerns at those times and did not develop or enforce discharge standards (U.S. Environmental Protection Agency 1999).

Real environmental regulation only occurred after a series of environmental disasters including the last Cuyahoga River fire in1968 and Love Canal (Ohio History Central 2005). EPA was established in 1970 in reaction to these and more localized problems. In 1972 the Clean Water Act was enacted and EPA followed with regulations implementing and enforcing that law in 1973 (U.S. Congress 1972).

Perhaps having the greatest impact on industrial discharges was the enactment and enforcement of the Resource Conservation and Recovery Act (RCRA) in 1976. The EPA regulations were embodied in Title 40, Code of Federal Regulations parts 239 through 282. RCRA set standards for waste and product releases to the environment. These regulations would have prompted industries to examine their waste stream to avoid fines and enforcement actions. Lastly, a Federal initiative in the 1970’s and 1980’s that may have affected metal concentrations was the Construction Grants program that sent money to the states for up-grading of sewage treatment works.

At the state level, in 1972 Massachusetts enacted the Wetlands Protection Act designed to regulate work in wetlands and waterways. Gradually, the State of Massachusetts has incorporated those portions of the Federal Clean Water Act that had been delegated to the State, into the Wetlands Protection Act (Commonwealth of Massachusetts 2009). Similar to the Clean Water Act and RCRA, the Wetlands Protection Act has been updated through time, increasing its effectiveness. In 1983 the jurisdictional area for regulation was expanded to include a 100-foot buffer zone surrounding wetland areas and other water resources.

In the early 1990's regulatory agencies came to the realization that storm water runoff from development and inhabited areas significantly impacted water quality in rivers and lakes (U.S. Environmental Protection Agency 1993; Taebi and Droste 2004). This has led to the establishment and expansion of programs such as the National Pollutant Discharge Elimination System (NPDES) that regulate storm water (U.S. Environmental Protection Agency 2011).

Storm water regulation under the Massachusetts Wetlands Protection Act was instituted in 1996 and has since expanded as well. In 1997 the Rivers Protection Act was added to afford additional protection to perennial streams providing for greater buffer zones and setting standards for stream crossings.

In 1995 EPA committed to a goal of making the Charles River safe for boating and swimming, based on bacterial standards, 100% of the time by Earth Day 2005. In support of the Clean Charles 2005 program, industrial discharges were virtually eliminated, water treatment plants were upgraded, and combined storm sewer outlets that discharged raw sewage to rivers were removed. The gauge of success is the number of days it is safe, from the perspective of bacterial counts, to boat or swim. When the program began in 1995, it was safe to swim just 19% and boat 38% of the time (U.S. Environmental Protection Agency 2005). In 2009, it was safe to swim 62% and boat 93% of the days, well short of its goal of 100% by 2005.

In 2006 and 2007 significant occurrences of blue-green algae, cyanobacteria, in the Charles River caused EPA to further regulate existing storm water discharges in three communities in the upper Charles River watershed (U.S. Environmental Protection Agency 2008; Tetra-Tech Inc. 2009). EPA’s decision document focused on phosphorous discharges from storm water as the probable cause of these algal blooms. The relationship between runoff and phosphorus concentrations was not conclusively established and other conditions may have contributed. The restoration and protection of sediment quality with respect to metals and other substances may contribute to better water quality in the Charles River

1.5 Conclusion

Considering the many regulations that have been established and implemented since the mid-1970’s it would be expected that improvement in Charles River would be reflected by improvements in the concentrations of metals in Charles River sediments. But during that period Massachusetts also experienced tremendous growth in residential homes throughout the State and in much of the Charles River watershed (Massachusetts Water Resources Authority 2005). This dissertation examined the trends of metal concentrations in sediments over a long period of time to gauge the success of environmental regulations and the impact of population growth and the associated infrastructure.

The upper Charles River watershed was selected as the location for collecting sediment cores for analysis. Sediment cores were collected in Echo Lake in Hopkinton, Massachusetts and 14 km downstream in Box Pond in Bellingham, Massachusetts. Because these locations were relatively close to one another and in an area of similar geology, the comparison of the sediment cores would not need to account for varying atmospheric deposition or geology.

Despite their proximity, the land use in the Echo Lake and Box Pond watersheds contrast dramatically. The Echo Lake watershed had but 16 residents until 1970, while the Box Pond watershed has been an urban industrial area since the 1870's. Analysis of the sediment cores from these locations in Chapters 3 and 4 allowed an estimation of the anthropogenic enrichment of metals due to the different land uses upstream of each sediment core location.

The concentrations of the metals in Echo Lake and Box Pond sediments were examined to determine the factors that may have altered the concentrations of select metals in sediments. These factors are also examined in the downstream surface sediment samples. The trends of metal concentrations and the relevant factors that control the concentrations suggest potential methods to protect and restore the Charles River and other, similar urban rivers.

CHAPTER 2

SAMPLING AND ANALYTICAL METHODS

2.1 Introduction

The only media sampled in this research was sediment. The management, processing and analysis of that sediment required careful handling to ensure that samples were homogeneous and representative of the sampled horizon. Each sampled horizon in a sediment core was processed and analyzed for geochronology, total organic carbon (TOC), and metals. This chapter describes the techniques used to ensure the representativeness, precision, and accuracy of the data.

2.2 Sampling Equipment and Collection of Samples

Sediment sampling consisted of collecting two sediment cores of greater than 30 cm length as well as 11 surface sediment grab samples. All sediments were collected in 15.24 cm diameter polybutarate tubes that varied in length from 10 to 50 cm in length and had a wall thickness of approximately 2 mm. End caps, used to secure the sediments during transit, were flexible, orange polyethylene caps that fit into the coring device with an overlap onto the tube wall. The methods for collection, processing and analysis were identical for both the sediment cores and the surface sediment samples except where noted below. Sediment cores were collected using a diver in Echo Lake and a remote sampling device in Box Pond. Surface sediments were collected by wading except for samples collected at the Charles River boat dock by use of a remote collection device.

The remote sampling apparatus was constructed in the University of Massachusetts machine shop to retrieve sediments in deep water. The remote sampling device was designed to connect to a 15.24 cm diameter polybutarate tube that would collect the sediment sample and consisted of a 2.54 cm thick end cap that attached to the core with an air-tight ring that was secured with six Teflon nuts and bolts. The cap was vented on top with a fitting that attached to a 5.08 cm diameter polyethylene tube with a shut-off valve. A push rod was secured at the top by a threaded rod attached to a 7.62 cm diameter polyvinylchloride (PVC) pipe. Each pipe was approximately 3 meters in length and could be threaded onto successive pipes as the sampling device was lowered. The depth of remote collection was limited only by the strength and confidence of the person collecting the sediment. A schematic diagram of the remote sampling apparatus is shown in Figure 2.1, below.

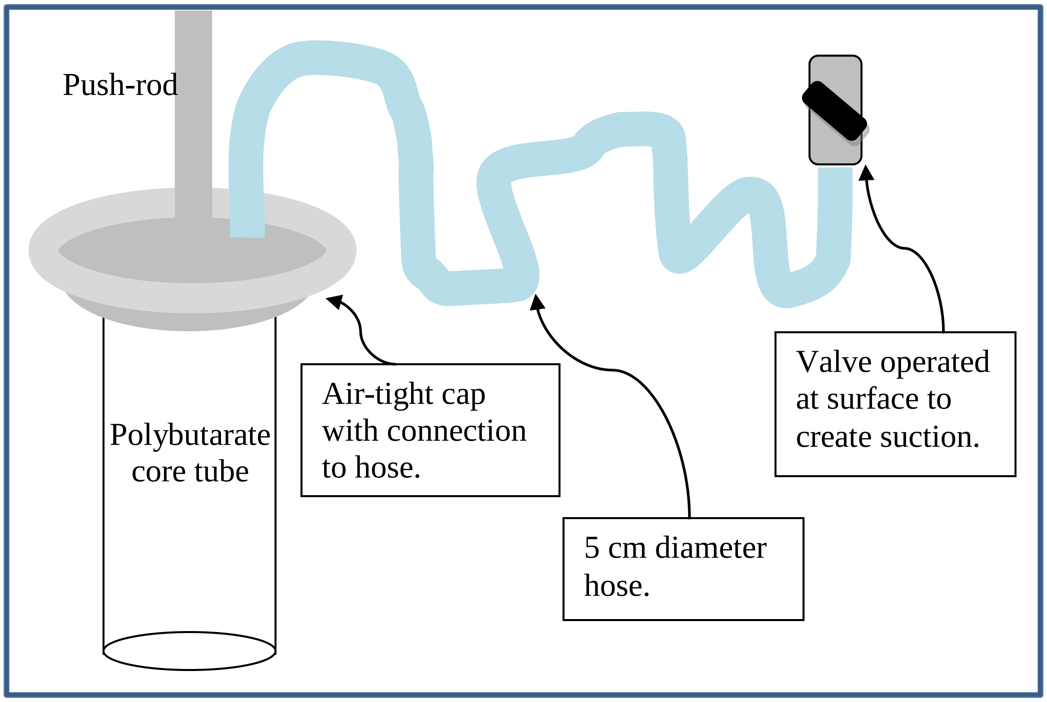


Figure 2.1. Schematic of the remote sediment sampling apparatus. Manufactured in the University of Massachusetts, Boston, machine shop.

The operational design of the remote sampling apparatus required the core tube to be pushed into the sediment from a boat or through a hole in ice using the PVC rods. During the lowering phase the valve attached to the clear flexible tubing was left open to expel air and water as the tube was lowered. Once the core tube reached the limit of penetration into the sediment, the valve was shut and the core tube carefully extracted and brought to the surface.

Prior to mobilizing to the field, sediment core tubes, end caps, and the remote sampler were acid-washed with 10% HCl, rinsed with deionized water and placed in plastic bags for transport. Additional acid-wash and distilled water were brought to the field for washing in between collection efforts.

As described in Chapter 1, two locations were chosen for the collection of sediment cores in impoundments on the Charles River. Eleven other locations were chosen along the length of the Charles River for the collection of surface sediment samples. The objective at each sediment collection site was to find a location that was undisturbed and representative of sediment deposition in that area. For the sediment cores, the deepest portion of each impoundment was sought using a fish finder. The surface sediment samples were taken in depositional environments that were not in deep impoundments but shallow water environments that dominated those stretches of the river. Geographic coordinates were determined by taking back azimuths onto known points and plotting on USGS quadrangle maps, those points were subsequently verified using GoogleEarth.

When the sampler was employed by a diver at Echo Lake, the clear polybutarate tube was driven slowly into the sediment by hand, capped on top, and then the bottom cap was placed by digging beneath the sediment to cap the bottom. This method was also used by wading at several of the surface sediment sites where the sample was collected upstream of the wading so as to minimize disturbance of the sediment surface.

The collection and handling of all sediment samples was identical. At each location the sediment coring device was lowered onto the sediment slowly to minimize suspension of the sediments and capture the unconsolidated layer of sediment at the top. The sediment coring tube was then advanced slowly into the sediment. The core and surface samples collected by hand had their bottom sealed by digging alongside and underneath the core tube and placing an end cap on the tube. When using the remote sampler, vacuum was relied on to maintain the sample in the core tube and the bottom was open during retrieval.

The sediment cores and surface samples were removed slowly to minimize disruption. Once collected, the sediment cores were inspected to ensure that the sample appeared undisturbed. The cores were constantly maintained in a vertical position, capped, and placed on ice for transport back to the lab for sectioning. The surface sediment samples were inspected after collection and then extruded in the field, placed in 250 ml jars, sealed, and placed on ice for transport back to the lab. The time interval between coring and processing at the lab was no greater than three hours for either sediment core and no greater than six hours for any surface sediment sample.

Each sediment core was measured as soon as it was collected and re-measured at the lab to determine if compaction had occurred during transport. All measurements made were positive values, downward, from the sediment-water interface. Prior to extrusion the overlap on the bottom cap was cut off with a razor blade. The bottom cap was then placed on the extruder. A cm-scale was taped to the core tube and downward pressure was applied to extrude the sediment sample at 0.5 cm intervals. The surface sediment samples were uncapped and extruded for sectioning at intervals that varied according to observations made during extrusion.

The equipment used for extruding the sediment cores consisted of an extruder that allowed the sediment to be pushed upward from the core tube in 0.5 cm intervals, a spatula constructed of high impact a 0.030 inch thick polystyrene, a 0.030 inch thick clear, polycarbonate scraper to remove sediments that adhere to the spatula. The extruder did not contact the sediment. The spatula and scraper were acid-washed with 10% HCl and rinsed with deionized water prior to use and were rinsed under a flowing distilled water tap between each sample horizon collection.

Each sediment core was sectioned by pushing the sediment upward in increments of 0.5 cm and slicing off each horizon with the polystyrene sheet and using the polycarbonate scraper to guide each section of sediment into a 250 ml polystyrene jar. Prior to sectioning of the Echo Lake core a considerable "fluff" layer was noted at the surface. After extruding most of the overlying water, the fluff layer was collected in two 0.5 cm layers using an acid-cleaned 50-ml syringe. Each 0.5 cm layer was collected from the upper-most portion of the overlying water. This water and fluff layer was also placed into separate 250 ml polystyrene jars.

2.3 Sediment Processing and Preparation for Analysis

The sectioned sediments were placed into a 250 ml polystyrene jar that had been previously labeled, weighed, cleaned in 10% HCl, rinsed with quart-distilled milli-Q water, and air dried under a Class-100 clean bench. Once each sample was in its jar it was immediately weighed. Each jar was then oven-dried at 60°C for approximately 72 hours. Those not immediately oven-dried, due to space constraints, were placed in a cold room. The oven-dried samples were weighed and visually inspected with the results recorded. After drying, all handling of samples occurred under a class-100 clean hood. All lab equipment that came into contact with the samples were acid-cleaned in 10% HCl, rinsed in quartz-distilled milli-Q water, and dried under a Class-100, laminar flow hood.

The dried sediment was homogenized by grinding with a Lexan rod under a Class-100 clean bench until it was reduced to a fine-grained powder. The lexan rod was approximately 8 cm in diameter and 15 cm long. The lexan rod was acid-washed in 10% HCl, rinsed in deionized water prior to first use and was rinsed under flowing distilled water between samples. The lexan rod was weighed periodically to within 0.01 g to ensure that pulverizing the samples did not abrade the rod. Once the sediment was sufficiently pulverized and homogenized, each jar was covered tightly and maintained for sub-sampling. Subsamples were collected for the following analyses: geochronology, metal digestion, and TOC analysis that are detailed below.

2.3.1 Preparation for Total Organic Carbon Analysis

Prior to analyzing for total organic carbon (TOC), carbonate and other inorganic carbon minerals were removed using a fuming method (Hedges and Stern 1984). Approximately 2 – 4 grams of sediments from each horizon were sub-sampled, transferred to 10 ml scintillation vials, and wetted with a small amount of quartz-distilled milli-Q water. The open scintillation vials were then placed in a covered desiccating jar with two small beakers containing approximately 15 ml of concentrated HCl and exposed to the acidic fumes for 24 hours thus removing inorganic carbon minerals. The open scintillation vials were then placed in a clean hood overnight to de-gas and dried in an oven at 60º C for three days. For analysis, approximately 2.5 – 5 mg of sediment were removed from the scintillation vials, weighed to an accuracy of 0.001 mg in pre-formed foil cups, and closed into a pellet-form using a custom built aluminum and brass pellet press.

2.3.2 Preparation for Metals Analysis

Sediment samples were prepared for analysis of metals and mercury using a microwave digestion method (Wallace et al. 1991). Sediment samples from each horizon were acid-digested by placing the dried, pulverized, homogenized sediment samples weighing approximately 200 mg, weighed to an accuracy of 0.1 mg on a Sartorius Analytical Balance (model No. 2743, Sartorius, North America, Inc., Edgewood, NJ), into 125 ml acid-cleaned Teflon vessels (Parr Instruments Model #4782) with 5 ml of aqua regia and 2-ml of concentrated, trace metal grade hydrofluoric acid. The aqua regia was constructed with concentrated trace metal grade hydrochloric acid and nitric acid.

The Teflon vessel was allowed to vent any evolved gases in a Class-100 hood for at least 30 minutes before being placed in a Parr Bomb container and heated at high power for 3 minutes in a 750 watt Kenmore microwave oven, model #87144, with a hand-wound turning apparatus that rotated the sample during microwaving to better expose the sample to heating. Once removed from the oven and after cooling in an ice bath for 1 hour, 10 ml of 1.5% boric acid (Certified ACS, Fisher) were added to the Teflon vessel which was returned to the microwave oven for an additional two minutes of heating at high power.

After the second cooling period of 0.5 hours in an ice bath, the contents of the vessel were added to a 125 ml trace metal clean, low-density polyethylene bottle and the Teflon vessel rinsed with a 1.5% boric acid solution prepared with quartz-distilled water. The rinse water was added to the 125 ml bottle sufficient to dilute to a total volume of 100 ml. The 125 ml bottle was then labeled with the sample designation and retained as a "stock solution."

The stock solutions were labeled and stored in a cool area. Each stock solution, including QA/QC samples were maintained in an up-right position, tightly sealed, and in a dark container. The stock solutions were sub-sampled to construct analytical aliquots for measurement by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) and the Mercury Cold-Vapor Atomic Adsorption (CVAA) instrument. In constructing any of the aliquots for analysis, care was taken to ensure that the stock solution was not shaken and that the covers were off for a minimal amount of time.

2.3.3 Preparation of Samples for Geochronology

The pulverized, homogenized sediments in the 250 ml jars were sub-sampled and placed into pre-weighed, 1 cm thick by 14 cm diameter petri dishes that had a nominal wall thickness of 1 mm. The sediments were stirred and leveled during packing into the petri dish to ensure that they were homogenous and that no voids existed. The caps were placed on the full petri dishes and then weighed to within 0.01 g. After weighing, each petri dish was taped shut and labeled.

2.4 Total Organic Carbon Analysis

TOC was determined with a Perkin-Elmer 2400 CHN Series II Elemental Analyzer (PerkinElmer, Waltham MA). A standard lab method (Kristensen and Anderson 1987) was used in operating the instrument. Pelletized samples, sample duplicates, blanks and standards were loaded into the auto-feed tray for analysis. Blank samples were prepared by pelletizing empty cups and placing one empty pellet every 10 samples (n = 20). The limit of detection was 0.01 mg TOC per gram of dry sediment and is based on three times the standard deviation of the prepared blank analyses. Analysis of acetanilide standard (PerkinElmer, Waltham, MA) occurred every ten samples and yielded a recovery of 99.995% with n = 19. Differences between replicate analyses proved to be less than 10% between samples. The TOC content of the sediment at each horizon as well as QA/QC analysis is reported in Appendix I and displayed graphically in Chapters 3 and 4.

2.5 Metal Analysis with Inductively Coupled Plasma – Mass Spectrometer

Prior to analysis, the digested sediment samples in the stock solution bottles were further diluted in 0.4 M HNO_3 (Optimal grade, Fisher Scientific). All metal samples, except mercury, were analyzed by ICP-MS (PerkinElmer ELAN6100 DRC, PerkinElmer) equipped with an Apex-Q sample introduction system (Elemental Scientific Inc., Omaha, NE). The instrument was prepared following standard optimization procedures before each daily analysis. The typical operation parameters under which the ICP-MS was run are listed in Table 2.1, below.

Table 2.1. Parameters used for ICP-MS analyses.

Nebulizer Gas Flow ranged 0.74-0.77 L/min, depending on daily optimization results.	**ICP RF Power**: 1100 Watts	**Integration Time**: 900 ms
Auxiliary Gas Flow: 1.2 L/min.	**Analog Stage Voltage**: -2100 Volts.	**Scan Mode**: Peak Hopping
Plasma Gas Flow: 15 L/min	**Pulse Stage Voltage**: 1600 Volts	**Scans**: 27
Lens Voltage: 5.75 Volts	**Dwell Time**: 100 ms	**Detector**: Dual

Analytical runs were performed in 2002, 2005 and 2009. In 2002 the Echo Lake and Box Pond samples were diluted 1:1000 for iron and aluminum and 1:100 for the remaining trace metals. It was determined that the dilutions were too great and that select samples should be re-run. Those samples were re-run in 2005 at a dilution of 1:200 for the iron and 1:25 for tin and zinc. Examining the 2005 results for the Box Pond samples, it was decided to rerun the entire sample set. Therefore, in 2009 Box Pond was re-run with Al and Fe diluted to 1:202 and the remaining trace metals to 1:37.

All samples analyzed, except the 2002 sample runs, used an internal standard to correct for instrument drift and interferences caused by the introduction system. All samples were spiked with an Indium (^{115}In) standard at a concentration to track the temporal variability of the signals.

The isotopes analyzed included the single isotope elements ^{27}Al, ^{55}Mn, ^{75}As, ^{88}Sr, ^{45}Sc, ^{52}Cr, ^{59}Co, and those with multiple isotopes such as ^{56}Fe, ^{57}Fe, ^{63}Cu, ^{65}Cu, ^{64}Zn, ^{66}Zn, ^{206}Pb, ^{208}Pb, ^{110}Cd, ^{111}Cd, ^{107}Ag ^{109}Ag, ^{118}Sn, and ^{120}Sn. In selecting those isotopes to carry forward in the reduction of the data, isobaric interferences and abundances were examined. Ultimately, both sets were carried forward, compared with respect to SRM recovery and duplicates, and the previous results. The results of the isotopes of each metal had few differences and there was substantial agreement with the 2002 runs. Those isotopes with the better agreement with SRM values were reported and included: ^{57}Fe, ^{65}Cu, ^{64}Zn, ^{206}Pb, ^{110}Cd, ^{109}Ag, and ^{120}Sn.

Digestion blanks were constructed by adding the acids and diluting solutions to the Teflon vessels and being subject to the same processing as samples. Values for digestion blanks were then adjusted to solid concentrations by assuming a value of 0.2 g of sediment in the calculations. This value was used to determine the limits of detection. These values are shown in Table 2.2.

Table 2.2. Detection limits of metals in sediment cores.

	Limit of Detection	
Element	**Box Pond**	**Echo Lake**
Al	0.12 mg/g	0.12 mg/g
Fe	0.01 mg/g	0.03 mg/g
Mn	11.10 µg/g	2.06 µg/g
Cu	0.25 µg/g	1.7 µg/g
Zn	0.86 µg/g	41 µg/g
Pb	0.04 µg/g	0.80 µg/g
As	0.27 µg/g	5.23 µg/g
Cd	0.01 µg/g	0.36 µg/g
Sn	0.9 µg/g	6.21 µg/g
Cr	5.4 µg/g	5.26 µg/g
Co	0.59 µg/g	0.28 µg/g
Ag	0.002 µg/g	0.04 µg/g
Sr	2.76 µg/g	1.13 µg/g
Sc	3.14 µg/g	1.76 µg/g

Based on 0.2 g sediment

Analytical accuracy was determined through the use of Standard Reference Materials (SRMs). The SRMs selected were BCSS-1 and PACS-1 from the National Research

Council of Canada. BCSS-1 is estuarine sediment from the Gulf of St. Lawrence while PACS-1 is harbor sediment from Esquimalt Harbor, British Columbia. The primary difference in the two SRM is that metal concentrations in the PACS-1 sediments were generally higher. Therefore, two ranges would be supplied to cover the range of values anticipated for Box Pond (high concentrations) and Echo Lake (low concentrations). A summary of the SRM recoveries for runs of each sediment core is provided in Table 2.3.

Table 2.3. Summary of Standard Reference Material recoveries. Echo Lake and Box Pond analytical runs.

Element	Core Location	Maximum Conc.	Average Conc.	BCSS-1 certified value	% Agree	PACS-1 certified value	% Agree
Al	Echo Lake	76 mg/mL	37 mg/mL	63 mg/mL	97.50%	65 mg/mL	102.44%
	Box Pond	68 mg/mL	48 mg/mL		103.20%		100.20%
Fe	Echo Lake	90 mg/mL	24 mg/mL	33 mg/mL	101.39%	49 mg/mL	96.64%
	Box Pond	42 mg/mL	25 mg/mL		111.30%		108.70%
Mn	Echo Lake	952 µg/mL	436 µg/mL	229 µg/mL	110.70%	470 µg/mL	104.52%
	Box Pond	597 µg/mL	345 µg/mL		125.73%		102.08%
Cu	Echo Lake	70 µg/mL	24 µg/mL	18.5 µg/mL	110.50%	452 µg/mL	100.60%
	Box Pond	470 µg/mL	143 µg/mL		106.51%		101.58%
Zn	Echo Lake	279 µg/mL	119 µg/mL	119 µg/mL	109.87%	824 µg/mL	102.52%
	Box Pond	682 µg/mL	290 µg/mL		119.19%		95.44%
Pb	Echo Lake	134 µg/mL	76 µg/mL	22.7 µg/mL	113.03%	404 µg/mL	103.96%
	Box Pond	270 µg/mL	121 µg/mL		115.73%		98.52%
As	Echo Lake	19 µg/mL	10 µg/mL	11.1 µg/mL	105.99%	211 µg/mL	91.23%
	Box Pond	40 µg/mL	13 µg/mL		106.00%		87.20%
Cr	Echo Lake	58 µg/mL	29 µg/mL	123 µg/mL	93.52%	113 µg/mL	91.02%
	Box Pond	247 µg/mL	96 µg/mL		113.21%		106.12%
Cd	Echo Lake	1.43 µg/mL	0.53 µg/mL	0.25 µg/mL	97.20%	2.38 µg/mL	104.07%
	Box Pond	5.3 µg/mL	2 µg/mL		104.59%		110.37%
Co	Echo Lake	19.1 µg/mL	5.9 µg/mL	11.4 µg/mL	110.14%	17.5 µg/mL	112.32%
	Box Pond	14.2 µg/mL	6 µg/mL		105.08%		92.25%
Sn	Echo Lake	15.6 µg/mL	2.9 µg/mL	1.85 µg/mL	61.30%	41.1 µg/mL	110.39%
	Box Pond	257 µg/mL	25 µg/mL		95.79%		109.92%
Ag, Sc & Sr	No SRM were available for these elements. They were run to gauge the crustal input (Sc and Sr) and anthropogenic activities (Ag) qualitatively.						

A summary of isotopes analyzed, limits of detection, replicate recoveries and SRM recoveries is presented in Tables II-1 and II-3 in Appendix II. The SRM recoveries, limits of detection, and blanks were examined to determine suitability for discussion in subsequent chapters. SRM recovery was acceptable (within 10% of the accepted value) for Al, Fe, Cu, As, Co, and Cd. The metals Mn, Zn, Pb, and Cr were within 25% of their accepted values for the BCSS-1 SRM in Box Pond sediments. A comparison of the range of concentrations of Mn, Zn, Pb and Cr in Box Pond sediments with the SRMs, shown in Table II.2 as well as by the maximum and average concentrations shown for each water body in Table 2.3, demonstrates that the PACS-1 SRM is more appropriate than the BCSS-1 SRM for these metals. The greatest disagreement was the BCSS-1 SRM for Sn in Echo Lake. Although the range of concentrations may also make the PACS-1 SRM more appropriate, caution should be exercised in examining the Echo Lake Sn data. All quality assurance and quality control measures are reported in Appendix II. Three elements had no SRM available, Sc, Sr and Ag. Sc and Sr were included in the analysis to qualitatively support the evaluation of crustal contribution.

2.6 Mercury Analysis via Cold Vapor Atomic Adsorption

For Hg analysis the stock solution was diluted and analyses performed using a CETAC Model 6000A Mercury analyzer with a detection limit of 1 ng/l in the final digestate using a method similar to method EPA Method 245.5. Blanks were run at a frequency of 1 blank to each 10 samples analyzed. Standards were run every five samples throughout the cold-vapor analytical run. The SRM selected was PACS-1, the same as used for the metals in the ICP-MS. For both sets of data, Echo Lake and Box Pond, SRM were < 10% of the certified values, analytical and digestion replicates were <5% except for the Echo Lake digestion replicates at 25% driven by one value. Table 2.4 summarizes the quality assurance and quality control measures for the Hg analysis, the details are provided in Appendix II.

Table 2.4. Summary of quality control and quality assurance for Mercury analysis.

	Echo Lake	**Box Pond**
Limit of Detection	8.91 ng/g	8.27 ng/g
Limit of Quantitation	29.71 ng/g	27.57 ng/g
Standard Reference Material average agreement	90.59%	103.36%
Digestion Duplicate average agreement	104.4%	103.47%

2.7 Geochronology

The sedimentation rate and age of each horizon in the core was determined from the dried samples in sealed 14cc petri dishes. Non-destructive, radioisotope methods were used in the determination of the age of each 5 mm interval using gamma detection techniques.

The radioisotope activities were determined by gamma detection on a Canberra model G2020R Low Energy Germanium (LEGe) detector with an active diameter window of 50.5 mm and an active area of 2000 mm^2. Signals from the detector were processed through a Canberra model 2026 Spectroscopy Amplifier and a Nuclear Data Inc ND575 ADC (Analog-to-Digital Converter). The Amplifier was set at a coarse gain of 10, fine grain 0.9510, with a shaping time of 4 µsec, a negative polarity, and set in gaussian mode. The coincidence was set to “off” on the ADC. Signals were analyzed through a Model 556A Acquisition Interface Module. The power supply was through a NIM/Bin Model 2100 and high voltage was supplied by a Model 31060 Programmable H.V. Power Supply set to –2.5 keV. Signals were processed using Genie 2000 software.

Samples were counted for a sufficient amount of time to either collect greater than 1000 counts or generate a one-sigma error less than 5%. Background and instrument drift were checked after every ten samples and approximately 10% of the samples were recounted for quality assurance.

Two standards were used to calibrate the detector. These included the 4350b standard and a standard pitchblende ore. Corrections for geometry and detector efficiency for the radioisotopes in this research, ^{210}Pb, ^{214}Pb, and ^{137}Cs, were found using the reference materials and were found to be as shown in Table 2.5.

Table 2.5. Overall efficiencies of the Low-Energy Germanium gamma detector.

Radioisotope	**γ Energy**	**Efficiency**
^{210}Pb	46 keV	0.5114%
^{214}Pb	295 keV	0.6835%
^{137}Cs	662 keV	1.40%

Branching efficiencies were found in the literature and incorporated intrinsically into the geometry and detector efficiency calculations. Self-absorption was calculated by the method of Cutshall (Cutshall et al. 1983). After the background, decay and yield corrections, the results were reported in units of dpm/g and Bq/g dry weight.

Radiometric dating techniques use a variety of models based on an assumed depositional characteristic to determine the dates of sediment horizons. The two basic divisions are constant rate and variable rate models.

The Constant Flux:Constant Sedimentation rate model (CF:CS) is a constant rate model based simply on the slope of the activity plotted against the amount of sediment deposited. To use this model, the activity is transformed by the natural logarithm and the amount of sediment can be expressed either in depth in centimeters or cumulative mass. Typically, the cumulative mass is the better to use as sediments become compacted with depth and diagenetic changes may alter the density of sediments.

The variable rate methods include the Constant Rate of Supply (CRS) and Constant Initial Concentration (CIC) models. These models assume either the amount of excess ^{210}Pb is the same every year irrespective of the amount of sediment deposited (CRS) or that the amount of sediment and radioisotope vary in a co-dependent fashion (CIC) (Appleby and Oldfield 1978).

In determining which model to employ for the cores, it was necessary to examine the amount of watershed versus the amount of surface water present at each location and character of the depositional area. Ultimately, all the models were used on each sediment core and the results compared. Appendix III describes the models used and how the dates were developed from those models. The dates of sediment deposition are plotted against the metal concentrations in Chapters 3 and 4 to yield a chronological concentration profile.

CHAPTER 3

ECHO LAKE WATERSHED

Abstract

A 43 cm long sediment core was collected from Echo Lake, a protected drinking water reservoir in Hopkinton, Massachusetts, and sectioned at 5 mm intervals. Radiometric dating, using gamma spectroscopy and the radioisotopes ^{210}Pb, ^{214}Pb, and ^{137}Cs, determined absolute dates of deposition for each interval. Each interval was then analyzed for TOC and the metals Al, Fe, Mn, Hg, Pb, As, Cd, Cu, Zn, Co, Cr, Sn, Ag, Sr, and Sc.

Increases in sediment Hg concentrations in the late 19th and early 20th century were determined to perhaps be the result of increased railway traffic within the watershed. Increases in sediment Pb concentrations in the latter half of the 19th century were due to atmospheric sources from outside the watershed. Pb concentrations increased through the 20th century until 1993 when concentrations began to decrease due to the phase-out of leaded gasoline under the Clean Air Act of 1970.

Residential development began in the watershed in 1970 altering the physical character of sedimentation and the lake bottom as well as the metal concentrations in Echo Lake sediment. The rate of sediment deposition in Echo Lake increased by more than four times the natural rate of deposition. After 1970 the sediment concentrations of

Hg, Pb, Cd, and As began increasing due to atmospheric fallout and storm water runoff, while an increase in Cu sediment concentration was due to a weed treatment performed in 1990. Because of these increases of sediment concentration, seven metals: Hg, Cd, As, Cu, Zn, Cr, and Pb, were determined to exceed regulatory guidelines established to assess potential harm to aquatic life.

3.1 Introduction

Echo Lake is a drinking water reservoir in Hopkinton, Massachusetts. Few lakes in eastern Massachusetts are unaltered by anthropogenic land use changes, but Echo Lake has been a protected drinking water reservoir since 1882. For much of its history, the Echo Lake watershed was unpopulated. Until 1968 there were fewer than 16 homes in the watershed and less than 5% of the watershed was altered by residential development or agriculture. After 1970, residential development began on the northern edge of the watershed, approximately 1 km from the lake. Residential development continued to expand during the 1980's and 1990's, but a protective natural buffer of approximately 500 m has been maintained around the reservoir. When the sediment core was collected in 1999, residential development had altered 39% of the watershed (Dichter 2005).

Three primary questions were examined with respect to Echo Lake: What are the natural background concentrations of metals in sediments prior to anthropogenic alteration? What alteration to the concentration of metals in sediment occurred as a result of anthropogenic land use changes in the watershed? Have those changes in sediment metal concentration affected water quality and aquatic life?

To answer these questions, a 43 cm deep sediment core was collected from Echo Lake and sectioned at 5 mm intervals. The date of deposition for each interval was determined with gamma spectrometry using the radioisotopes ^{210}Pb, ^{214}Pb, and Cs^{137}. Sediments from each interval were acid-fumed and analyzed in a Perkin-Elmer CHN analyzer to determine the concentration of TOC. A total microwave acid digestion of sediments from each interval was performed to obtain suitable stock solutions for metal analysis. Al, Fe, Mn, Pb, As, Cd, Cu, Zn, Co, Cr, Sn, Ag, Sr, and Sc were analyzed via ICP-MS, while Hg was analyzed using CVAA. The sample preparation, analytical methods, quality assurance, and quality controls are discussed in Chapter 2.

3.2 Echo Lake Study Area

3.2.1 Echo Lake Watershed Characteristics

Echo Lake is an impoundment created by a 10 m high, granite dam filled by groundwater and three small streams in Hopkinton, Massachusetts. Its watershed covers 3.7 km^2 of which the lake covers 39 hectares. Echo Lake is the headwaters of the Charles River and lies at an elevation of 106 m above sea level and 125 km upstream, as the river runs, from the Charles River dam which separates the river from Boston Harbor and the Atlantic Ocean.

Echo Lake is approximately 9 m deep at its deepest point when the reservoir is full, but otherwise has large areas that can become exposed during dry summers. Its average depth is approximately 2 meters and has an approximate volume, when full, of 8x10^8 l. The measured flow of the Charles River as it emerged downstream of the Echo Lake dam in 1996 was 0.014 $m^3 s^{-1}$ (Wohlers 1998). From evidence gathered during the sediment core collection it appears that the lake bottom in the area of the deepest point of the reservoir is thermally stratified during the summer months and no benthic vegetation exists in the area where the core was collected.

The 500-million year-old Milford Granite underlies Echo Lake and much of south-central Massachusetts. In this area the Milford Granite is a pale gray color, with small amounts of biotite and quartz (Zen 1983). The general soil type in the area is the Chatfield-Hollis, a well-drained glacial soil that is present in sloping terrains. One of the distinguishing characteristics of this soil is that it is typically underlain by bedrock, just 20 to 40 inches below the surface, making the soil rather poor for farming, woodlands, or development (Taylor 1998). The watershed of the lake is forested with a mix of pine and hardwood that range from sapling to mature trees.

At the time of the sediment core collection in 1999 approximately 39% of the Echo Lake watershed consisted of land used for residential homes with the remaining land consisting of either forest (51%) or the lake itself (10%) (Dichter 2005). The majority of the 240 homes in the watershed at the time of sediment core collection were greater than 1 km from Echo Lake. The Echo Lake watershed is shown as the dark-grey shaded area on Figure 3.1.

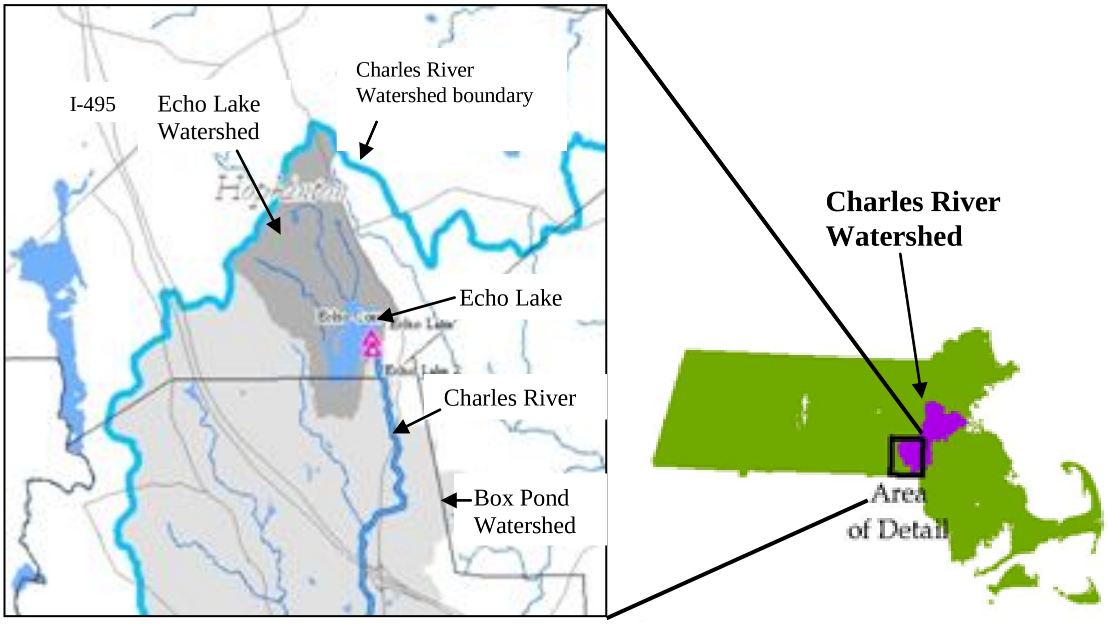


Figure 3.1. The Echo Lake watershed, the dark grey area in the center of the map, is the headwaters of the Charles River. The river flows southward from Echo Lake towards Box Pond. The Box Pond watershed is shown in a light grey color.

3.2.2 History of Land Use in Echo Lake Watershed

In pre-colonial times, before the river was dammed, the area of Echo Lake was a wetland. Sometime before 1831, a small dam, Sheffield's sawmill, flooded the area that was to become Echo Lake (McAdow 1992). Before the 1850's that dam was breached and the area reverted to, and was maintained as, a hayfield until 1882 (Bowker 2005). In 1872 a railroad line was built 70 m east of Echo Lake to connect Milford, Massachusetts to Hopkinton, Massachusetts (Milford Historical Commission 1980).

In 1881 the Milford Water Company purchased the area that was to form Echo Lake, and the surrounding land, as a water supply and buffer zone, respectively. In 1882 a six-meter high dam was built, but after a severe drought in 1900 a new ten-meter high dam was built on the same location in 1902, which still stands (McAdow 1992). Until 1968 the river ran in a natural, 4 km long channel to the treatment plant in Milford, before being collected, treated, and then distributed as drinking water. Due to water quality problems during high river flow events, a pipe was installed at the base of the dam in 1968 to transmit drinking water from Echo Lake, directly to the treatment plant (Papuga 2004). Since the early 1900's the Milford Water Company has restricted access to the lake, not allowing any recreational use, and has maintained a natural, forested buffer zone greater than 500 m, in most places, that is posted to prevent trespassing (Papuga 2004).

3.3 Sediment Core Collection and Description

The Echo Lake sediment core was collected by divers David Shull and Peter Edwards on August 6th, 1999 at the deepest point found in the lake. The sediment core location was determined from a boat using an electronic depth finder and recorded as N42° 11' 32.67" and W71° 30' 31.83" using a compass, triangulating from known landmarks and then checking against a USGS map. The sediment core collection location was found to be 6.4 meters deep at the time of collection by electronic depth finder.

The sediment core was collected in mid-summer while the lake level was depressed approximately 2.5 meters below its usual level. The water column was extremely turbid, with what appeared to be a bloom of plankton, and the divers disappeared from view at a depth of less than 1.5 meters. Both divers stated that within a short distance of the surface the water was completely dark. Although the surface water temperature was quite warm, 21.1ºC, the divers reported that within 0.5 meter of the lake bottom there was a sharp transition in water temperature to 12.8ºC as shown on a dive watch (Shull 1999).

The diver collected the sediment core by gently pushing the corer in, capping the top, and then digging under the bottom to put on the bottom cap. The diver reported that there was additional peat below that which the core intercepted (Shull 1999). The core was brought to the surface, maintained in an upright position, measured, placed in a bucket, and surrounded with ice. A second core was collected in an identical manner at that time as well from an area close to the initial core. The sectioning and processing of the sediment cores is described in Chapter 2.

A 1-cm layer of water overlying the sediment was collected in 0.5-cm sections capturing the unconsolidated sediments above the sediment/water interface. Sediment layers were then collected in 5 mm horizontal intervals. A Munsell Soil Color Chart was used to characterize the colors of the sections described below (Macbeth 1994) and the presentation is in the form of "(hue, value/chroma)." The sectioning and character of the sediment core will be described from the top of the sediment core to the bottom.

From the surface down to 7.5 cm the sediments were black (gley, 2.5/N) and devoid of structure or organisms. The sediments were loosely consolidated at the surface, and became more consolidated with depth. From the surface to 3 cm the sediments had an anaerobic smell but below 3 cm the anaerobic smell gave way to an earthy smell. This stratum, from the surface to 7.5 cm depth, was termed "Muck."

The stratum from 7.5 cm to 19.8 cm was black to dark brown (7.5YR, 2.5/1-2), with many small, fiberous roots, hence it was termed the "Root" stratum. Beginning at 15 cm a number of small, 2-3 cm diameter gray (gley, 6/5G), clay-like balls were found that persisted until 17.8 cm. The numerous roots indicate that at the time of deposition of these intervals, the deepest part of Echo Lake was dominated by rooted vegetation. Figure 3.2 is a photo of typical sediments in the Root stratum.

Figure 3.2. Echo Lake sediments in the root stratum.

The Terrestrial stratum was beneath the Root Zone, from 19.8 cm to 23.8 cm depth, and contained leaves, twigs, and grasses mixed with the sediment. This material was deposited when the surrounding area was used as a hayfield in the mid-1800's (Bowker 2005). The top of this section would appear to have been deposited in 1882 when the first of two water supply dams were built, trapping sediments that contained the terrestrial debris.

The Peat stratum contained the lower-most sediment. Peat grows above water and therefore formed before the area was dammed. The diver reported that substantial peat underlay the core when he dug through it to place the bottom cap. The presence of a thick layer of peat indicates that before becoming a lake, this area may have been a wetland since the glaciers retreated 13,000 years ago. The upper layers of the peat held considerable amounts of sediment within the peat matrix which diminished with depth in the core. The total length of the sectioned core was 43 cm; however, sectioning stopped at 35.7 cm when the peat matrix dominated and little sediment was evident.

3.4 Results

The concentrations of Al, Fe, Mn, Pb, As, Cd, Cu, Zn, Co, Cr, Sn, Ag, Sr, Sc, Hg, and TOC, as well as the absolute date of sediment deposition, were determined for each of the 5mm intervals of the sediment core. The dates assigned to each of the intervals extend from the sediment/water interface at 1999 to the bottom of the sediment core 35.7 cm, approximately 1754. The methods and materials used in the analysis of this sediment core are documented in Chapter 2. The results and quality assurance and quality control are in Appendix I for TOC, Appendix II for metals, and Appendix III for geochronology. The stratigraphy and assigned dates of deposition are shown on Table III-2 in Appendix III.

Figures 3.3 through 3.6 superimpose the strata comprising the sediment core along-side the concentration profiles and the year of deposition to better relate the sediment concentration to the environmental conditions during the deposition of that sediment. The strata present in the sediment core reflect the history of Echo Lake: first as a wetland (Peat) until 1850's, then as a field (Terrestrial) until 1882, and lastly as a lake (Roots and then Muck). The thickness of each stratum shown in the figures is relative to the date of deposition and not their actual thickness. An unconformity, labeled as a "Disturbed" stratum is shown within the sediment column. This stratum represents an erosion event or a period of slow deposition and is discussed in Appendix III.

Within the lake sediments, the Disturbed stratum divides the Root stratum into two units: an “Upper Root” stratum that was deposited from 1969 to 1983, and a “Lower Root” stratum deposited from 1882 to 1919. During processing of the core there was no visual indication of the Disturbed stratum. The Disturbed stratum was discovered through radionuclide dating and, as discussed in Appendix III, was perhaps the result of bioturbation, erosion, or depositional shading. Although it represents only 2 cm of sediments, the Disturbed stratum spans 48 years of deposition, from 1920 to 1968. Within the Disturbed stratum the concentrations are accurate but the dates of deposition are not believed to be accurate.

Below the Disturbed stratum, the accuracy of the dates derived from the radiometric dating model, the CF:CS model, was adjusted to account for the Disturbed stratum. The assumptions inherent in adjusting the CF:CS model prevented assigning uncertainty, but the modeled dates from 1919 to the bottom of the sediment core are believed to be accurate. The adjusted CF:CS model accurately dates the change in strata from terrestrial sediments to lake sediments when the dam was built in 1882. The CF:CS model was extended to portions of the core that pre-date 1882, based on the assumption that the depositional rate determined in the sediments between 1919 and 1882 did not change radically.

Figure 3.3 displays the concentration trends for Al, Sc, Sr, and Co. These metals have been used for determining the crustal contribution of metals due to erosion from native soils and rock (Feng et al. 2004). Figure 3.4 displays the concentration trends for Fe, Mn, Cr and TOC. These metals and TOC provide insight into the redox environment of the sediments (Lovley 1991; Stumm and Morgan 1996). Figure 3.5 displays the concentration trends of Hg, Pb, As and Cd. These metals have wide-spread anthropogenic uses and are most commonly associated with toxic effects in aquatic environments (Stumm and Morgan 1996). Figure 3.6 displays the concentration trends of Cu, Zn, Sn and Ag. These metals are also commonly used in many anthropogenic materials (Davis et al. 2001). Despite their common use, these metals may have toxic properties to aquatic life and affect the overall quality of sediments and surface waters (U.S. Environmental Protection Agency 1997).

Figure 3.3. Sediment concentration profiles of Al, Sr, Sc and Co.

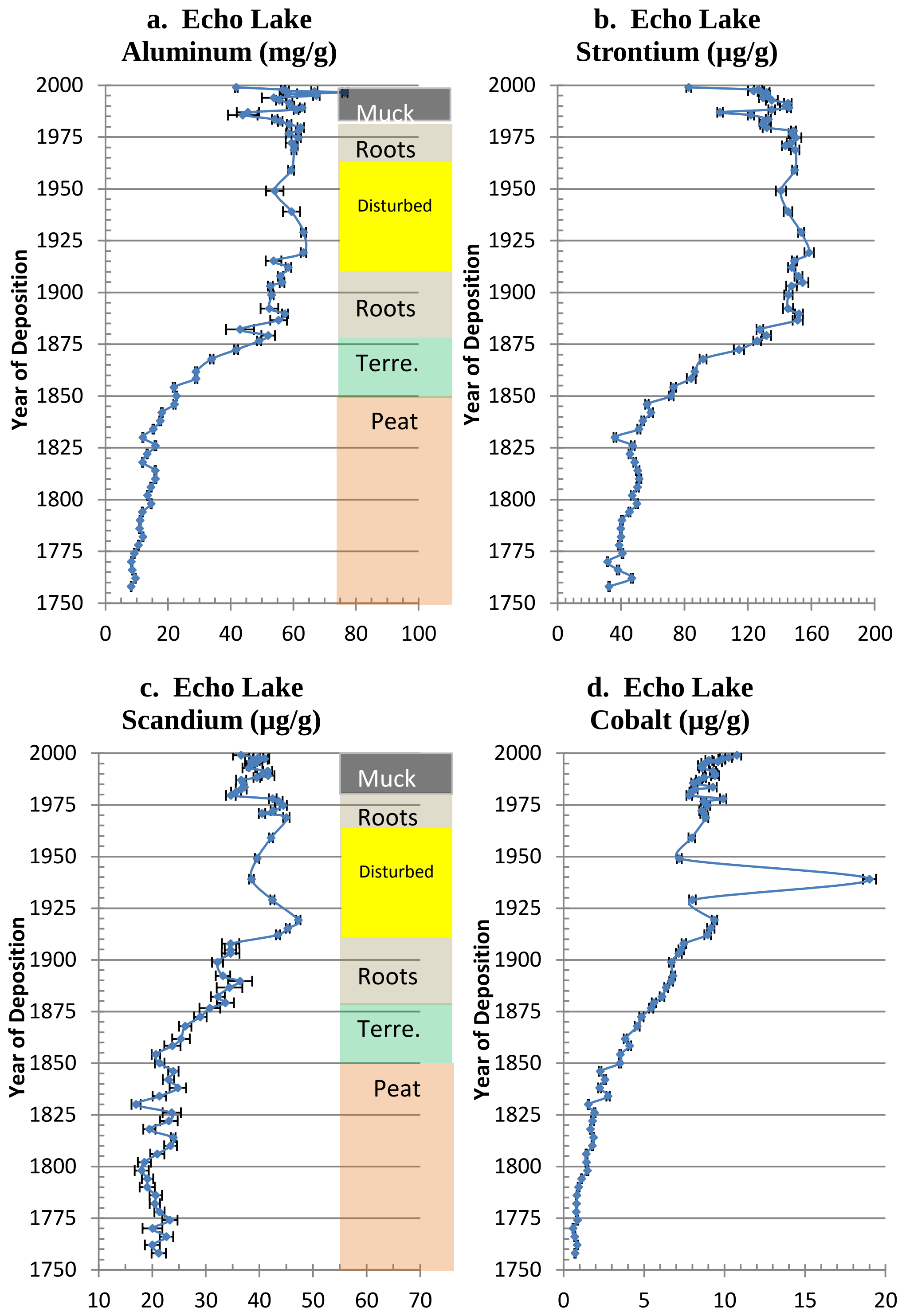
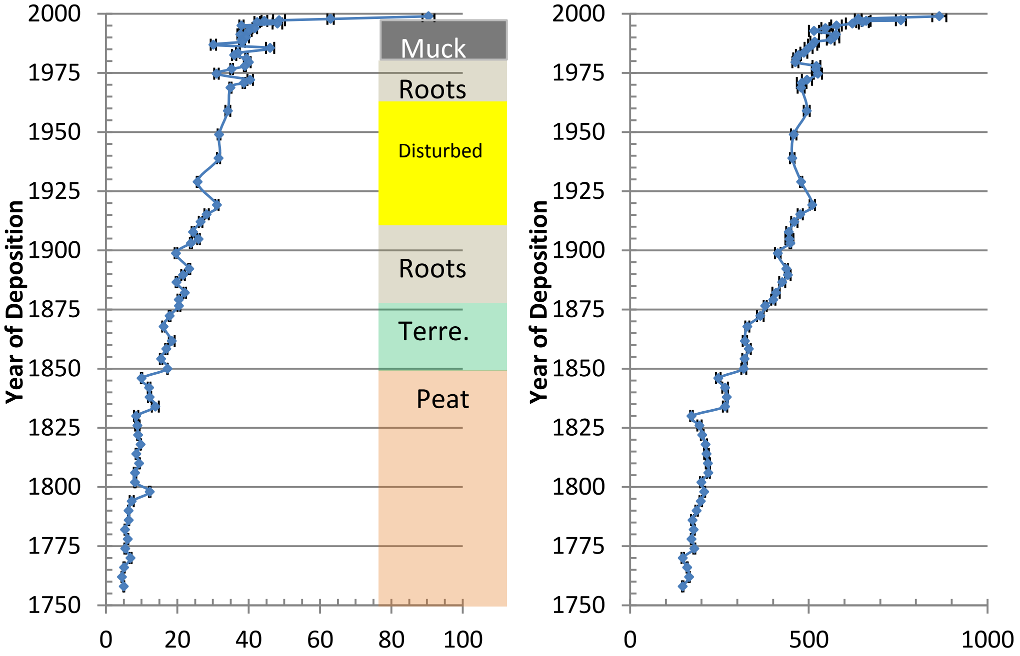
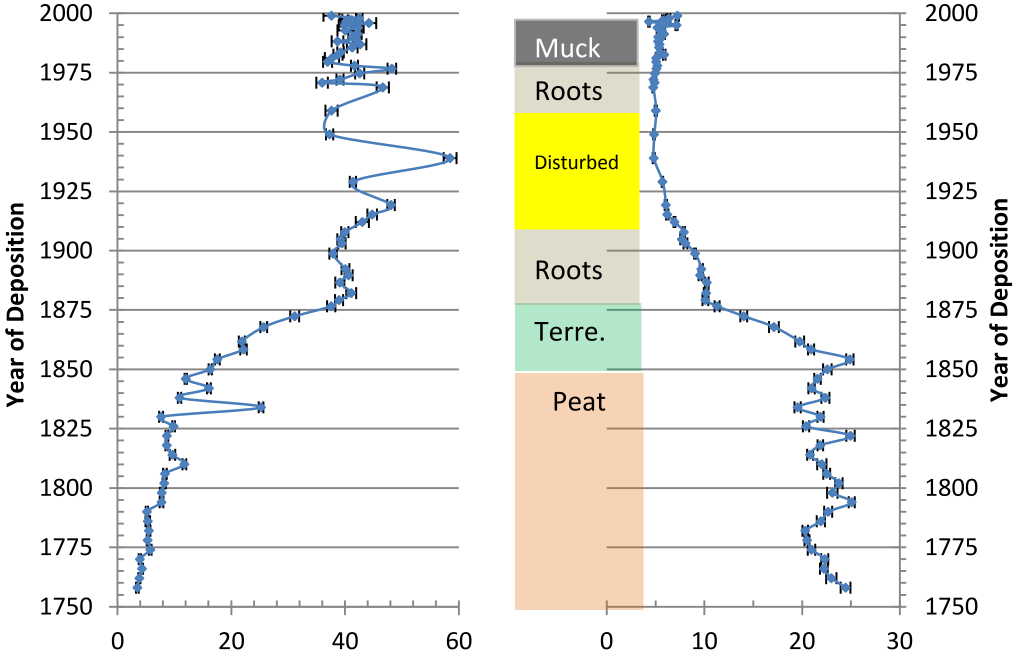


Figure 3.4. Sediment concentration profiles of Fe, Mn, Cr and TOC.


a. Echo Lake
Iron (mg/g)

b. Echo Lake
Manganese (µg/g)


c. Echo Lake
Chromium (µg/g)

d. Total Organic Carbon
(moles/kg)

Figure 3.5. Sediment concentration profiles of Hg, Pb, As, and Cd.

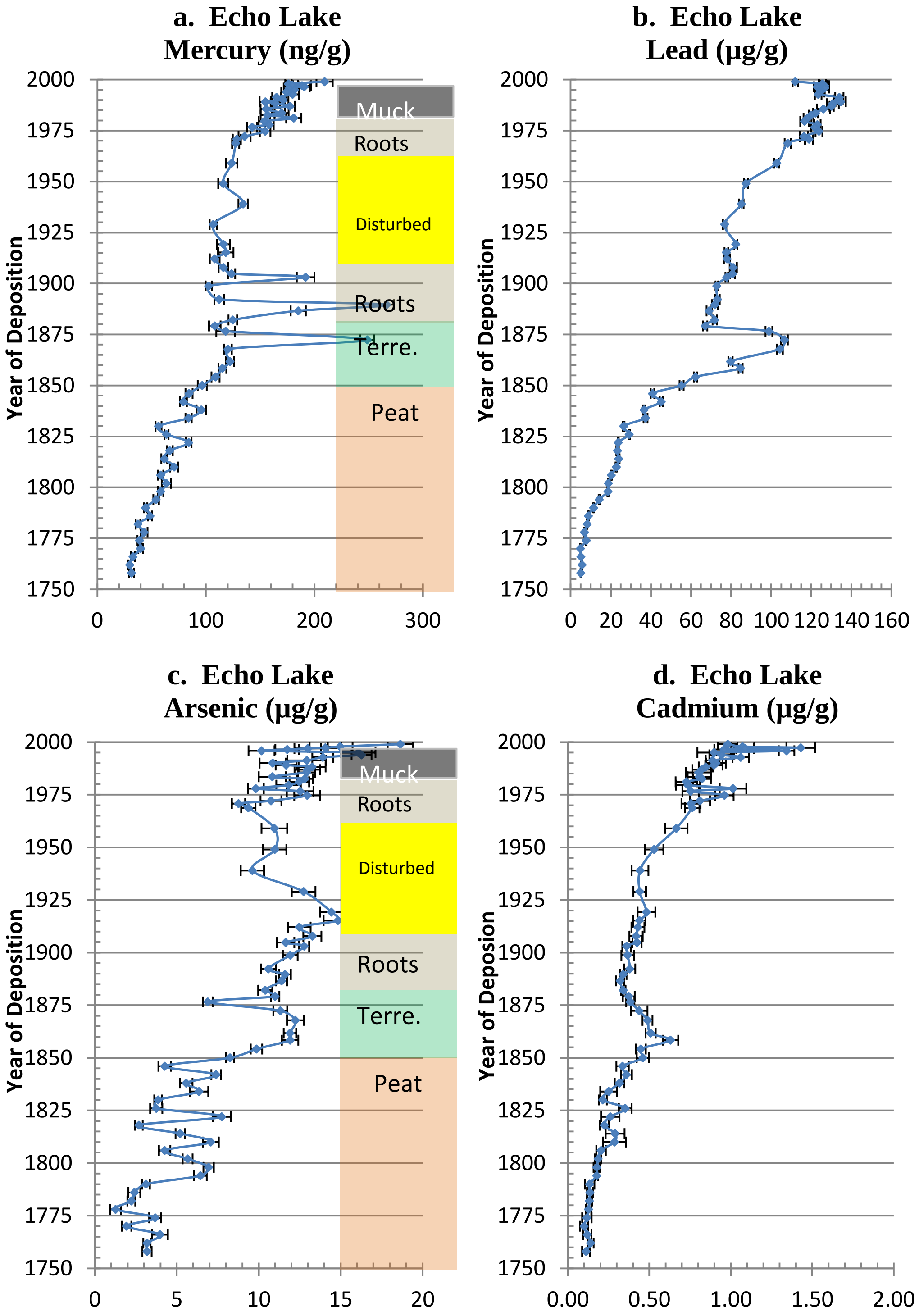
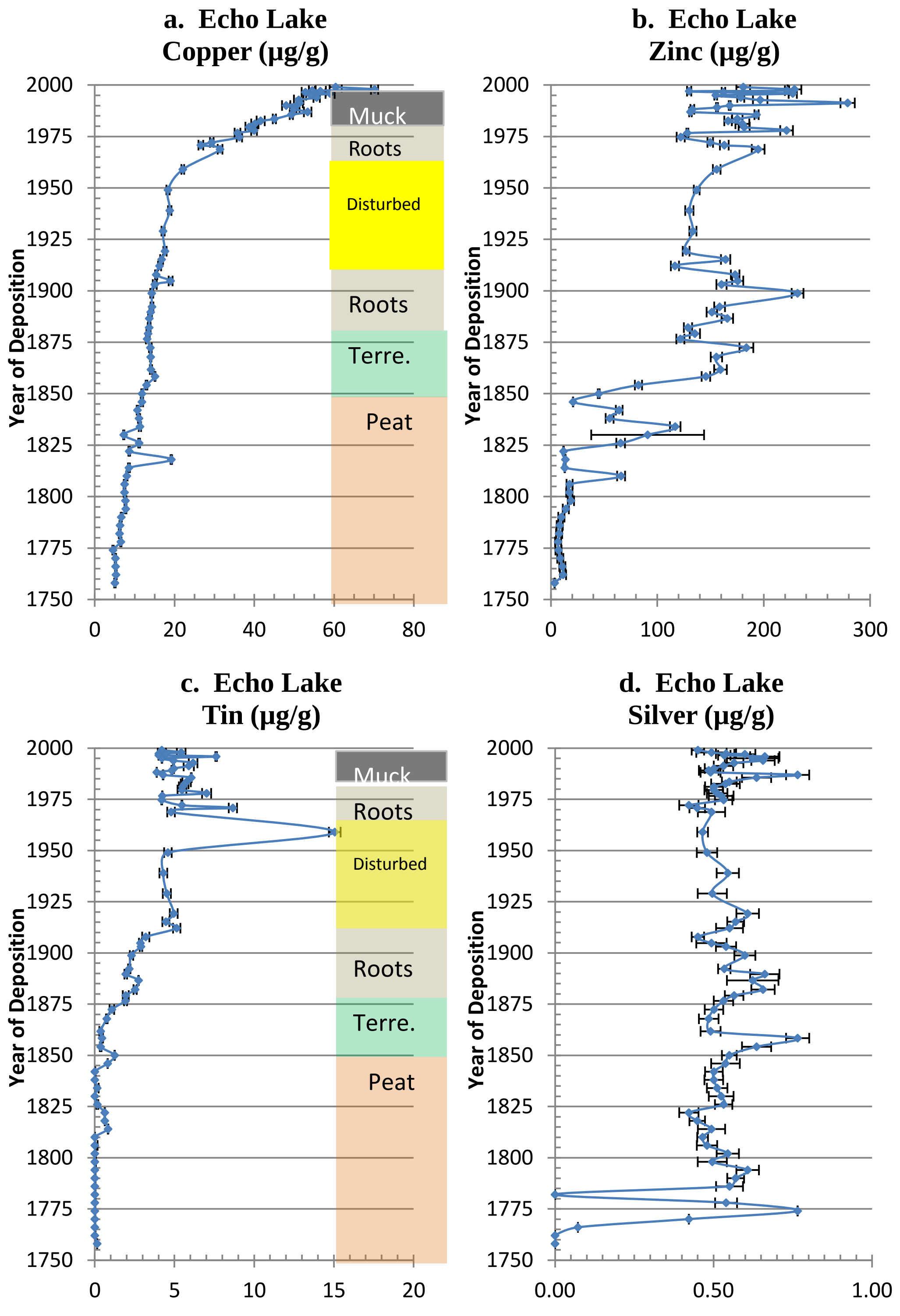


Figure 3.6. Sediment concentration profiles of Cu, Zn, Sn, and Ag.



a. Echo Lake Copper (µg/g)

b. Echo Lake Zinc (µg/g)

c. Echo Lake Tin (µg/g)

d. Echo Lake Silver (µg/g)

3.5 Discussion

The sediment concentration trends in Figures 3.3 through 3.6, with the exception of TOC, share a common character: low concentrations in the Peat stratum, increases in concentration through the Terrestrial stratum, and relatively consistent concentrations in the overlying lake sediments. This trend is due to the transition from atmospheric deposition in the Peat stratum to fluvial deposition, where runoff may contribute additional metals in the lake sediments.

The concentration profiles seen in lake sediments for Al, Sr, Sc, Co, Cr, As, Ag, Zn, and Sn are generally constant, with no consistent trends. This would indicate that there was no anthropogenic addition of these metals into the Echo Lake watershed. The concentration profiles for Hg, Pb, Cd, and Cu reveal anomalies at distinct intervals that may provide insight into land use changes that have occurred in the Echo Lake watershed.

Potential sources of metals to the Echo Lake watershed include atmospheric deposition from natural and industrial sources from the early 1800's to the present. Other, more local, sources of metals may include disturbances of the watershed such as when the railroad line was completed from Milford to Hopkinton in 1872, when the Echo Lake dam was built in 1882, and when the height of the dam was increased in 1902. After 1902 little activity occurred in the area until a pipe was installed in the bottom of the dam in 1968. In 1970 residential subdivision in the watershed began and the road network serving those homes began to expand.

The potential sources of anthropogenic metals from atmospheric fallout include coal-fired electrical power generators in the mid-west U.S. and industries in and near the City of Worcester and Millbury, Massachusetts (Wallace et al. 2004). Worcester, 25 km west of Echo Lake, is noted as having a significant steel manufacturing capability, glass works, munitions manufacture, and many milling and casting operations beginning early in the19th century (Stone 1930). Located 21 km west of Echo Lake in Millbury, Massachusetts is a waste-to-energy facility that has operated since 1987, incinerating up to 1.3×10^6 kg of residential and commercial wastes each day (Massachusetts Department of Environmental Protection 2011). Industrial emissions and incineration of residential and commercial wastes can be a significant source of many metals including Pb, Cd and Hg to the atmosphere (Golomb et al. 1997; Chillrud et al. 1999).

To address the questions posed in Section 3.1, based on an examination of the results shown in Figures 3.3 through 3.6, the examination of the sediment metal concentration profiles is divided into four sections:

1. The background conditions that existed before anthropogenic alteration in the watershed.
2. The anomalies found in the concentration profiles in Hg and Pb that occur before 1970.
3. The trends and anomalies observed for Hg, Pb, Cd, As, and Cu after residential subdivision begins in 1970.
4. The potential effects that the concentrations and trends for Hg, Pb, Cd, As and Cu may have on aquatic life and human health.

3.5.1 The Background Contribution of Metals to Sediment in Echo Lake

The contribution of background metals, the portion that results from weathering of native rocks and soils in the watershed and from atmospheric fallout, must be determined to ascertain the contribution of metals from other sources. Because the Echo Lake watershed had few disturbances before 1969, and those after 1969 were from a singular source, residential development, it was selected as the background sampling location.

In this research two background concentration values were developed: atmospheric fallout due only to natural conditions before industrial development, and the contribution of metals to lake sediments after 1882 and before 1919. The natural background concentrations of metals due to atmospheric fallout were determined by examining sediments that were dated to be deposited during the period 1762 to 1782 before industrial expansion in New England. The background conditions between 1882 and 1919 provide a baseline of concentrations when industry was active in New England but before residential development (Stone 1930; Cronon 1983).

The ideal method to determine background concentrations would be to examine the concentration of metals in sediments that pre-date anthropogenic alteration. This method is flawed for Echo Lake because prior to 1831, Echo Lake was a peat bog that had existed perhaps since the end of the last North American glacial period. The deposition of metals in a peat bog is different from a lake (Stumm and Morgan 1996; MacKenzie et al. 1998). Peat bogs lack the fluvial contribution, homogenization, and aerobic environment found in lakes (MacKenzie et al. 1998; Kalff 2002). The reducing conditions in peat bogs, created by the abundant organic matter, cause Fe, Mn and many of the trace metals to become soluble, whereas Hg, Pb, Cd, As and Sn have significant tendencies to bind with sulfur (-SH) and nitrogen (-NH) groups common in organic matter and peat (Stumm and Morgan 1996). The result is that peat deposits provide a record of the atmospheric contribution of Hg, Pb, Cd, As, and Sn but that the record of other metals may be unreliable (MacKenzie et al. 1998). Table 3.1 shows the average concentration and deposition rate of Hg, Pb, Cd, As and Sn for sediments estimated to have been deposited during the period 1762 to 1782 when the future coring location was a peat bog and atmospheric fallout from industry was either minimal or non-existent.

Table 3.1. Average sediment concentration and deposition rates for Hg, Pb, Cd, As, and Sn from natural atmospheric sources to the sediments in Echo Lake.

	Average Sediment Concentration Echo Lake 1762 – 1782	**Average Deposition Rate (g m^{-2} yr^{-1})**
Hg	37.1 ± 4.8 ng/g	4.9 x 10^{-6}
Pb	6.4 ± 1.4 µg/g	8.3 x10^{-4}
As	2.7 ± 1.1 µg/g	3.4 x10^{-4}
Cd	0.12 ± 0.01 µg/g	1.6 x10^{-5}
Sn	0.15 ± 0.04 µg/g	2.0 x10^{-5}

Both the average sediment concentration and average deposition rate for each metal are provided to enable comparison with other research. Research that did not obtain the dates of deposition cannot develop deposition rates. Deposition rates are derived from concentrations and the overall delivery of sediment by multiplying the concentration of each metal by the mass of sediment in a unit area and then dividing by the number of years each interval represents.

The values in Table 3.1 represent the contribution of volcanic emissions and aeolian erosion to Echo Lake sediments. The natural atmospheric background Hg sediment concentration determined for Echo Lake in Table 3.1, 4.9 µg m^{-2} yr^{-1}, compares well to other research that found the historic atmospheric deposition of Hg in other New England lakes before 1850 ranged from 5 to 17 µg m^{-2} yr^{-1} (Kamman and Engstrom 2002). The concentration of Pb in pre-industrial Echo Lake sediments shown in Table 3.1, 6.4 µg g^{-1}, agrees with concentrations of pre-industrial Pb in Canadian peat deposits which ranged from 0.3 to 52.5 µg g^{-1} (Kylander et al. 2009).

Once the dam was built in1882 and until 1919, the last sediment interval that was dated with confidence until 1969, there were no disturbances in the Echo Lake watershed likely to impact the concentration of metals (Bowker 2005). The sediments deposited after 1882 were formed in a reservoir. These sediments record the contribution of the natural materials of the watershed and atmospheric fallout from the growing industries in the area (Stone 1930; Kalff 2002). Table 3.2 provides average concentrations for each metal in each stratum as shown in Figures 3.3 through 3.6. The background contributions of metals from natural sources and industrial atmospheric fallout during the period 1882 to 1919 are shown in the row listed as “Lower Root.”

Table 3.2. Average sediment concentration for each metal in each stratum.

Strata / units	Al mg/g	Sr ug/g	Sc ug/g	Co ug/g	Fe mg/g	Mn ug/g	Cr ug/g	Cu ug/g	Ag ug/g	Zn ug/g	Hg ng/g	Pb ug/g	As ug/g	Cd ug/g	Sn ug/g	Date of top
Muck	59	131	39	9.2	42	580	41	53	0.58	182	174	127	13.0	0.98	5.10	1999
Upper Root	60	142	41	8.6	37	491	41	36	0.50	168	149	119	11.3	0.82	5.66	1983
Disturbed	59	147	41	7.73	31	472	44	19	0.50	139	120	88	11.1	0.52	4.47	1968
Lower Root	55	148	37	7.5	24	447	41	15	0.57	159	115	76	12.3	0.39	3.20	1919
Terrestrial	35	97	26	4.4	18	346	26	14	0.57	129	130	82	10.4	0.47	1.02	1879
Peat	13	45	21	1.4	8	200	8	8	0.43	29	58	19	4.4	0.21	0.15	1846
Crustal Average	82	320	14	17	39	775	92	28	0.053	67	50	17	5	0.09	2.1	

Table 3.2 also provides three useful comparisons. First, it allows a comparison of each stratum to average crustal concentrations in the literature. Table 3.2 allows a comparison of the two depositional environments: the wetland peat and the lake sediments. Lastly, it is an indication of metals with anomalous increases above natural concentrations indicated by the Lower Root stratum and the crustal averages. These comparisons were more easily explored by dividing the metals in this research into two broad groups based on their geochemical behavior and how they move through a watershed. These groups are the lithophiles and atmophiles (Stumm and Morgan 1996).

The lithophiles move through a watershed primarily by transport in streams in particulate or dissolved form. The lithophile metals examined in this research include: Al, Fe, Mn, Sr, Sc, Co, Cr, Cu, Zn, and Ag. In the Echo Lake watershed these metals are largely derived from the glacial till and the Milford Granite that make up the underlying geologic materials. As shown in Table 3.2, Al, Sr, Sc, Co, and Cr have relatively constant, average concentrations in Echo Lake sediments, which represent background concentrations, from 1882 until the core was collected in 1999. But several other lithophile metals, Fe, Mn, Ag, Cu and Zn do not share that character and have different concentration profiles that indicate changes in deposition or chemistry.

Fe and Mn have concentrations that gradually increase in younger sediments with little variation as shown in Figures 3.4a and 3.4b. Both Fe and Mn are sensitive to redoximorphic reactions that occur in sediments (Lovley 1991). These redox reactions cause particulate and mineral forms of Fe and Mn to become soluble and move within the sediment column, re-precipitating in aerobic environments typically at the sediment/water interface as hydroxides (Stumm and Morgan 1996). The preponderance of organic matter, especially in the peat, and the presence of a thermocline at the time of the collection of the Echo Lake sediment core, indicate that such redox reactions are likely.

The potential for re-mobilization of Fe and Mn is reinforced by the observation that the sediments in the upper 9 cm of the sediment core changed from a black color to a brick-red color 24 hours after collection and exposure to the air. The reaction that occurred was either dissolved Fe^{2+} in pore water, or iron sulfide species in the sediments, or both, oxidizing after exposure to air during processing and drying of the sediment core. The concentration profiles for Fe and Mn in Figures 3.4a and 3.4b are perhaps an expression of the re-distribution of Fe and Mn due to redox reactions and not diagnostic of deposition due to historic water quality.

Based on the concentration profiles in Figures 3.3 through 3.6, the redistribution of other metals did not likely occur. The Echo Lake sediments are typical of many freshwater environments where the sediments have an upper layer, generally less than 1 cm thick, that is aerobic and underlain by an anaerobic layer where respiration takes the form of sulfate reduction and methanogenesis (Boudreau and Jorgensen 2001). Sulfate reduction leads to the formation of stable metal sulfide complexes and the order of stability is generally: Hg>>Cu>Pb>Cd>Zn>Ni, which are more stable than Fe and Mn sulfide complexes (Stumm and Morgan 1996). Other research performed in Echo Lake found that the majority of the metals in sediments were bound as sulfides (U.S. Environmental Protection Agency 1997). The preservation of anomalous concentration peaks for Hg and Pb indicate that the metal phases associated with sulfides, other than Fe and Mn, are stable and the concentrations are representative of when that sediment was deposited.

A comparison of the Ag concentrations to the crustal average from the literature found that the Echo Lake concentration is more than 10 times that average. This anomaly persists throughout the entire sediment core. The consistent concentration of Ag shown in Figure 3.6d indicates that natural mineralization is a possible source.

The Milford Granite, which underlies the entire Echo Lake watershed, is listed as "…granite to granodiorite…" throughout its range, but zones of pegmatite and other mineralization were also found to exist (Zen 1983). In1881 there was an attempt to mine gold in the area southwest of Echo Lake which proved uneconomic. Topographic maps of North Milford note a "Silver Mine Hill" and a road up the hill as "Silver Mine Hill Road" (U.S. Geological Survey 1895). No information has been found regarding the type of deposit that the gold works was trying to exploit. These associations indicate that the above-average concentration of Ag may be the result of a low-grade ore deposit of Ag.

Atmophiles move through the atmosphere as particulates, aerosols, and methylated forms (Stumm and Morgan 1996). Atmophiles enter the atmosphere via natural processes such as volcanic emissions as well as industrial discharges to the atmosphere. The lithophiles are also capable of transport as atmospheric particulates, but the distances are typically much shorter than that of atmophiles (Stumm and Morgan 1996). The atmophile metals examined in this research include: Hg, Cd, Pb, As, and Sn.

Because there are no industrial sources in the Echo Lake watershed, atmospheric fallout of anthropogenic metals such as Hg, Pb, As, Cd and Sn was a regional effect that should be present throughout the Charles River watershed. Therefore, the sediment concentrations in the Lower Root stratum should provide the background concentrations and average deposition rate for each of the metals during the period from 1882 to 1919 due to the geology and regional atmospheric fallout. Table 3.3 takes the average values provided for the Lower Root stratum and develops an average deposition rate.

Table 3.3: Average background concentrations and deposition rates for metals in Echo Lake sediments from 1882 to 1919.

	1882 to 1919	
	Background Concentration	**Average Deposition Rate in Echo Lake ($g/m^2/yr$)**
Al	55 ± 5 mg/g	9.8 ± 3.3
Sr	148 ± 8 µg/g	0.026 ± 0.008
Sc	37 ± 5.5 µg/g	$6.8 \times 10^{-3} \pm 2.9 \times 10^{-3}$
Co	7.5 ± 1.2 µg/g	$1.4 \times 10^{-3} \pm 6.0 \times 10^{-4}$
Cr	41 ± 3 µg/g	$7.4 \times 10^{-3} \pm 2.5 \times 10^{-3}$
Cu	15 ± 1.8 µg/g	$2.8 \times 10^{-3} \pm 9.8 \times 10^{-4}$
Ag	0.57 ± 0.07 µg/g	$1.0 \times 10^{-4} \pm 2.7 \times 10^{-5}$
Zn	159 ± 31 µg/g	$2.8 \times 10^{-2} \pm 6.6 \times 10^{-3}$
Pb	76 ± 4.5 µg/g	$1.4 \times 10^{-2} \pm 4.4 \times 10^{-3}$
As	12.3 ± 1.4 µg/g	$2.2 \times 10^{-3} \pm 8.5 \times 10^{-3}$
Hg	115 ± 7 ng/g	$2.2 \times 10^{-5} \pm 6.4 \times 10^{-5}$
Cd	0.39 ± 0.05 µg/g	$7.1 \times 10^{-5} \pm 2.8 \times 10^{-5}$
Sn	3.2 ± 1.1 µg/g	$6.1 \times 10^{-4} \pm 3.8 \times 10^{-4}$

Deposition rates in Table 3.3 are corrected for sediment focusing by dividing actual deposition rates by 2, based on the observed inventories of ^{210}Pb as discussed in Appendix III. Sediment focusing is the movement of sediment to deeper locations in a water body, thereby increasing the apparent rate of sedimentation (Davis and Ford (Jesse) 1982).

Two background values for metals in Echo Lake sediment were developed in Tables 3.1 and 3.3. Table 3.1 represents the concentrations and deposition rates for Hg, Pb, As, Cd and Sn from natural, atmospheric sources prior to industrialization. Table 3.2 provides a comparison of average concentrations for each stratum to determine if anomalies are present for any of the metals. Table 3.3 presents the background concentrations for metals in sediments deposited prior to residential subdivision but after industrialization in the region and therefore were affected by the anthropogenic, atmospheric fallout.

3.5.2 Mercury and Lead Concentrations in Sediment before 1970

The profiles in Figures 3.3 through 3.6 in sediments deposited after 1882 but before 1970 are generally constant in concentration, hence their use as background values in the preceding section. The exceptions to constant concentration in this period are the Hg and Pb concentration profiles which display significant peaks in concentration at discrete intervals in the sediment column. Hg provided three narrow peaks in the late 19th and early 20th centuries, while Pb had a broad peak that began in 1860 and ended before lake sediments were deposited in 1882.

Because there was no industry or other land use in the watershed that would have created these peaks, the source must be anthropogenic atmospheric discharges. Coal has been determined to be a significant source of Hg, Pb and several other metals to the atmosphere (Szpunar 1992; Stumm and Morgan 1996). The industrial revolution in the late 19th century used coal as a primary fuel as did railway transport in eastern Massachusetts (Sanborn Map Co. October 1910).

The Hg concentration profile in Figure 3.5a shows a steady sediment concentration, with the exception of three narrow peaks, each spanning 5 to 7 years. The geochronology dates these three peaks as 1872, 1887 to 1889, and 1903. These dates correspond to when the railway tracks from Milford to Hopkinton, Massachusetts were laid 70 m east of Echo Lake in 1872, when the first dam was built in 1882, and when the existing dam was enlarged in 1902 (Milford Historical Commission 2004). For each of these projects, the number of rail trips by coal-fired locomotives would have increased tremendously to deliver men and materials to the work areas. The coincidence of these activities and deposition times indicate that the likely source of the three Hg peaks in Figure 3.5a is the result of local burning of coal in locomotives.

Figure 3.5b shows a broad peak of Pb that began in 1861, increased through 1872 and then decreased rapidly beginning in 1877. This peak period encompassed the American Civil War and ends with the close of the Indian Wars in the western United States beginning in 1880. Worcester, Massachusetts was a significant munitions manufacturer and because Pb was the principle component of the projectiles at that time, that activity may have served as the source of this peak of concentration (Stone 1930). After 1880, the concentrations of Pb slowly increase through 1919.

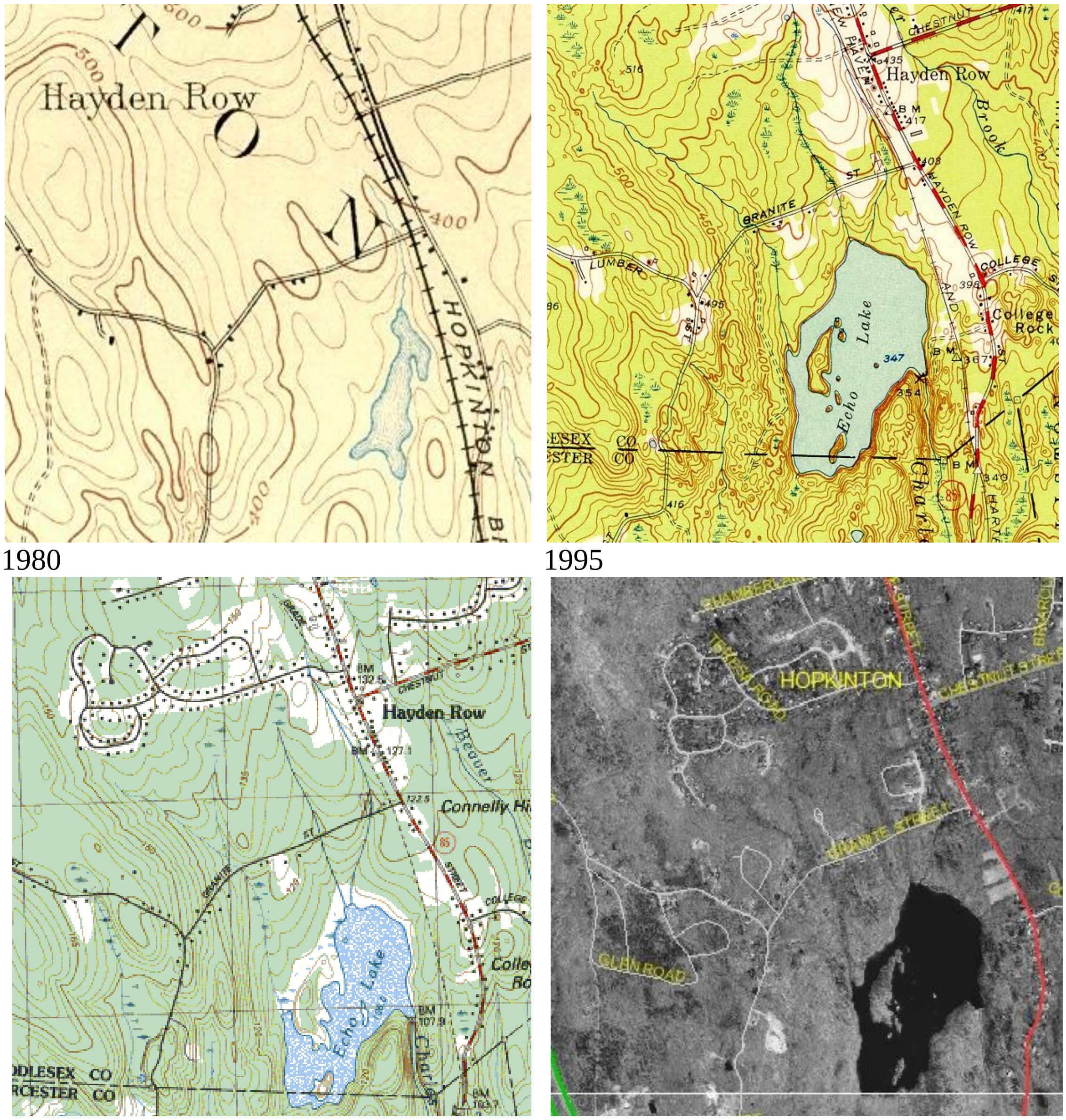
Leaded gasoline was introduced in automobiles during the 1920’s to increase octane and lubricate automobile engine parts (Radford University). The concentrations shown for the years 1929 to 1959 show an increasing trend, but because this period of deposition may have been disturbed, it is unlikely that the dates of deposition are accurate.

The conclusion is that the increases in Hg and Pb concentration are the result of atmospheric fallout. The discreet increases in Hg concentration are due to emissions from locomotives near the lake during periods of construction. The broad increase in Pb concentrations from the 1860s until the 1880s is due to atmospheric fallout from munitions manufacturing in Worcester. After 1900 automobiles become an increasing source of Pb to Echo Lake sediments. The average concentrations and deposition rates for Hg and Pb, with two of the three Hg peaks removed, were shown in Table 3.3. The first Hg peak in 1872 pre-dated lake sediments and did not need to be subtracted.

3.5.3 The Supply of Metals to Echo Lake Sediment after 1970

The greatest physical change to the Echo Lake watershed, other than the creation of the lake in 1882, was the expansion of residential areas beginning in 1970. Before 1970, the Echo Lake watershed held 16 or fewer homes and it was crossed by only three main roads that covered a total of 3.7 kilometers. When the sediment core was collected 29 years later there were 240 homes and nearly 12 km of roads. Assuming an average road width of 9 m, paved surfaces covered approximately 3.3 ha prior to 1970 and 10.3 ha in 1999. The scope and timing of residential land use, compared with the sediment metal concentration profiles offers insight into contributions of various sources and the effects of the buffer zone maintained by the Milford Water Supply Company around Echo Lake. Figure 3.7 shows the extent of land use in the Echo Lake watershed in 1886, 1953, 1980, and 1995, respectively. Each map or photo in Figure 3.7 shows the Echo Lake watershed with some minor portions of the adjoining watersheds.

Figure 3.7. Echo Lake, the majority of its watershed, and the extent of residential land use for 1886, 1953, 1980 and 1995. Each map or photo is approximately 2.5 km on a side. The year of the map or photo is shown on the upper left side of each map.


1886

1953

1980

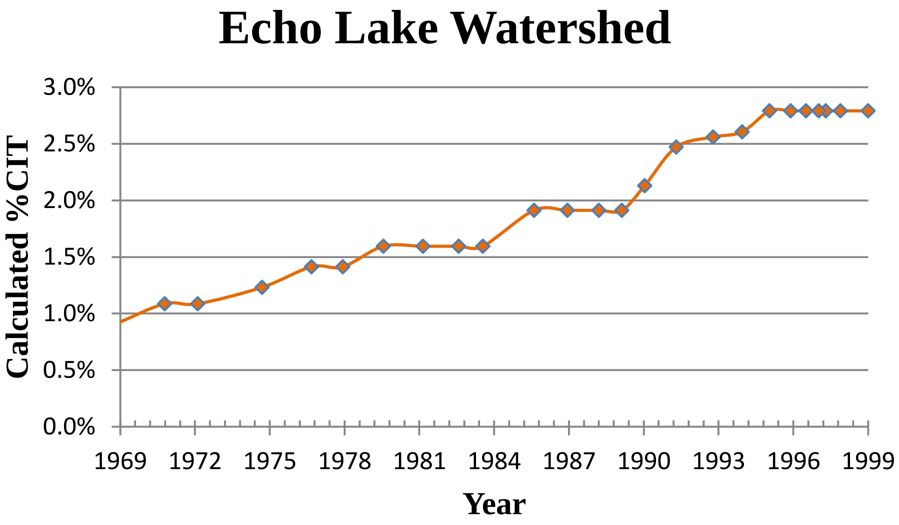
1995

The 1886 map shows a much smaller Echo Lake behind the original, six-meter high dam built in 1882. In 1902 the original dam was replaced by a ten-meter high dam in the same location which enlarged the lake to the extent seen in the 1953 map.

Residential land use increased from 16 homes in the watershed in 1968 to 240 when the sediment core was collected. During that period the length of roads increased from approximately 3,700 m in 1968 to 11,500 m in 1999. The number of homes and road lengths were estimated from the building permits issued each year in the Echo Lake watershed (Hopkinton Planning Department 2004). Recent research has used the percentage of Commercial, Industrial and Transportation network (%CIT) as a measure of urbanization and impervious surface coverage (Chalmers et al. 2007). This is also a frequently collected demographic statistic for communities (Commonwealth of Massachusetts 2012). For comparison to downstream locations, the above estimates of homes and road length were used to construct a similar statistic for the period of interest, 1970 to 1999, in the Echo Lake watershed.

For the Echo Lake watershed there are no commercial or industrial activities. Therefore, the %CIT estimate was constructed by multiplying the road lengths at each interval by an assumed width of 9 m. The resulting values resulted in a calculated %CIT of 0.9% in 1969 and 2.8% in 1999. These values compare favorably with other nearby communities with similar distributions (Commonwealth of Massachusetts 2012). For 1999, Hopkinton, Massachusetts, where the Echo Lake watershed lies, was listed as 5.2% CIT, but the Echo Lake watershed is more rural than the community in general. The trend of %CIT use developed for the Echo Lake watershed, based on building within the watershed, is shown in Figure 3.8 (Hopkinton Planning Department 2004).

Figure 3.8. Estimate of the amount of impervious surface created by the transportation network in the Echo Lake watershed, 1969 to 1999.



The increase in the calculated %CIT from 1970 to 1999 was only from 0.9% to 2.8%, respectively. But during this time the overall area altered for residential development expanded from approximately 5% to 39% of the watershed and the amount of road network had tripled (Dichter 2005). It was determined that the apparently small increase in %CIT in the Echo Lake watershed altered Echo Lake sediments both physically and chemically.

3.5.3.1. Changes in Physical Sedimentation in Echo Lake

The growth of residential land use impacts, as discussed in Chapter 1, impacts physical characteristics of a watershed. The primary alterations to hydrology cited included higher storm flows and lower base flows. Perennial streams become more intermittent and water temperatures rise in receiving water bodies. This translates into increased scour of stream channels and increased deposition in lakes (Dunne and Leopold

1978). Erosion from construction sites also contributes to sedimentation (Siver et al. 1996).

The alteration to the upland areas in the Echo Lake watershed is shown in Figure 3.7. Comparing the 1953 map to the 1980 map, it is apparent that the Charles River View subdivision in the northern portion of the watershed has altered substantial amounts of upland areas and filled wetland areas as well. Figure 3.8 shows the growth of this subdivision which began construction in 1970, expanded in 1975, and again in 1980. By 1980 there were 56 homes built or under construction in the Charles River View subdivision. Another 55 homes were added during the 1980's.

The increase in construction increased the amount of sediment delivered to Echo Lake. Figure 3.9 plots the deposition rate of sediment in the Echo Lake core by mass, the Mass Accumulation Rate (MAR), compared to the stratigraphy and year of deposition.

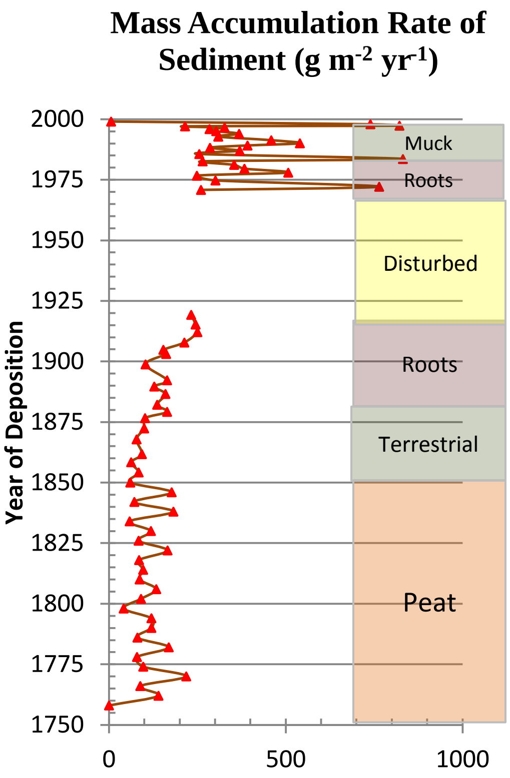
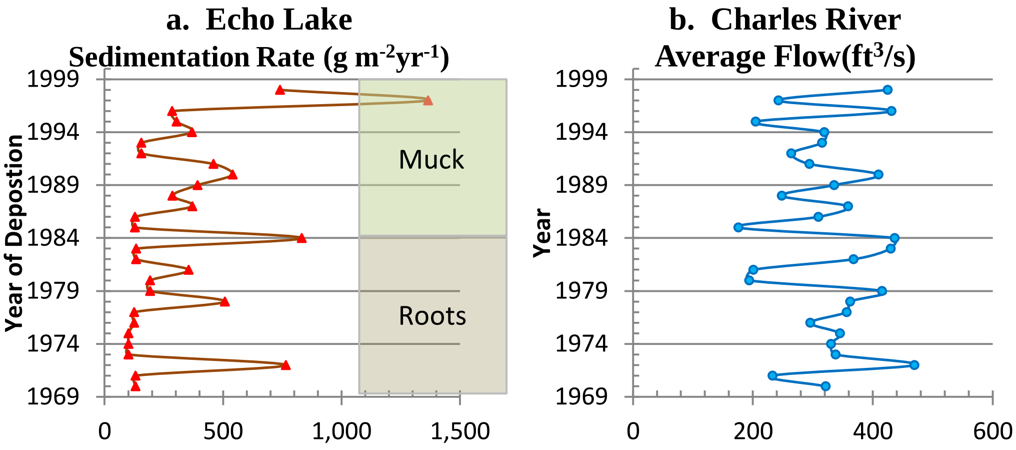


Figure 3.9. Sedimentation rate of Echo Lake, adjusted for sediment focusing.

Figure 3.9 shows the MAR at the coring location, corrected for sediment focusing. The MAR in Echo Lake increased from an average of 177 g m^{-2} yr^{-1} in sediments that pre-date 1919, to an average of 417 g m^{-2} yr^{-1} in sediment deposited after 1970. The variability increased in the post-1970 sediments as well, with three periods that exceeded 750 g m^{-2} yr^{-1}. The gap from 1919 until 1968 is the Disturbed stratum which was the result of either an erosion event in 1968 or a period with very low deposition. Those values were not plotted.

The variations shown in the MAR after 1970 displays a number of interesting anomalies. A regression of the %CIT developed in Figure 3.8 against the MAR found no agreement, R^2 = 0.02. Focusing on only the post-1970 period, Figure 3.10 plots the deposition rate for sediment from 1970 to 1998 (a), and the flow of the Charles River at the Dover, MA U.S. Geological Survey (USGS) gauging station (b).

Figure 3.10. Comparison of the Echo Lake sedimentation rate from 1970 to 1998 to the flow of the Charles River at the USGS gauging station in Dover, Massachusetts.



The average annual flow of the Charles River at the USGS gauging station in Dover, MA, 30 miles downstream of Echo Lake, was used in Figure 3.10b to approximate potential runoff in the Echo Lake watershed. Correlation of the sediment mass and Charles River flow also found little agreement, 0.02, but the peak sediment deposition years: 1972, 1978, 1984, and 1990, match the peak average annual flow in the Charles River in Figure 3.10 with the exception of 1997.

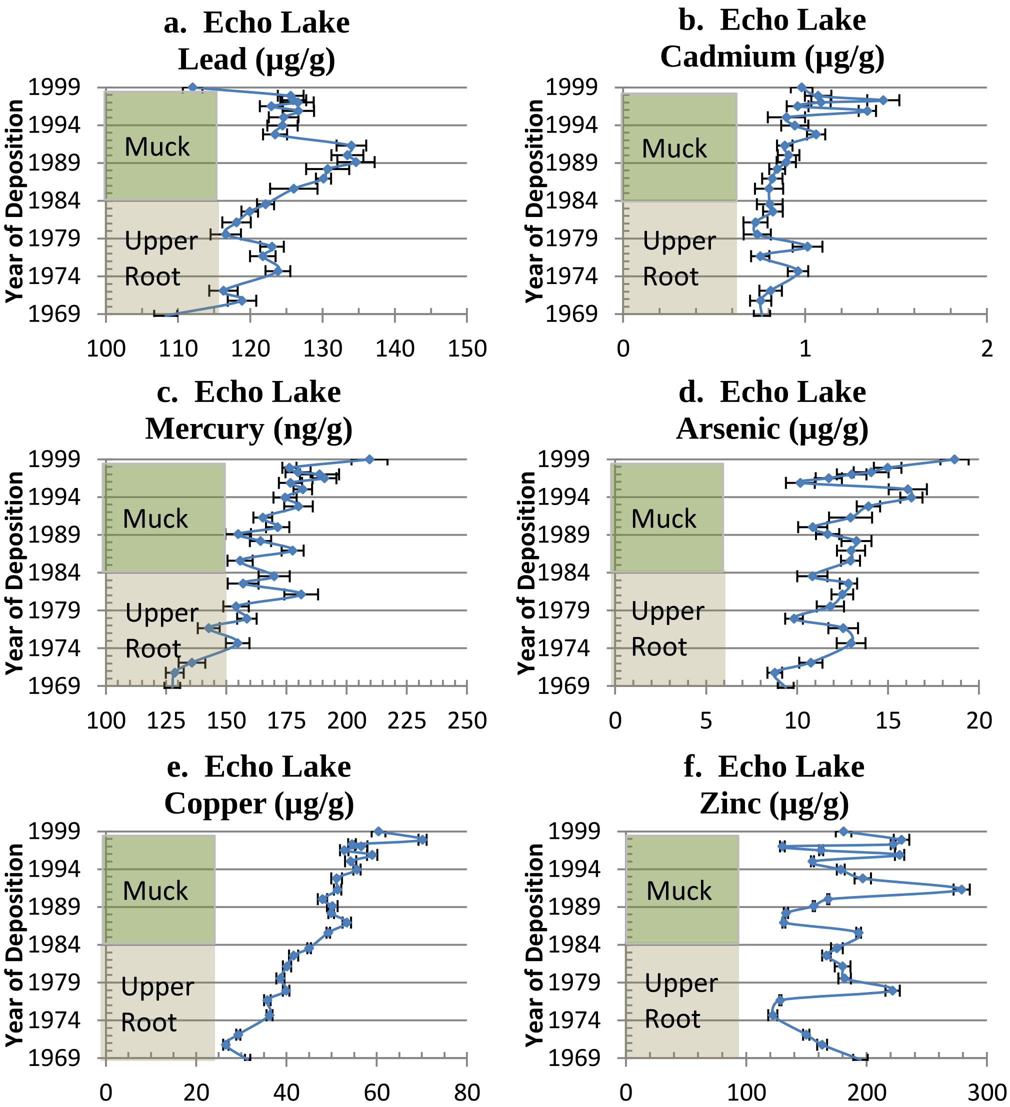
The agreement of peak deposition years with peak flows is a measure of the supply of easily eroded materials from construction sites. The step-wise changes in Figure 3.8 shows construction phases which would present the greatest potential for increases in sedimentation. The primary increases in %CIT and road length occur when residential construction occurs in 1971, 1975, 1980, 1984, 1990 and 1995 which correspond with the increases in MAR shown in Figure 3.10.a.

The sediment column shown in the concentration profiles, Figures 3.3 through 3.6, documents a profound change in Echo Lake itself. From 1882 to 1983 the bottom of Echo Lake was dominated by rooted, aquatic plants. In 1984 the rooted plants disappear and the deposited material transitions to an amorphous black sediment termed “Muck.” The deposition of Muck continued until the collection of the sediment core. The largest MAR occurred in 1984, nearly 1 kg m^{-2} yr^{-1} adjusted for focusing, more than 5 times the average deposition rate. The 1984 interval coincides with the extirpation of rooted vegetation in Echo Lake and a change in the character of deposited sediments to muck. It was also estimated that from 1983 to 1985 roadways increased from approximately 4200 m to 6000 m and the number of houses increased from 100 to 135 (Hopkinton Planning Department 2004).

3.5.3.2. Changes in Echo Lake Sediment Chemistry

The concentration profiles shown in Figures 3.3 and 3.4c show little variation in concentration in lake sediments from 1882 to 1999. This demonstrates that despite the large increase in MAR noted above, much of the increased sedimentation is due to erosion of native materials, either erosion from construction sites or scouring of the channels of the intermittent streams that drain to Echo Lake. After 1970 only Hg, Pb, As, Cd and Cu display increases in concentration in younger sediments. A closer inspection of these concentration profiles, focusing on the period after 1969, is provided in Figure 3.11.

Figure 3.11. Concentration profiles for: Pb, Cd, Hg, As, Cu, and Zn in Echo Lake sediments for the period from 1969 to 1999.



The metals Pb, Cd, Hg, As and Cu are frequently cited as common contaminants in storm water runoff from residential areas (National Oceanic and Atmospheric Administration 1999; Davis et al. 2001). Although these metals all increase in concentration in progressively younger sediments after 1969, there are unique characteristics among them that indicate possible sources and processes.

Pb, Hg, As, and Cd are atmophile metals. Sources of these metals can include natural and anthropogenic emissions to the atmosphere, as well as common building materials such as roofing, paint, and treated lumber, in residential areas (Davis et al. 2001). A linear regression of concentrations against both the number of homes and the length of roadway present in the watershed, represented by %CIT, had strong R^2 values for Hg (0.66) and Cd (0.49), but Pb had a weaker association ($R^2 = 0.25$).

The Pb concentration profile in Figure 3.11 a. is unique. After 1969, Pb concentrations rise until a peak is reached in 1991 and then concentrations decline in 1993. A primary source of Pb was atmospheric fallout from burning gasoline (Davis et al. 2001). Tetraethyl lead was a common additive to gasoline beginning in the 1920's, by the 1970's the largest use of Pb was in gasoline. Due to health concerns, the phase out of leaded gasoline began in 1975 when the first cars that used unleaded gas were produced (Radford University). In 1996, leaded gas use was banned and through that time, although leaded gas was available, gradually fewer cars were able to use it (U.S. Environmental Protection Agency 2011).

The Pb profile in Figure 3.11 a. parallels the characteristics of gasoline use after 1970. In 1979, an economic slump coupled with a disruption of the oil supply, greatly limited available gasoline, apparently causing a decline in concentration of Pb in sediments during that time (Schwenk 2001). With improving economic conditions through the 1980's gasoline use increased along with concentrations of Pb. These relationships helped determine the possible sources of the other atmophile metals.

To determine the contribution of each source the values for background developed in Tables 3.1 and 3.3 were examined with respect to the atmophile metal concentrations in the post-1970 sediments. In 1969, with only 16 homes in the watershed, it was assumed that there was minimal contribution of these metals from inside the watershed. Table 3.4 compares the concentrations and percentage increases over diagnostic horizons in the Echo Lake sediment core.

Table 3.4. Sediment concentrations of atmophile metals after 1969.

	Pb	**Hg**	**Cd**	**As**	**Sn**
Natural Background (µg/g)[a]	6	0.037	0.12	2.7	0.15
Industrial Background (µg/g)[b]	70	0.078	0.27	9.6	3.05
Concentration in 1969 (µg/g)	108	0.128	0.76	9.4	4.78
Increase of Concentrations from 1919 Background to 1969	54%	64%	181%	-2%	57%
Concentration in 1986 (µg/g)	126	0.156	0.80	12.9	6.5
Increase of Concentrations from 1969 to 1986	17%	22%	5%	37%	36%
Concentration in 1991 (µg/g)	134	0.165	0.89	12.9	5.9
Increase of Concentrations from 1986 to 1991	6%	6%	11%	0%	-9%
Concentration in 1993 (µg/g)	123	0.180	1.06	13.9	6.2
Increase of Concentration from 1991 to 1993	-8%	9%	19%	8%	5%
Average Concentration 1996-1998 (µg/g)	126	0.182	1.18	12.8	5.1
Increase of Concentration from 1993 to 1996-1998 Average	2%	1%	11%	-8%	-18%

[a] Values from Table 3.1.
[b] Values from Table 3.3.

Table 3.4 shows that the atmospheric contribution of industry, compared to its background for the period 1882 to 1919, had substantially increased by 1969. Much of this increase may be due to the increase of automobile emissions. But after automobile Pb emissions were virtually eliminated in 1993, Pb had only declined 8%. The increase of sediment concentration of the other atmophile metals during this period verifies that the decrease in Pb sediment concentrations is not due to other factors.

This would indicate that either the contribution of Pb from the residential area has greatly increased or that Pb deposited in watershed soils by past emissions is gradually being transported to the lake sediments. Although Pb was eliminated in paints in 1977, it is unlikely that homes would immediately contribute to Echo Lake sediments (U.S. Consumer Product Safety Commission 1977). By 1977, only 52 homes had been added to the watershed and all of these were greater than 1 km from Echo Lake. During this period the calculated %CIT had increased from 0.9% in 1969 to 1.4%.

Table 3.4 also compares the concentrations and the relative changes in atmophiles at another diagnostic juncture, the creation of a nearby atmospheric source. In 1987 the Wheelabrator trash to energy facility began operations 21 km west of Echo Lake in Millbury, Massachusetts. The Wheelabrator facility incinerates approximately $1.3\text{x}10^6$ kg of residential and commercial waste from 39 surrounding communities each day (Massachusetts Department of Environmental Protection 2011). A comparison of concentrations in 1986 to the 3 year average from 1996 to 1998 finds an increase in Cd sediment concentrations of 48%. Only Hg increases during this time, by 17%, while the concentrations of other atmophiles remain stable (Pb) or decrease (As and Sn). It is notable that during the period 1986 to 1996 the %CIT went from 1.9% to 2.8%, a 48% increase that parallels the increase in Cd concentration during this time.

Cd is geochemically similar to Hg, and occurs in coal in small quantities (Szpunar 1992). A possible source of Cd is the incineration of nickel-cadmium (NiCad) batteries that may be incorporated into residential wastes. The Wheelabrator facility has more recently targeted the removal of batteries from its waste stream, primarily to remove Hg (Wheelabrator 2009). Other research has found that although residential building materials may contain Cd, they are insignificant sources compared to atmospheric fallout (Davis et al. 2001). In Figure 3.11b, Cd appears to have no consistent increase in concentration until 1987 or 1988. Sediment from 1970 to 1987 had an average concentration of 0.81 ± 0.09 µg/g. Sediment deposited after 1988 had an average concentration of 1.03 ± 0.19 µg/g, a 20% increase in concentration and a greater than 50% increase in variability over the 1970 to 1987 sediments.

The Echo Lake Hg deposition rate ranged from 10.2 µg m^{-2} yr^{-1} in 1969, to 130.4 µg m^{-2} yr^{-1} in 1998, an average deposition rate of 64.2 µg m^{-2} yr^{-1} for the 30 year period. These values are in close agreement with the rate of atmospheric Hg deposition during the 1990's in Vermont and New Hampshire lakes which ranged from 21 to 83 ug m^{-2} yr^{-1} (Kamman and Engstrom 2002). Deposition rates of Hg as high as 86 ug m^{-2} yr^{-1} were also observed in another lake in eastern Massachusetts (Wallace et al. 2004). The suspected sources of Hg in the 2004 Wallace study were coal-burning power plants in the mid-west and nearby medical waste incinerators (Wallace et al. 2004).

The concentration of As in sediments increases over the period from 1970 to 1999, but concentrations are very low, 9.4 µg/g in 1969 and 15 µg/g in 1999. The thin soils of the Echo Lake watershed prevented the establishment of orchards and therefore historic agriculture is not a likely source of As (Bowker 2005). The deposition rate of As in Echo Lake sediments deposited in the early 1970's was approximately $3x10^{-3}$ to $8x10^{-3}$ g m^{-2} yr^{-1}. This value compares well with average As deposition rates, $2x10^{-3}$ µg m^{-2} yr^{-1}, determined in a number of rural areas in the 1970's (Galloway et al. 1982). The increases in As sediment concentration parallels that of other atmophile elements in Table 3.4 indicating a potential atmospheric source.

In sediments deposited in the 1990's the deposition rate for As increases, averaging 0.0046 g m^{-2} yr^{-1} which is in agreement with monitoring performed during the same time period at a station approximately 40 km to the northeast which determined a rate of 0.004 g m^{-2} yr^{-1} (Golomb et al. 1997). Monitoring in a rural area in neighboring New Hampshire had As deposition rates that were as low as $3.2x10^{-10}$ g m^{-2} yr^{-1}, well below the rates determined in Echo Lake (Pike and Moran 2001). Because the New Hampshire watershed lacked nearby industry, the importance of atmospheric sources is apparent. Therefore, it is likely that the source of As increases in Echo Lake sediments is atmospheric emissions.

There is a similarity in concentration profiles of Cd, Hg, and As in Figure 3.11b, c and d, respectively. Correlation analysis of the metal concentrations found some agreement between the profiles for Hg and Cd (0.52), Hg and Pb (0.49) and Hg and As (0.56) indicating that these metals share a similar method of transport and incorporation into the sediments, most likely atmospheric deposition and collection in storm water. Hg and As share a saw-tooth profile, but the origin of this pattern is not found in the data. Hg shows a period of 3 years between troughs and peaks, As varies from 1 to 8 years.

Correlation with average annual flow or deposition rates found nothing diagnostic. These differences may indicate that although atmospheric deposition is the likely source of these metals, different watershed or sedimentation processes affect the concentration profiles of Hg, Cd and Pb.

Table 3.4 highlights general trends among atmophiles that indicate that atmospheric fallout is the primary source of these metals to Echo Lake sediments. The less-than-expected decline of Pb indicates that sorption onto watershed soils and then subsequent long-term erosion of these soils in storm water is an important contributor to sediment metal concentrations. The behavior of the other atmophiles in the Echo Lake watershed may parallel this behavior. This behavior has been demonstrated to occur in other similar watersheds for Hg and Pb where more than 70% of Hg and 90% of Pb were delivered to Big Round Top Pond in Rhode Island through runoff from the watershed (Chalmers et al. 2007).

Table 3.4 also demonstrates that environmental regulation has had some effects on sediment metal concentrations. The clearest example is the 1993 decline of Pb sediment concentrations due to the Clean Air Act. The emission of Pb was the only metal directly regulated under the Clean Air Act (CAA), but the slowing of the sediment concentration increases, especially after 1993, evident in Table 3.4 indicate that regulating the particle size may be reducing the concentrations of atmophile metals in sediments.

Cu is the only lithophile metal to show a consistent increase in sediment metal concentration (Davis et al. 2001). The Zn concentration profile is included in Figure 3.11 f. because Zn is commonly found associated with Cu in storm water and overall average concentrations shown in Table 3.2 indicate an increase in concentration in younger sediments (Davis et al. 2001).

Cu is present in building materials and may also be added to storm water by abrasion from automobile brakes (Stead-Dexter and Ward 2004). Zn, a lithophile like Cu, is a significant constituent of residential building materials such as galvanized metal and roofing and a common component in automobile tires. It is typically present in sediment affected by storm water runoff and commonly associated with Cu (Davis et al. 2001). Table 1.2 in Chapter 1 showed that the primary sources of Cu in the Maryland watershed was automobile brakes (47%) and exterior paint and materials on house siding (22%). The primary sources for Zn included house siding and galvanized materials (59%), and automobile tire wear (25%). The anthropogenic contribution of Cu and Zn to those sediments from the Maryland watershed was 3.8×10^{-3} and 6.5×10^{-2} g m^{-2} yr^{-1}, respectively (Davis et al. 2001).

The Maryland watershed had deposition rates of Zn more than an order of magnitude greater than Cu mirroring results in other research (Chalmers et al. 2007). Table 3.2 does show an increase in Zn. An average of Zn sediment concentrations for the periods 1969 to 1975 and 1996 to 1998 found an increase in concentration from 157 to 194 µg/g, a 23% increase, while the %CIT increased by greater than 200%. The lack of a definitive increase for Zn comparable to Cu as shown in Figures 3.6a and b and 3.11e and f, indicates that building materials and storm water runoff are not primary sources of Cu to Echo Lake. A regression of Cu and Zn yielded a contradictory result. Although the sediment concentration of Cu agreed well with the %CIT (R^2=0.82), Zn sediment concentrations found no relationship (R^2=0.10).

The deposition rate of Cu and Zn in Echo Lake sediments during the 1990's was 1.9×10^{-2} and 7.4×10^{-2} g m^{-2} yr^{-1}, respectively. Although the Zn sediment deposition rate in Echo Lake was similar to that of the Maryland research, Cu was greatly enriched. The concentration profiles for Cu and Zn were dissimilar as well. Figure 3.12e and f, respectively show that while Cu increases consistently after 1970, Zn has no discernable trend. Cu clearly has another source other than storm water runoff.

It was discovered that in 1990 Echo Lake had been treated with an unknown amount of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) to treat a noxious bloom of vegetation (Papuga 2004). The weed growth may have been due to the runoff of nutrients from residential areas. In the previous section the amount of sediment supplied to the lake bottom was shown to have increased dramatically after 1969, and perhaps was responsible for the extermination of rooted aquatic benthic plants in 1984.

Typical treatments for floating aquatic plants in drinking water reservoirs attempt to attain a concentration of 0.5 mg/l $CuSO_4$ over a target area of the lake surface area to avoid a massive kill that would increase biological oxygen demand (Aqua Doc Lake & Pond Management 2009). Assuming that 10 hectares of Echo Lake, a quarter of the lake surface, was treated to a depth of 1 meter to attain a 0.5 mg/l dose approximately 20,000 g of Cu would be required. During treatment, the active Cu is incorporated by the plant. The plant then dies and is conveyed to sediments with the Cu.

If the 20 kg of soluble Cu was distributed through the post-1969 sediment column the total mass of Cu in those sediments would be 0.051 g m^{-2}. Subtracting that amount of Cu from the total inventory of Cu in post-1970 sediments, 0.12 g m^{-2}, yields a difference of 0.07 g m^{-2} over 30 years or an average Cu deposition rate of 2.3 x 10^{-3} g m^{-2} yr^{-1}. This compares well with the Maryland site value of 3.8 x 10^{-3} g m^{-2} yr^{-1} (Davis et al. 2001).

The increasing concentration trend shown by Cu in Figure 3.11e shows the trend beginning in 1971. However, the first and only treatment with copper sulfate was in 1990 (Papuga 2004). Because the copper sulfate is in soluble form when applied, it penetrated the sediments and was sorbed to the underlying sediments at the aerobic/anaerobic interface. When the copper sulfate was applied in 1990, the 1971 horizon was only 6.5 cm below the sediment surface. A peak of concentration appears in the 1987 horizon, which in 1990 was only 1.5 cm from the surface. Interestingly, the typical thickness of aerobic layers in sediment are from 0.5 to 2 cm in depth (DiToro 2001). Diffusion and travel through pore water since that time has allowed the Cu to be incorporated in newly deposited sediments as they were added. An increase in sediment concentrations due to copper sulfate addition has been observed in other areas (Serdar 1995).

Approximately 88% of the Cu increase in post-1970 sediments appears to have been added through weed treatment. The remainder is most likely due to storm water runoff from roadways and building. The lack of a clear trend in Zn concentrations, yet an overall increase in concentration through time indicates that although storm water supplies these metals from road runoff, watershed processes affect the sediment concentrations of Cu and Zn.

3.5.4 The Potential Effect of Metals in Echo Lake Sediment on Biota

The increase in concentration of Hg, As, Pb, Cd, and Cu in sediments during the period from 1970 to 1999, raises the prospect of possible environmental harm. The toxic properties of Hg, As, Pb, Cd, and Cu in sediments are well known (U.S. Environmental Protection Agency 1997). The significance of ERL and ERM values was discussed in Chapter 1. Table 3.5 displays the metals investigated in this research with the established ERL and ERM values as well as the crustal averages. These values are offered for comparison to the background concentration (from Table 3.3) that provide an indication of what would be expected from atmospheric fallout, and the average concentrations in the upper 7.5 cm of sediments that have been deposited since 1984.

Table 3.5. Comparison of sediment metals concentrations in Echo Lake to crustal averages and regulatory guidelines. The bold values exceed the ERL or ERM established for sediments.

	Average[a] Crustal Concentration (µg/g)	Echo Lake Sediments Background Concentration (µg/g)	 Average Concentration 1984 to 1998 (µg/g)	ERL[b] (µg/g)	ERM[b] (µg/g)
Cr	92	**41** ± 3	**41.2** ± 1.5	39	270
Hg	50	0.115 ± 0.007	0.174 ± 0.001	0.180[c]	1.060[c]
Pb	17	**76** ± 4.5	**127** ± 4.1	55	99
As	5	12.3 ± 1.4	**13.1** ± 1.8	13	50
Cd	0.09	0.39 ± 0.05	**0.98** ± 0.19	0.7	3.9
Cu	28	15 ± 1.8	**53** ± 5.8	41	190
Zn	67	**159** ± 31	**182** ± 43	110	550

[a] (Rudnick and Gao 2003), [b] (Ingersoll et al. 1996), [c] (U.S. Department of Commerce 2012).

Table 3.5 demonstrates that several metals exceed regulatory guidelines. Pb exceeds the ERM, and Cr, As, Cd, Cu and Zn exceed the ERL in the upper 7.5 cm of sediment (1984 to 1999). The trend in Hg concentration is increasing and the 1999 horizon exceeded the ERL, 209 µg/g. The sediment concentration trends for Hg, As, Cd, and Cu appear to be increasing. Although Pb is not increasing, the average concentration of Pb in the core after 1993 is 125 ug/g, still well above the ERM of 99 ug/g. Cu may continue to diffuse from the sediments and, providing there are no further weed treatments, may decrease in concentration in the future.

With respect to Hg, Cd and As exceeding ERM values, regressing the %CIT against the concentration found that greater than 1500 additional homes would need to be built in the watershed to exceed the ERM for any of the other metals. Buildout for the Echo Lake watershed is unlikely to exceed 500 homes, based on the amount of surrounding developed land and the zoning for the area (Hopkinton Planning Department 2004).

Although the concentration of Pb exceeds the ERM and Hg, Cd, Cu, Zn, Cr and As exceed the ERL, other research has examined Echo Lake sediments and determined that most of the metals are bound as sulfides and therefore unlikely to be bioavailable and cause toxicity (U.S. Environmental Protection Agency 1997). Yet, the potential for resuspension of these sediments and deposition in other environments may pose a risk to aquatic organisms (Simpson et al. 1998; Rogers et al. 2002).

3.6 Conclusions

This research determined the background concentrations of selected metals in Echo Lake sediments during two periods: the natural, atmospheric deposition of Hg, Pb, As, Cd and Sn before industry was established in the late 18th century, and the concentrations of metals in lake sediments between 1882 and 1919. Anthropogenic impacts to Echo Lake sediments prior to 1919 were found for Hg and Pb. Narrow peaks of Hg concentration were probably the result of increased local railroad traffic during three distinct intervals. A broader peak of Pb was delivered through atmospheric deposition likely due to discharges from industrial sources in Worcester, MA, approximately 25 km to the west.

Despite a 500 m protected buffer zone, Echo Lake sediments have been impacted both physically and chemically after residential land use began in 1970. Erosion from construction sites nearly 1 km from the lake increased the mass accumulation rate of sediment and the concentrations of Hg, Pb, Cd, As, Cu, and Zn. Runoff, perhaps from residential areas, also required that the lake be treated with Cu to address nuisance vegetation, causing Cu to exceed regulatory guidelines in Echo Lake. Atmospheric fallout and the increase of impervious area was the likely, primary source of the increase in concentration of Hg, Pb, Cd, and As. Regulatory guidelines for aquatic life are exceeded for Pb, As, Cu, Cr and Zn which, except for Pb, have an increasing concentration trend. Although Hg did exceed the regulatory guideline in 1999 and the trend of concentration indicates that it will continue to exceed that standard.

This research found that changes in land use affected the concentrations of metals in sediments by introducing additional allochthonous metals through the atmosphere and that the residence time of all metals in the watershed was altered by the collection and conveyance of metals through storm water. The metals that were formerly retained in soils of the watershed are being transferred more quickly to the river sediments, but those metals are retained behind the Echo Lake dam rather than being conveyed to the ocean. The sediment metals may be a future source of impairment to the environment either through re-suspension or diffusion.

CHAPTER 4

BOX POND WATERSHED

Abstract

A sediment core collected from Box Pond, in Bellingham, Massachusetts, contained metals from residential and industrial sources. Radiometric dating of the sediment core using ^{210}Pb, ^{214}Pb, and ^{137}Cs revealed that the sediments spanned the time period from 2000 at the top of the core, to 1905 at the bottom of the core. Industrial sources such as paint manufacturing contributed Cr, Hg, Pb, Cd, Zn, Cu and Sn, and glass and mirror manufacturing most likely contributed As and Ag. The concentration of these metals from industrial sources declined after 1970 due to either economic conditions or increased environmental awareness. As the contribution of metals to sediments from industry declined after 1970, other sources, including population, may have contributed additional metals such as Cu and Ag causing concentrations to either continue increasing or remain close to their peak industrial concentration. The Milford Sewage Treatment Works may have also altered sediment metal concentrations in Box Pond during expansions and other work. High concentrations of metals in historic sediments upstream of Box Pond may have been re-suspended in 1987 after expansion of the Sewage Treatment Works. Continuing high concentrations of metals in sediments are likely due to the re-suspension and deposition of sediments and soils containing high concentrations

of metals. The metal concentrations for Cu, Hg, Pb, Cr, Cd, Zn and Sn in the Box Pond sediments exceed regulatory guidelines, indicating that these sediments may adversely affect aquatic life. A means of quantifying the flux of anthropogenic metals into the watershed and the residence time of those metals is needed to protect and restore the Charles River.

4.1. Introduction

The Charles River traverses a complex geologic terrain, has varied anthropogenic atmospheric fallout sources along its length, and has an industrial history of nearly 400 years. But the upper watershed of the Charles River, the Box Pond watershed, provides a unique opportunity to characterize the behavior of metals in sediments.

The Box Pond watershed contains several different land uses, has a common geology, and is relatively small which minimizes differences in atmospheric fallout. Sediment cores collected in two impoundments of the Charles River contained anthropogenic metals that reveal the effects of land use. Echo Lake is the headwaters of the Charles River and a sub-watershed of the Box Pond watershed. The sediment core taken from Echo Lake served to define the background contribution of metals. Only 14 km downstream of Echo Lake, a sediment core was taken from Box Pond in Bellingham, Massachusetts to determine the effects of more than 150 years of industry and changing land use. The metal concentrations in the dated sediment core taken from Box Pond were contrasted against those of Echo Lake to determine the changes in concentration as compared to changes in land use and other anthropogenic factors such as environmental regulations.

A comparison of the concentrations of metals in sediments in Box Pond with the concentrations of the metals deposited at the same time in the background sediment core collected at Echo Lake facilitated the examination of three questions in this research:

1. What is the anthropogenic contribution to sediment metal concentrations in the Box Pond sediments from various industrial and urban sources?
2. What has been the effect of environmental regulations on metal concentrations in sediments?
3. What are the potential effects of those sediment metals on aquatic organisms in Box Pond?

These questions were addressed by collecting a sediment core from Box Pond and sectioning it at 5 mm horizontal intervals. The date of deposition of each interval was determined by gamma detection of ^{210}Pb, ^{214}Pb, and ^{137}Cs. Total organic carbon (TOC) was determined for each interval by collecting a subsample from each interval and acid fuming the sediment to remove carbonate minerals. Metal concentrations were determined from stock solutions prepared from total acid microwave digestion of additional subsamples.

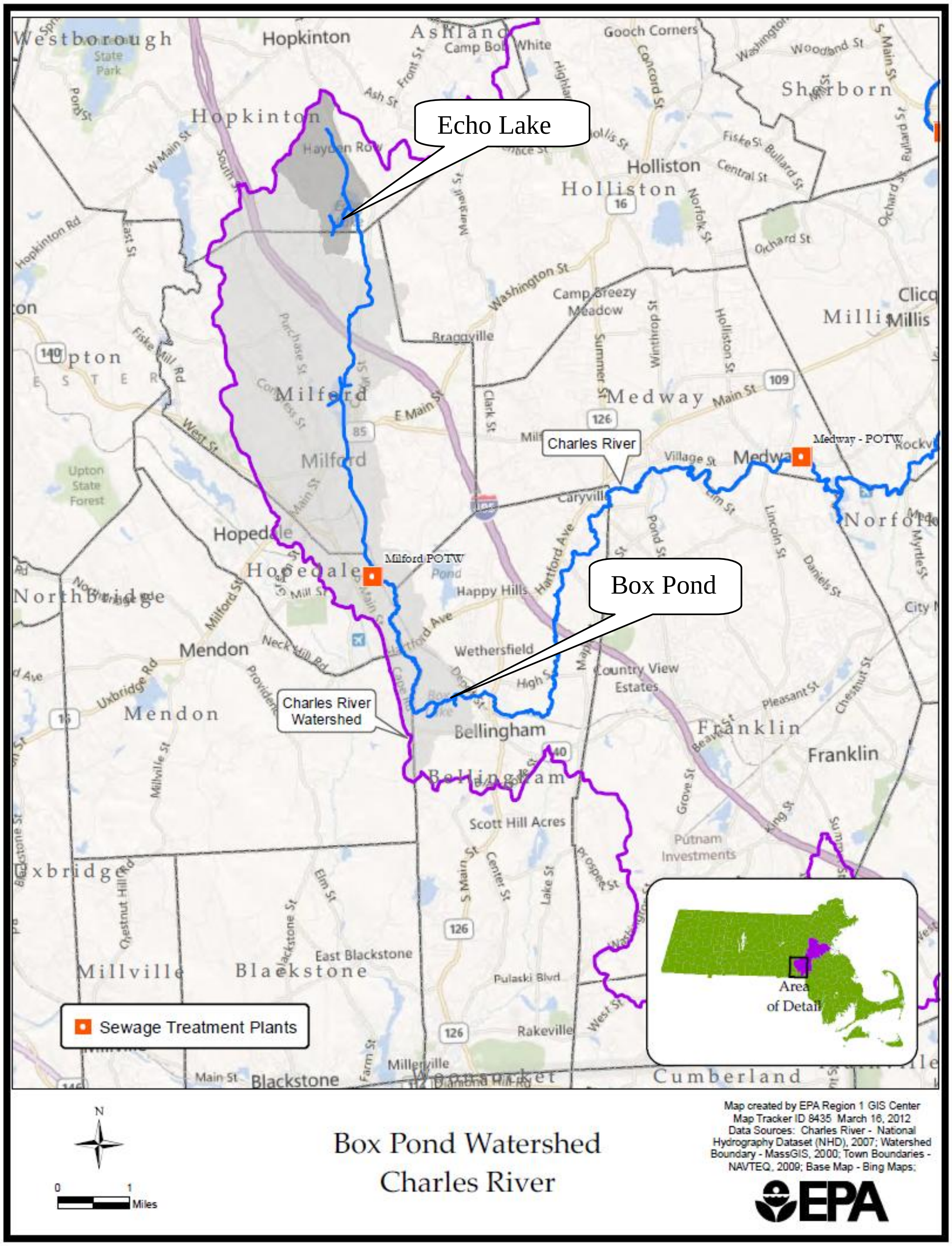
The microwave digestion method used aqua regia, hydrofluoric acid, and boric acid to completely digest the subsample and produce a stock solution. Mercury (Hg) concentrations were determined using cold vapor atomic adsorption (CVAA) of aliquots of stock solution. The metals aluminum (Al), iron (Fe), manganese (Mn), chromium (Cr), Cobalt (Co), lead (Pb), cadmium (Cd), arsenic (As), tin (Sn), copper (Cu), zinc (Zn), strontium (Sr), scandium (Sc) and silver (Ag) were determined for each interval using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The analytical methods, quality assurance, and quality controls are discussed in Chapter 2.

4.2. The Box Pond Study Area

The total area of the Box Pond watershed is 38 km^2, approximately 5% of the 767 km^2 Charles River watershed. The Echo Lake sub-watershed covers 3.7 km^2, approximately 10% of the Box Pond watershed. The span of the Box Pond watershed, including that of Echo Lake's, is approximately 14 km, north to south, and 8 km, east to west (Dichter 2005). The small size of the Box Pond watershed increases the probability that the contribution of anthropogenic atmospheric fallout is more likely to be homogeneous.

The watersheds of Box Pond and Echo Lake share a common geology. The Milford Granite underlies both watersheds minimizing the differences in autochthonous metals expected in stream sediments at either sediment core location. The Milford Granite is a pale grey biotite quartz granite that underlies a large portion of central Massachusetts (Zen 1983).

The Box Pond watershed is shown as two, gray-shaded areas, light and dark, on Figure 4.1. The darker shaded area is a sub-watershed of Box Pond, that of Echo Lake, the headwaters of the Charles River, where the background core was collected. The remainder of the Box Pond watershed, downstream of Echo Lake, is shown in a lighter shade of grey.



Box Pond Watershed
Charles River

Map created by EPA Region 1 GIS Center
Map Tracker ID 8435 March 16, 2012
Data Sources: Charles River - National Hydrography Dataset (NHD), 2007; Watershed Boundary - MassGIS, 2000; Town Boundaries - NAVTEQ, 2009; Base Map - Bing Maps;

Figure 4.1. The Box Pond watershed, in light grey, also contains the Echo Lake watershed, shown in dark grey.

A significant portion of the water in Echo Lake is sent southward through a pipe for distribution as potable water use in Milford, Massachusetts. The small amount of water that escapes Echo Lake forms the Charles River at the base of the dam and flows southward towards Milford through mostly forested terrain that contains narrow, bordering riparian wetlands. Approximately 2.6 km south of Echo Lake, the Charles River flows beneath Interstate Highway 495 and enters Milford Pond. Milford Pond is bordered on the northern bank by a large residential area, on the eastern bank by a closed municipal landfill that is now a park, and on the western bank by several industries. The Charles River exits Milford Pond to the south and enters a large urban area, where it is heavily channelized and, in some portions, contained in underground pipes.

Milford became a major manufacturing center in the mid-1800's. The industries were located along the Charles River, in particular Milford Pond. The larger industries initially included granite quarries and stone works, as well as shoe manufacturing and woolen mills. In the early 20th century, industries such as paint manufacturing, electronics, metal works, and glass and mirror manufacture came to the area. Milford also served as a transportation hub with many coal-burning trains operating between Providence, Rhode Island and Worcester, Massachusetts until at least 1910 (Milford Historical Commission 1980). As of 2001, Milford was an urban city of 25,000 with residential and commercial sections surrounding the river and industry remaining clustered near the west bank of the Charles River and Milford Pond.

The river emerges from Milford and flows through an area of light residential development and forest. Approximately 2 km south of Milford and 4 km upstream of

Box Pond, the Milford Sewage Treatment Works, a publically-owned treatment works (POTW) discharges the water originally taken from Echo Lake for use as potable water, back to the river. The river continues to flow southward in a narrow channel, past a ruined dam near what is now Hartford Avenue, where a woolen mill burnt to the ground in the 1860's and was not re-built.

Box Pond is a narrow, shallow impoundment created by a dam near Depot Street in Bellingham, Massachusetts. Box Pond is approximately 1.3 km long and is no more than 100 m wide at its widest point. Its depth is quite shallow, and based on a number of short surveys with a fish finder, no more than 2 m at the deepest with an average depth of approximately1.5 m. As the Charles River flows eastward from the dam at Box Pond it is still a small stream approximately 3 to 5 meters in width and approximately 20 to 30 cm in depth but the rate of flow can be quite rapid. Three kilometers downstream of Box Pond, the Charles River turns north, towards Boston.

4.3. Sediment Core Collection and Description

The Box Pond core was collected on January 12, 2001, 6 m upstream (west) of the dam spillway at 42º 05' 41.35" N, 71º 29' 05.20" W. This location was selected as it was the deepest point found near the dam spillway. It was believed that this location would be undisturbed because it was unlikely for boats to anchor so close to the spillway. The depth was found to be 1.7 meters by sounding. At the time of sampling the water ran vigorously over the dam, the location where the sediment core was collected was covered with 15 cm of ice, and the ice pack and the surrounding terrain were mantled with at least

20 cm of snow. The location of the sediment core collection point and the character of the surrounding area are shown on Figure 4.2.

Figure 4.2. Box Pond, December 31, 2001. The coring location is marked.

Prior to taking the core a sounding of the vigorously flowing surface water was taken using a YSI-85 multi-meter. The water profile had the following values:

Table 4.1. Surface water profile at Box Pond sediment core sampling point, January 12, 2001.

Depth (m)	**Temp (°C)**	**Dissolved O_2 (mg/l)**	**pH**	**Salinity (‰)**
0.2	0.24	18.41	6.11	0.1
0.5	0.89	10.57	5.96	0.39
1.1	1.3	8.19	5.98	0.58
1.4	1.59	6.69	6.08	0.6
1.6	1.63	5.99	6.11	0.61

The Box Pond sediment core was collected using a remote sampling device described in Chapter 2. Immediately after collection the sediment core had an uneven surface that varied from 29.5 to 31.2 cm in thickness with no suspension of sediments apparent and no benthic vegetation noted. When re-measured at the lab, the sediment core measured an even 30 cm, indicating some redistribution of the upper section during transportation. The sediment core was placed on the extruder and sectioned at 0.5 cm intervals for processing and analysis.

4.4. Results

Radiometric dating found that the Box Pond sediment core spanned an uninterrupted interval from 1905 at the bottom of the core, to the date of collection, January 2001. Moving downward from the surface water/sediment interface the sediment was a loose, black muck. At a depth of 15 cm, corresponding to a date of deposition of 1951, the muck became more clay-like in consistency. At a depth of 26 cm, corresponding to a date of 1914, the black muck ended abruptly and was replaced by coarse sand. The bottom of the core, which was medium sand, was dated at 1905.

Figures 4.3 through 4.6 display the concentrations of each metal in Box Pond sediments with their year of deposition. The concentrations of the same metals in the background sediment core collected from Echo Lake are plotted alongside Box Pond for comparison. Also displayed on the concentration profiles of Cr, Hg, Pb, As, Cd, Cu, Zn and Ag are the regulatory guidelines established for those metals. These guidelines were established to allow a preliminary screening and assessment of the potential for impacts to aquatic life (National Oceanic and Atmospheric Administration 1999). As explained in Chapter 1, the Effects Range Low (ERL) and Effects Range Median (ERM) values were established as guidelines to evaluate the potential for sediment toxicity to aquatic organisms. Quality control and quality assurance measures are described in Chapter 2 and the methods used for determining the geochronology are described in Appendix III.

Figure 4.3 shows the sediment concentration profiles for Al, Sr, Sc and Co. These metals are typically used for determining the crustal contribution of metals due to erosion from native soils and rock. Figure 4.4 shows the sediment concentration profiles for Fe, Mn, Cr and TOC. These metals and TOC provide insight into the chemistry of the depositional environment. Figure 4.5 shows the sediment concentration profiles for Hg, Pb, As and Cd. These metals have wide-spread anthropogenic uses and are most commonly associated with toxic effects. Figure 4.6 shows the sediment concentration profiles for Cu, Zn, Sn and Ag. These metals are typically associated with anthropogenic discharges. At high concentrations these metals may also adversely affect aquatic life.

Figure 4.3. Sediment concentration profiles of Al, Sr, Sc and Co.

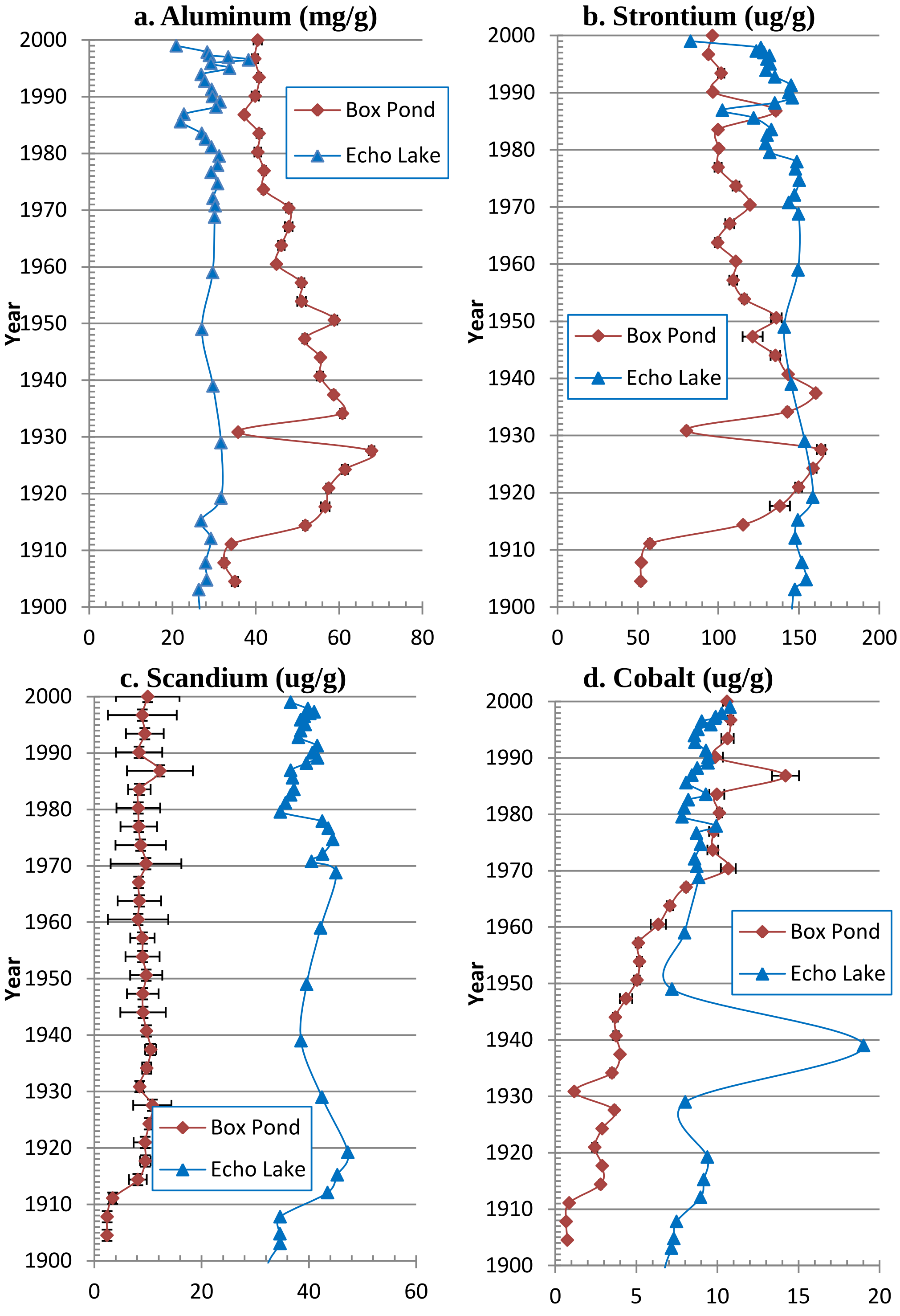


Figure 4.4. Sediment concentration profiles of Fe, Mn, Cr, and TOC.

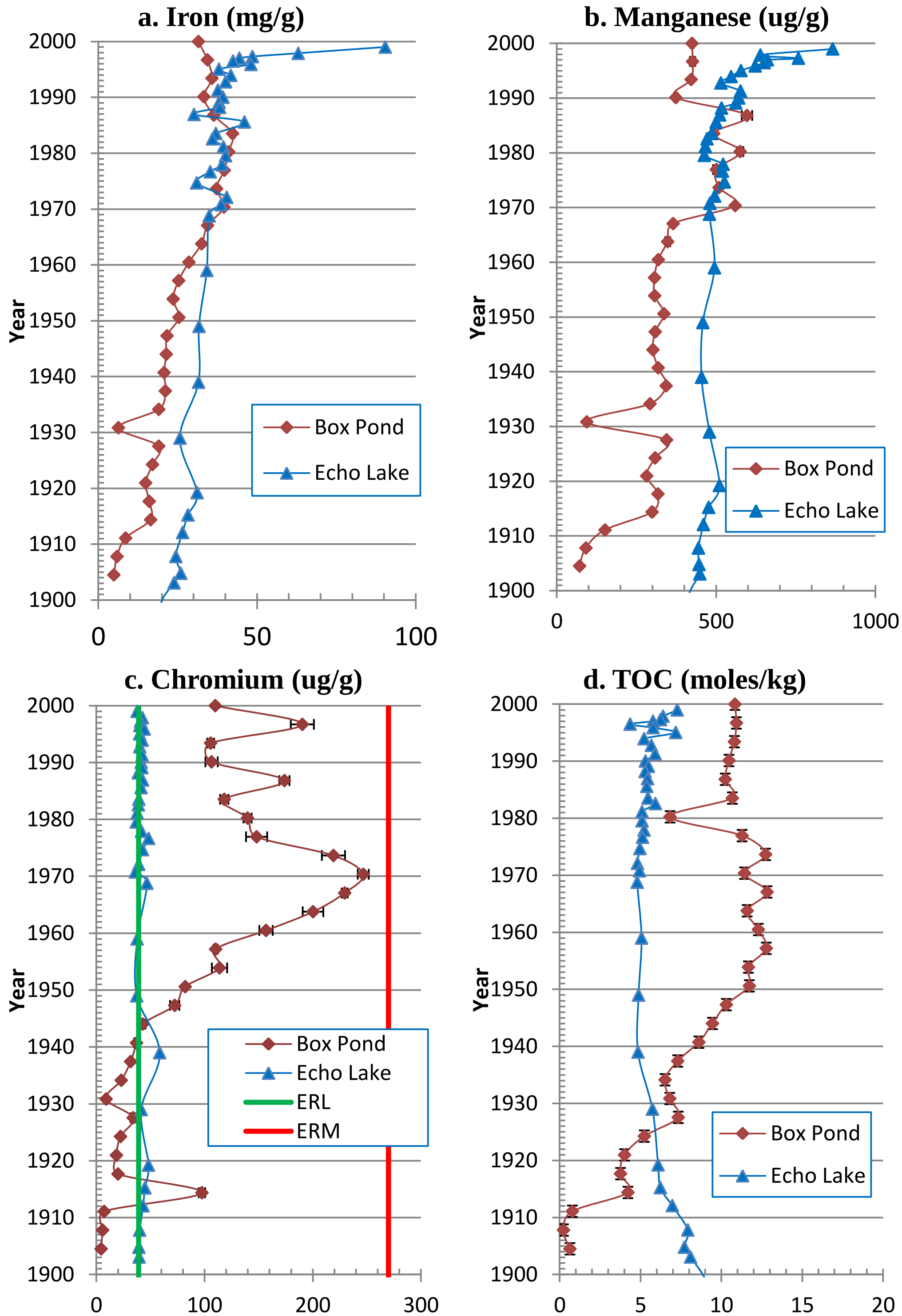
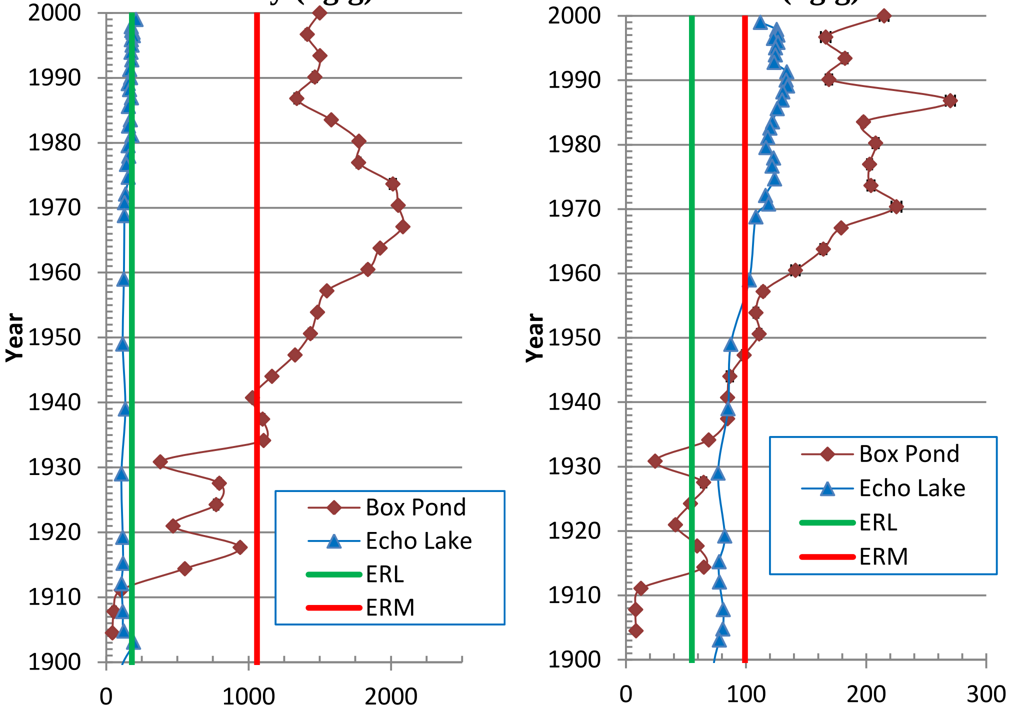


Figure 4.5. Sediment concentration profiles of Hg, Pb, As, and Cd.

a. Mercury (ng/g) **b. Lead (ug/g)**



c. Arsenic (ug/g) **d. Cadmium (ug/g)**

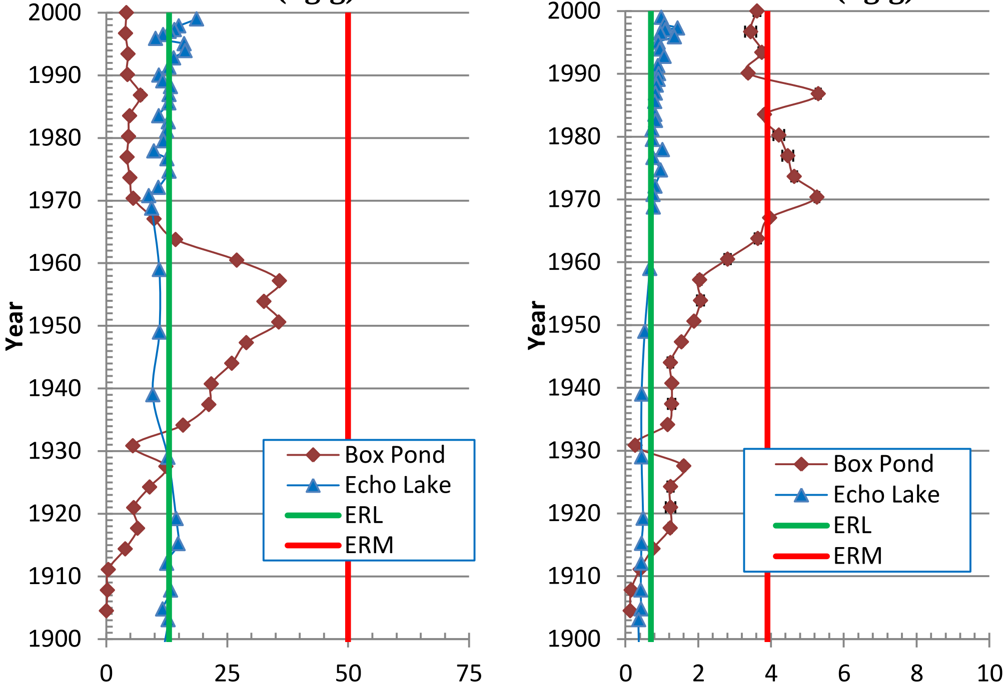
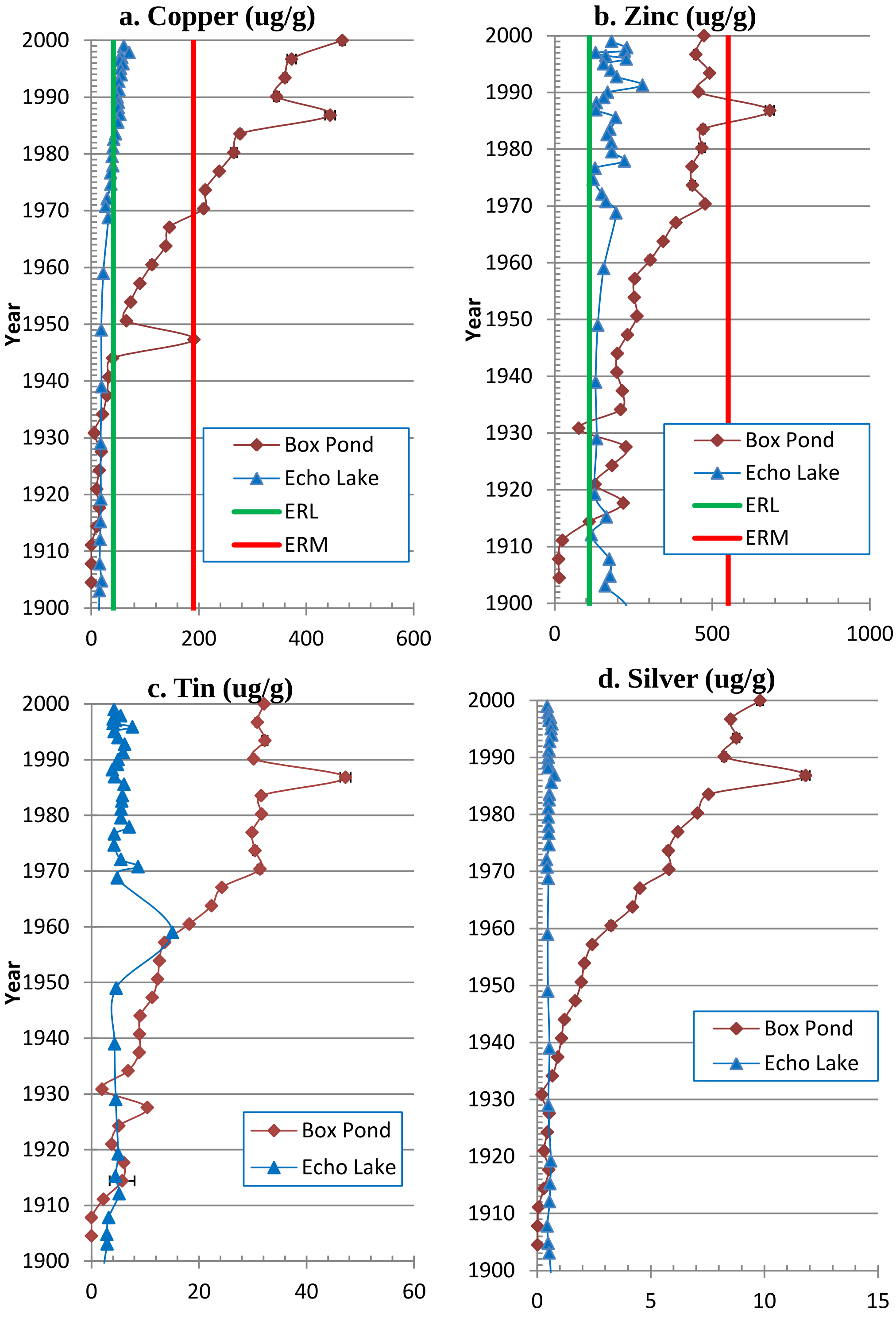


Figure 4.6. Sediment concentration profiles of Cu, Zn, Sn, and Ag.



4.5 Discussion

In Figure 4.3 the crustal source metals, Al, Sr, and Co, have concentration profiles that are similar to those of Echo Lake. Comparing the mass accumulation rate (MAR) for Box Pond and Echo Lake in Figure 4.7 finds that the geology and weathering within the Box Pond watershed is similar to that of Echo Lake, with some exceptions, since 1970.

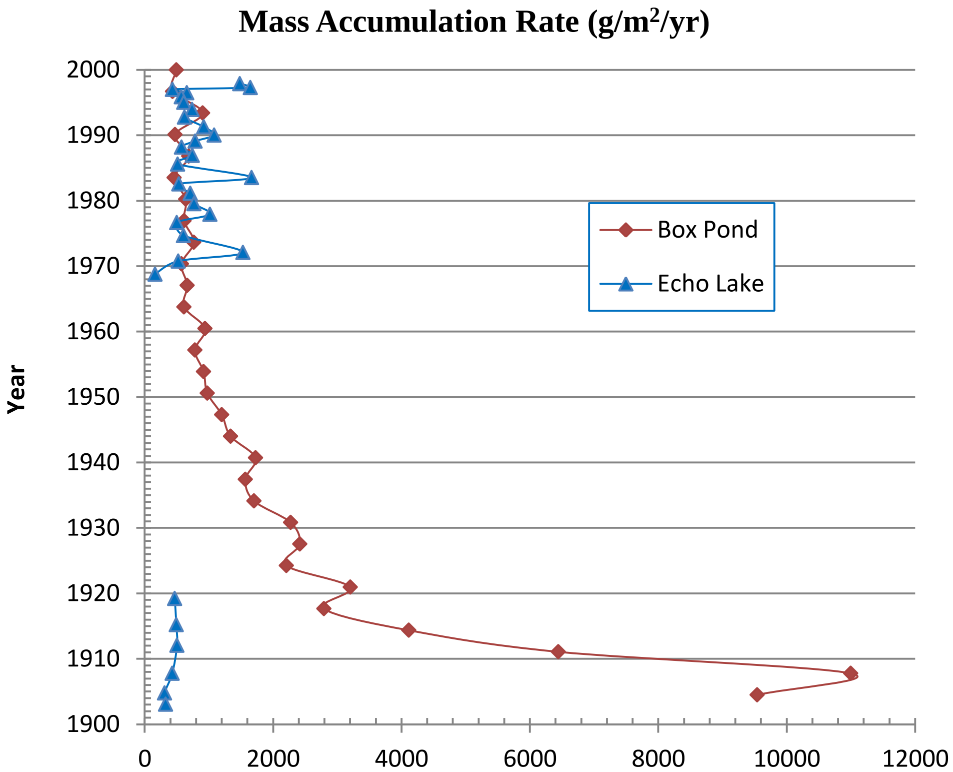


Figure 4.7. Mass accumulation rate in Box Pond and Echo Lake.

In Box Pond, sediments below the 1918 horizon are fine-grained sand, which greatly affects the MAR. Quarrying of the Milford Granite was the dominant industry in the area from 1870 to 1930 and is the likely source of the large MAR for Box Pond from 1905 to 1940. Quarrying would not increase the concentrations of metals but would affect the MAR. The effects of quarrying decline through the mid-1960's although quarrying has remained active through the present. The Echo Lake MAR profile is missing the period from 1920 to 1967 because that period is an unconformity for the Echo Lake sediments.

The concentration profiles of many metals in Box Pond sediments differ greatly over the metal concentrations in sediments that were deposited contemporaneously in Echo Lake. These differences are the result of the contrast in the anthropogenic uses in each watershed during those periods.

4.5.1 Anthropogenic Addition of Metals to Sediments

The concentration of metals in Box Pond sediments that differ significantly from the sediment concentrations in the background location include: Cr, Hg, Pb, As, Cd, Cu, Sn, Zn, and Ag. Although the concentration profiles of each of these metals display subtle differences, they may be divided into two groups. The first group, Cr, Hg, Pb, Cd, Sn, and Zn share a common profile in that their concentrations increase beginning in the mid-1940's, peak in 1970 and then either remain constant or decrease in younger sediments. The concentrations for these metals are also much greater than those of the background location. This behavior may be due to the metal contribution of a single source. The second group: As, Cu and Ag display distinct concentration profiles that indicate potentially different sources of these metals.

4.5.1.1. Sources of Cr, Hg, Pb, Cd, Sn and Zn

Although there are many sources of anthropogenic Cr, Hg, Pb, Cd, Sn, and Zn to sediments, the increase in concentration for each of these metals occur shortly after 1944, coinciding with the beginning of paint manufacturing near Milford Pond in the mid-1940's. The Benjamin Moore Paint manufacturing facility, the largest of these firms, began operating in 1948 and is still present on the west bank of Milford Pond.

According to anecdotal evidence from residents that lived in the area, during the 1950's and 1960's Milford Pond was frequently un-natural colors that were likely the result of disposal of waste paint pigments (Papuga 2004). The primary use of metals in paint is pigmentation. The color white is attained using Pb or Zn. Orange is the product of Cr and Fe, Co can impart a blue color, Cd or Cr and Pb are used to obtain yellow, and Cu has been used to make green and blue. Paris green was a popular pigment produced from As until the 1960's (Hawley 1977). Hg, Sn and Cu have also been used for anti-fouling paint for boats (Hawley 1977). EPA banned the use of Hg for marine paints in 1972 (Hawley 1977). EPA also banned the use of Hg in all paints in 1990, where the primary use had been as a fungicide (U.S. Environmental Protection Agency 2012). Cu replaced Hg as an anti-fungal additive.

The concentration profiles for Cr, Hg, Pb, Cd, Sn, and Zn show increases in concentrations that began in 1948 and peaked in 1970. After 1970 the concentrations of these metals then either declined or remained stable. The halt in the rise of concentrations in post-1970’s sediment may be due to changes in business practices, economic conditions, or perhaps public pressure.

In eastern Massachusetts, the general economy struggled through the 1970’s which may have either caused a reduced demand for paint during the 1970’s or perhaps caused the manufacturing operations for some of the paint lines to move to other locations (Schwenk 2001). Changes in manufacturing technique or material handling may have occurred in 1970 that stopped or re-directed discharges to the Charles River.

The decline in metal concentrations after 1970 may have also been due to a rising environmental awareness among the public. Following the first Earth Day in April 1970 and the creation of EPA by Congress in July 1970, public awareness would have increased. Complaints from the public regarding the changing colors of the pond, or the increased awareness by the paint manufacturers may have increased their diligence in handling wastes.

Environmental regulation was not the cause of the 1970 decline as EPA was only formed in December, 1970. Although many environmental regulations were enacted in the early 1970’s, such as the Clean Water Act (1972), implementation of those laws occurred several years later. For instance, the increase of Pb in Box Pond sediments stopped in 1970, yet the ban on the use of Pb in paint was implemented in 1977 (U.S. Consumer Product Safety Commission 1977). EPA announced the phase out of Pb in gasoline in December 1973 and that ban was not complete until 1996.

The dating of the sediment core is crucial in assessing these dates and sources. The confidence in the assigned dates is strong. The Box Pond sediment core was found to present a strong ^{137}Cs peak at 1964 and the assigned uncertainty using the excess ^{210}Pb gamma detection techniques was less than 1 year for the entire sediment core as shown in Table III.1.

As shown in Figure 4.5b, the concentration of Pb in Box Pond approximates Echo Lake's concentration until 1957, after which the concentration in Box Pond nearly doubles. The delay between the start of paint production in the late 1940's and the increase in Pb after 1957 could be due to the nature of the waste Pb, which could be bound with other paint components and perhaps have a greater residence time in Milford Pond.

After the 1970 peak, the concentration of Pb remains steady for more than 10 years potentially due to the travel time of the Pb-particulates from Milford Pond to Box Pond. The 1987 peak may be due to an upstream erosion event that will be discussed later as it has implications for all metals. After 1987, Pb concentrations begin to decline parallel to those in Echo Lake. This may be due in part to the Clean Air Act eliminating the discharge of Pb from automobile emissions.

The Box Pond Hg sediment concentration profile in Figure 4.5a displays key differences from the background Hg sediment of Echo Lake. The Box Pond sediments show a relatively constant concentration of Hg in sediments from 1914 to 1940 that are approximately six times the concentration of Echo Lake sediments being deposited in the same period. Possible sources of this increase are the manufacturers that made electrical switches in the Milford area or dental amalgams. The population of Milford from 1910 to 1940 was 12,000 to 15,000 and poor practices in the disposal of dental amalgams may also account for this increase in concentration (Wallace et al. 2004). The population of the Echo Lake watershed during the same time was approximately 20 to 40 persons and there were no businesses or industry active in the Echo Lake watershed.

After 1944, the concentration of Hg in sediment increased dramatically, coincident with the start of paint manufacturing in the area. The same increase in concentration after 1957 that occurred for Pb also occurs for Hg. The appearance of Hg in the Box Pond sediments in 1944 indicates that the Hg was mobile in the water column and easily distributed. By 1970 the concentration of Hg in sediment was nearly 20 times the value in Echo Lake. Similar to Pb, there is no definitive reason for the decline in concentration of Hg in Box Pond sediments after 1970 other than those cited above. The concentration of Hg continued to decline until 1987. After 1987 the concentration profile for Hg remains approximately 7 times that of Echo Lake but appears to parallel the increase in concentration found in Echo Lake. This indicates a continuing source of Hg that is increasing at the same rate throughout the watershed. This may be the result of atmospheric fallout.

Cr, Cd, Sn and Zn display sediment concentration profiles that are remarkably similar and bear many of the same features of Hg and Pb, a steady rise in concentration after 1944, a larger rate of concentration increase after 1957, a peak at 1970, and then either steady or declining concentrations. Zn and Sn appear to slightly increase after 1970 which may be due to additional anthropogenic discharges from automobile tires and building materials (Davis et al. 2001). Sn has uses in plating of steel and manufacture of bronze. These uses are prevalent in food canning and in plumbing fixtures (Hawley

1977). It is unknown if antifouling paints using organotin were produced and discharged in the Milford area. Paint manufacture continued through at least the early 1980's and Benjamin Moore, a major manufacturer of paint, maintained a facility on the west bank of the Charles River as late as 2011 (Goyette 1982).

4.5.1.2. Sources of As, Cu and Ag

Although As, Cu and Ag may be used as pigments in paint as described in the preceding section, the concentration profiles of these metals differ greatly over those of the other metals. Paint manufacture may still be one source, but the difference in the concentration profiles suggest that processes in the water column or sediment act on those metals differently.

The sediment concentration profiles of Cu and Ag in Figures 4.6a and 4.6d, respectively, appear identical. A comparison to the background concentrations and an examination of the scales reveal subtle differences that may be diagnostic of sources. Cu has a concentration similar to its background until 1947. The increase in sediment concentration in Box Pond is continuous and at the time of core collection was greater than 4 times the concentration of Echo Lake sediment Cu. Because Cu is an important pigment in paint and is also used as a fungicide and anti-fouling paint for boats, its simultaneous increase with the start of the paint industry indicates that paint may be the primary source at that time. The continued increase in sediment concentration after 1970 may be due to a new source such as automobile brakes or corrosion from residential plumbing (Davis et al. 2001). During ICP-MS analysis the isotopes of ^{65}Cu and ^{63}Cu were measured and are shown in Figure 4.8.

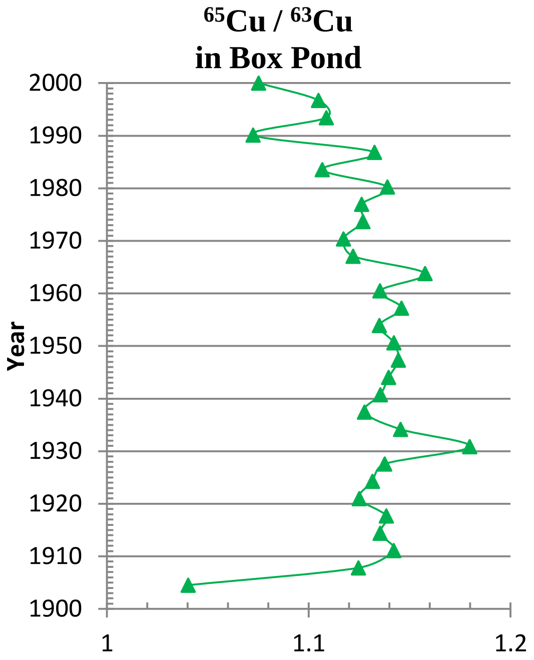


Figure 4.8. Ratio of ^{65}Cu relative to ^{63}Cu in Box Pond.

The change in isotope ratio suggests that the source of Cu after 1980 differs from that before 1980. For instance, prior to 1908 and the beginning of public sewage collection and treatment, the ratio of concentrations of ^{65}Cu and ^{63}Cu indicated that ^{63}Cu was more prevalent. Figure 4.8 shows a break in the general trend after 1980, suggesting that another source of Cu, more enriched in ^{63}Cu was deposited in Box Pond sediment at that time. That source may be automobile brakes or Cu dissolved from plumbing in homes.

The sediment concentration for Ag in Box Pond departs from the background concentration in the mid-1930's and increases continuously thereafter. The beginning of the increase in Ag concentration is before paint manufacturing began, but approximately when glass manufacture was operating and is perhaps result of the disposal of wastes from the production of mirrors. An examination of the isotopes ^{107}Ag and ^{109}Ag revealed no indication of a change of sources in the sediment column. Although paint may use Ag as a pigment, the timing of the increase and the increase to over 10 times the background indicated that another, unknown source is likely.

Industrial discharges of Ag, such as in jewelry or photography, are unlikely as Ag is a valuable metal and typically easy to recover in these processes (Hawley 1977). Other potential sources include the use of cosmetics by the population, as well as textile and medical industries where it is used as a bactericide (Hawley 1977). High quality mirrors using silver are made in the Box Pond watershed by the company Saint-Gobain, but the date when manufacture began and material handing processes is unknown (Goyette 1982).

Arsenic has a sediment concentration profile unlike any other metal in Box Pond. Figure 4.5c shows that the sediment concentration begins increasing after 1931, increasing consistently until the 1950’s, and then rapidly falls until 1970 when sediment concentrations become constantly lower than the background location. In 1935 the Milford landfill opened on the eastern shore of Milford Pond. Landfills are a potential long-term source of many metals including Fe and As (Lovley 1991).   The source of Fe is the material deposited into the landfill and the source of As may be either redox mobilization from the aquifer materials, rat poisons, or industrial wastes deposited in the landfill. Milford landfill closed in 1976 (Richer and Holdridge 2009).

Although it is possible that the rise in As sediment concentrations is due to the landfill, it is also possible that an industrial use of As may be a factor. Arsenic was used in paint pigments such as Paris Green which was discontinued by all manufacturers in the 1960's due to the recognition of its toxicity (Paris Green was also a rat poison). Glass manufacture in Milford by several companies, one of which was Ball Brothers, used As to minimize bubbles in glass, although this process too has since found a safer replacement (Hawley 1977). The decline of As concentrations through the 1960's was due most likely to a recognition of the dangers in handling As and the availability of safer alternatives.

Another possible source of As may have been lake weed treatments. In the late 1950's and early 1960's the State of Massachusetts authorized a pilot program that used various aquatic weed control chemicals, including sodium arsenite, in several lakes in the state (Commonwealth of Massachusetts 1953). However, no records were found regarding such treatment in Box Pond or Milford Pond.

4.5.1.3. Sources of sediment metal trends and peaks

For all of the metals there are common trends and peaks that are diagnostic of sources and factors that affect the concentration of metals in sediments. The critical turning points for nearly all of the metals are 1914, 1928 and 1931, 1944 and 1947, 1957, 1970, and 1987. The increase in concentration in 1914 is due to the transition from sand to organic-rich silt shown in the concentration of TOC in Figure 4.4d. For all metals, concentrations increase through 1928 and then decline dramatically in 1931. In 1928 the

POTW increased capacity, although details of the work were unavailable, such work on the POTW may have created the potential for flushing of settling ponds. The subsequent 1931 decline in sediment concentration that is present in the concentration profiles for all metals and TOC could be the new treatment lagoons absorbing much of the new flow.

The concentration profiles of all metals resume their general trends after the 1931 decline and remain relatively constant in concentration until 1944 or 1947 after which a general increase in concentration occurs. It is possible that some of the increase in sediment metal concentrations after 1941 could be due to increased production of many metal items in World War II. But the largest increase after 1944 for many of the metals is likely due to production at the paint companies.

In 1957 the POTW increased capacity again, but unlike 1928, rate of increase in concentrations for all metals appear to increase after this date, perhaps due to the general economic expansion in the late 1950's and early 1960's (Schwenk 2001). Concentrations increase until 1970 and then either decline or remain relatively constant except for Cu and Ag.

After 1970 the most prominent feature is a peak at 1987. Twelve of the fifteen metals have a concentration peak in 1987 and for nine of the fifteen metals it is their maximum concentration in the sediment record. In 1986 the POTW was upgraded to include tertiary treatment. Tertiary treatment typically produces a discharge that is almost potable. The subsequent increase in sediment metal concentration in 1987 could be due to either flushing of the old sedimentation ponds, or the discharge from the POTW being re-routed to a new location, disturbing sediments containing high concentrations of metals, when the old ponds were emptied. The estimated flow from the POTW may have been higher than typical flows and in the existing narrow channel would be capable of disturbing existing, historic sediments and depositing them in Box Pond in 1987 (Simpson et al. 1998).

Approximately 1 km upstream of Box Pond, and downstream of the POTW, a woolen mill operated during the 1800's, burned down in 1868, and was not re-built (Partridge 1919). Woolen mills discharge many waste dyes and metal-containing "liquors." Table 4.2 compares the concentrations of Box Pond sediments for 1987 to sediments at a Superfund site woolen mill in Corrina, Maine (U.S. Environmental Protection Agency 2004).

Table 4.2. Comparison of maximum sediment metal concentrations, Eastland Woolen Mills Superfund Site in Corrina, Maine and Box Pond sediments deposited in 1987.

	Superfund Site µg/g	**Box Pond Sediment µg/g**
As	16	7.1
Cd	56	5.3
Cr	390	174
Cu	49	445
Pb	330	270
Hg	1.2	1.3
Ag	0.56	11.8
Zn	2600	683

Table 4.2 shows that the metals in the Superfund Site sediments and Box Pond sediments have very similar concentrations of metals, most notably Hg and Pb. The changes in operations at the POTW in 1928, 1957, and 1987 coinciding with changes in the concentration, or rate of concentration increase, for many of the metals in Box Pond

sediments, indicates that the POTW exerts a significant influence on metal concentrations.

The POTW does not accept raw industrial discharges and discharges treated water at an average approximate rate of 1 m^3 min^{-1}. The discharge limits are based on an allowable flow of $18x10^6$ l day^{-1} (monthly average) and include the discharge of total suspended solids (TSS) of 100 to 800 kg day^{-1}, as well as dissolved components including Al (1500 g day^{-1}), Cu (300 to 500 g day^{-1}), and Pb (68 g day^{-1}) (Commonwealth of Massachusetts 2010). There is no requirement to determine the concentration of the TSS component of the flow. The uncharacterized TSS may be the source of the excess concentrations of Hg, Pb, Cd, Cr, Cu, Zn, Sn and Ag that continue to the top of the sediment core. The concentrations of all these metals in sediments that were deposited after 1970 and up to 2000 greatly exceed those of the background location, Echo Lake.

Although the POTW is a tertiary treatment plant, releases of untreated water can occur. On August 9, 1999, following a one-inch rainstorm the previous night, Box Pond, 4 km downstream of the POTW, had a distinct sewage smell. Because the POTW accepts residential sewage, and there is an industrial pretreatment program that addresses industrial discharges, the concentration of metals discharged may also be a function of population (U.S. Environmental Protection Agency 1999).

The % Commercial, Industrial and Transportation (%CIT) is used by several authors to gauge the effects of land use as it is a measure of altered and impervious area (Chalmers et al. 2007; Coles et al. 2010). In Chapter 3 an estimate of the %CIT for the Echo Lake watershed was calculated because the watershed is small and the land use changes relatively recent and can be estimated using maps and building permits. The Milford area does not share that character and no historic values of %CIT are available, nor are there any reasonable means of estimating such a value. Moreover, the %CIT value may not be appropriate in the instance of historic industrial discharges. To examine sediment metal concentrations as industrial discharges are controlled after 1970 requires a common metric of measure. Population remains the singular available statistic that may provide insight to sediment metal concentrations. The growth in population of Milford is shown below on Figure 4.9.

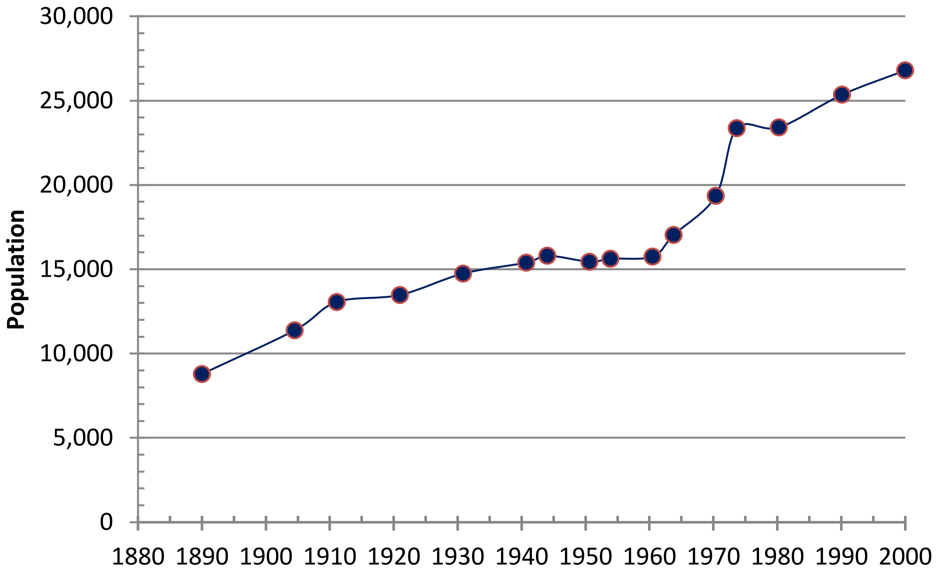


Figure 4.9. Historical population of Milford, Massachusetts, 1905 to 2001.

Population density and the amount of disturbed watershed is an indicator of water quality and hence sediment concentrations due to the storm water runoff from impervious areas (Chalmers et al. 2007; Coles et al. 2010). The population of Milford was higher than the Echo Lake watershed, which had only 16 homes until 1969. The population density in of Milford in 1934 was less than 350 people km^{-2}, but the majority of those people lived in high density dwellings in Milford (Milford Historical Commission 1980). The higher population density concentrated the watershed impacts and equated to less impervious area as the development patterns of modern suburbs was not prevalent until after 1945. This may be why Box Pond sediment concentrations of Cr, Pb, Cd, As, Cu, Sn, Zn, and Ag generally approximated the Echo Lake background concentrations until the 1940s despite a much larger population. Prior to 1940, significant portions of the Box Pond watershed, perhaps as much as 90%, may have been in an unaltered state. Figure 4.10 shows the sediment concentrations of Hg and Cu relative to the population.

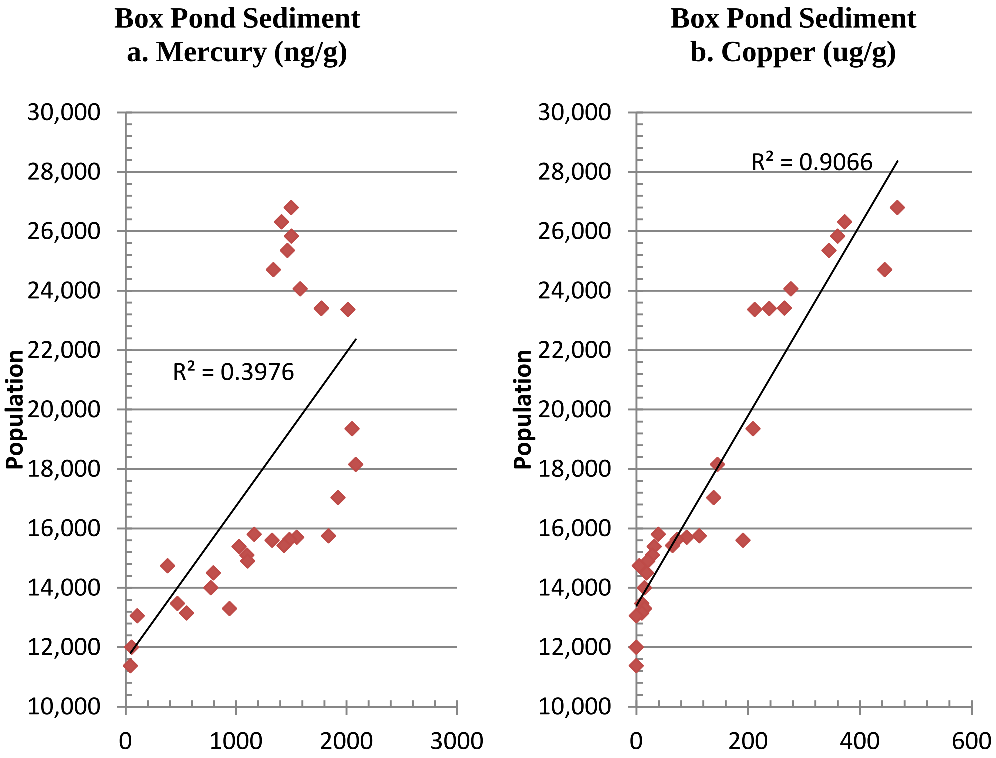


Figure 4.10. Comparison of the concentrations of Hg and Cu in Box Pond sediments to the population of Milford, MA.

Figure 4.10 contrasts the concentration of Hg and Cu with the population over the length of the sediment core. The industrial discharge dominates the Hg profile between the populations of 15,000 and 23,000 in Figure 4.10 a., which corresponds to 1940 and 1980, respectively. But an examination of trends before 1940 and after 1987, before and after industrial influences, indicates that the concentration may be affected by population. The Hg concentration profile in Figure 4.10 a. shows linearity that may be a function of population from 1905 until the population was approximately 15,000, corresponding to the early 1940's. This would correspond to the period before paint manufacture began. During this time period many products containing Hg were available to the public (Hawley 1977). Milford was a large city through this period and it is likely that dental offices were common. Dental fillings may have contributed Hg to the waste stream of the POTW (Wallace et al. 2004). The relationship between Hg and population from 1905 to 1944 has an R^2 value of 0.76 and the slope of the regression, or rate of increase in concentration during this period, is approximately 29 ng yr^{-1}.

The Hg profile assumes a linear increase after the population is 24,708 in1987 to the top of the sediment core in 2000 that approximates that of the 1905 to 1944 interval. A regression of this period found an increase in concentration of 11 ng yr^{-1} and an R^2 of 0.6. Caution should be used regarding this regression statistic as the number of observations is small (n=4) and these sediments are close to the surface water increasing the potential for bioturbation and other processes that may affect the concentration of Hg. The average concentration of Hg in the period after 1987 (>1400 ng g^{-1}) is well above that of Echo Lake, which had an average concentration of 175 ng g^{-1} for the same period. By comparison Lake Cochichewick, a reservoir 60 km northeast of Box Pond that has a heavy atmospheric input of Hg but no past industry in its watershed, has an average Hg concentration of 550 ng g^{-1} for the period after 1980 (Wallace et al. 2004). This would suggest that either industrial discharges of Hg have not been eliminated upstream of Box Pond or that historic sediments in the Charles River below Milford Pond, but above Box Pond are re-suspended and serve as the source of continued high Hg concentrations.

The R^2 value for Cu in Figure 4.10 b. indicates that there is some relationship with population and less with an industrial source. However, that may be correlation and not causation. The profile and concentrations of Cu in Box Pond are similar to those of Lake Cochichewick that had been treated with copper sulfate for a blue-green algae bloom in 1993 (Wallace et al. 2004). Because Box Pond is a recreational pond it is probable that multiple weed treatments could have occurred, generating the present concentration profile.

It must be noted that the Cu concentration profile mimics that of Ag, and Ag is not used as a weed treatment and, as discussed earlier, may be the result of disposal of personal care products or industry. The Cu profile, similar to the other metals, has a 1987 peak perhaps due to discharge from the POTW.

In Figure 4.9 1974 corresponds to the largest jump in population in the watershed. The increase in population density and the building required to accommodate that increase may have generated the continuing increase in Cu concentration. A linear regression of Cu compared to population after 1974 yields an R^2 of 0.92 if the data point at 1987 is excluded. Therefore, the steady increase in Cu concentration could be the result of industrial discharges until the 1970's and thereafter the population continued to contribute to the increase through automobile brake wear, the corrosion of residential plumbing, and perhaps the use of cosmetics.

4.5.2 The Effect of Environmental Regulation

The general conclusion regarding the effectiveness of environmental regulations in Section 4.5.1.1 is that they provided little direct relief from increasing concentrations with the exception of the phase out of leaded gasoline. Economic conditions or perhaps the increased public awareness may have caused the decline in concentrations after 1970. But it was also pointed out that many effects may be subtle. For instance, banning Pb and Hg in paints would not have an immediate effect on sediment metal concentrations, but such a ban may affect future concentrations of these metals in sediment. Many environmental regulations are only beginning to mature into more effective regulation. For instance, the National Pollutant Discharge Elimination System (NPDES) has been phased in through the 1990's and has not fully addressed storm water runoff as of 2010 (U.S. Environmental Protection Agency 2010).

Two communities in the Box Pond watershed, Milford and Bellingham, Massachusetts, are the subjects of these tightening standards and litigation is likely to result due to the projected cost of nearly $220 million to businesses within the three affected communities (Benson 2011). Although the regulation of these three communities targets nutrients, the overall effort is to minimize contributions of storm water flow to the river (U.S. Environmental Protection Agency 2008). Despite the well-understood connection between impervious surfaces and the quality of storm water flow, the EPA's 2008 decision document exempts the local, state and federal governments and thus exempts road runoff which perhaps contributes a sizeable share of the storm water.

Metal concentrations can impact aquatic organisms and hence the water quality of a water body (Singleton and Guthrie 1977). Because metal concentrations frequently parallel the concentrations of other contaminants found in storm water, metals may be an indicator of sediment impaired by nutrients and synthetic organic compound such as pesticides and other compounds harmful to human health (Breault et al. 2000; U.S. Environmental Protection Agency 2000; Coles et al. 2004). Whereas metals are found to present a significant legacy in the deposited sediments behind Box Pond dam, it is likely that nutrients and contaminants that may impair the Charles River are also found within these sediments.

Therefore, more effective regulations may be possible by further defining the relationship between metals, nutrients, and other contaminants in sediments, as well as the processes that may allow sediments to release those materials to a water body. Characterization of the emitting sources and the existing reservoirs of contaminants would greatly assist in addressing problems with water quality in the Charles River.

4.5.3 The Potential Effect of Box Pond Metals on Aquatic Life

A consequence of the increase in metal concentrations is the potential for toxic effects on aquatic life in Box Pond sediments and sediments downstream. Regulatory agencies assess sediment toxicity through the use of screening benchmarks such as the

Effects Range Low (ERL) and Effects Range Median (ERM). The average concentration of each of the eight metals having ERL and ERM values is shown in Table 4.3 for the entire Box Pond sediment core, and the sediments that post-date 1970.

Table 4.3. Comparison of the average concentrations in the Box Pond sediment core to the Effects Range Low and Effects Range Median values.

Element	**units**	**Average Crustal Conc.**[a]	**Average Concentration 1905-2000**	**Average Concentration 1970-2000**	**ERL**[b]	**ERM**[b]
Cr	µg/g	92	96	135	39	270
Hg	ng/g	50	1219	1510	180[c]	1060[c]
Pb	µg/g	17	121	201	55	99
As	µg/g	5	12.0	4.8	13	50
Cd	µg/g	0.090	2.39	3.93	0.7	3.9
Cu	µg/g	28	140	362	41	190
Zn	µg/g	67	290	499	110	550

[a] (Rudnick and Gao 2003), [b] (Ingersoll et al. 1996), [c] (U.S. Department of Commerce 2012).

Within Table 4.3 some associations are evident. First, all the metals, with the exception of As, exceed their ERL values through the entire core. The only metal to decline in the post 1970 sediments is As, which falls drastically in concentration during the 1960's. All seven metals exceeded the ERL and Pb, Hg, and Cu exceeded the ERM. It is evident that Box Pond sediments may adversely impact aquatic organisms.

In 1996 EPA collected sediment from Box Pond and examined the ratio of total metals in the sediment to those bound in the sulfide phase, acid volatile sulfides (SEM/AVS), commonly used as a means of assessing bioavailability. EPA also collected a sediment sample and conducted toxicity tests using aquatic organisms. The EPA analysis of metals in Box Pond sediments found concentrations of Cu, Hg, Pb, and Zn in agreement with the values found in this research. The SEM/AVS result, 0.28, indicated that much of the metals were bound in the sulfide phase and therefore not bio-available. The EPA toxicity test of the Box Pond sediment corroborated this finding with the result that 89% of the test organisms *Chironomus tentans* and 96% of *Hyallela azteca* organisms survived the 10-day test indicating no toxicity in these sediments (U.S. Environmental Protection Agency 1997).

Although metals in Box Pond sediment may not adversely impact aquatic organisms in its present state, re-suspension of these sediments may have toxic effects further downstream. Although the metals in Box Pond are maintained in the sulfide phase, redistribution downstream may alter the particulate-metal complex and create a more bio-available complex that affects organisms in other stream environments (Rogers et al. 2002).

4.6 Conclusions

The concentrations of Cr, Hg, Pb, As, Cd, Cu, Zn, Sn and Ag in Box Pond sediments were greatly elevated above the background concentrations in Echo Lake. Several industries have operated and discharged metals in the Box Pond watershed, but it is likely that paint manufacturing is responsible for the majority of those metals. Although the concentrations of metals in more recent sediments are lower than in the period from the mid-1940’s to 1970, the metals with established guidelines to assess potential toxicity to aquatic organisms exceeded toxicity threshold values. This indicates that the potential for sediments to adversely affect aquatic life in Box Pond and further downstream.

In Box Pond the long-term high concentrations of Hg, Pb and other metals may likely be the result of the contribution of sediments and soils that are eroded from upstream sources and were deposited in Box Pond. The association of metal concentrations and land use is obscured by this contribution and use of the land use metric of %CIT was ineffective because of the historic industrial discharges.

Population may still be a factor in metal concentration trends in sediments deposited after 1970. The concentration profile of Hg increases with population after 1987 that may be the result of dental amalgams and other sources within the population. The discharge resulting from work at the POTW may have impacted nearly all metal concentrations in Box Pond in 1928, 1957, and 1987. In 1987 the expansion of the treatment plant may have re-suspended historic, heavily contaminated sediments and distributed the metals further downstream and to Box Pond.

Although environmental regulations may have not had a direct, significant impact on metals in sediment, the relationships between the sources and reservoirs of allochthonous, anthropogenic metals may be significant with respect to future environmental regulation. The high concentrations and increases in metal concentrations in Box Pond sediments is the result of sources that include atmospheric fallout transmitted by storm water, direct industrial discharges, discharge from a sewage treatment works, and the erosion or re-suspension of soils and sediment that contain metals discharged in the past. The development of methods to determine the flux of anthropogenic metals into a watershed and the factors that affect the residence time of those metals in the watershed would greatly enhance environmental regulation not only of metal concentrations but other contaminants as well.

CHAPTER 5

COPPER, ZINC, LEAD AND MERCURY IN THE CHARLES RIVER

Abstract

The concentrations of Cu, Zn, Pb and Hg in the upper 3 cm of sediments at 13 locations along the Charles River were examined to determine the concentrations and likely sources of these metals that were deposited over an approximate 10-year period. The concentrations of these metals were found to exceed regulatory guidelines for toxicity throughout much of the river and were higher than other similar urban water bodies. The population density and the percentage of Commercial, Industrial and Transportation network (%CIT) for each community bordering the river was compared to the concentrations of these metals. It was determined that the %CIT, a function of storm water runoff, was related to the sediment metal concentrations. Simple regression models were developed for Cu and Hg that demonstrated the relationship of total organic carbon to their concentrations in sediments. The models indicated that improvements in storm water management may decrease the concentrations of metals in Charles River sediments. Decreasing the concentration of metals in sediments may improve overall conditions in the river and decrease future difficulties in managing sediments that are behind dams.

5.1 Introduction

Surface sediment samples were collected along the length of the Charles River from the headwaters in Echo Lake, in Hopkinton, Massachusetts, to the Charles River Basin in Boston, Massachusetts in June 2001. These samples provided an estimate of the concentrations of metals contributed from anthropogenic sources during an approximate ten-year period from 1990 to 2000. The metals copper (Cu), zinc (Zn), lead (Pb), and mercury (Hg), were the focus of this sampling effort because they are commonly associated with anthropogenic discharges to waterways and are known to adversely affect aquatic life (National Oceanic and Atmospheric Administration 1999; Davis et al. 2001; Wallace et al. 2004). These metals were also chosen because sediment cores collected in the upper watershed indicated that all four metals exceeded concentrations that may have toxic effects on aquatic life downstream of those locations. There were three main objectives in examining the surface sediment samples:

1. Determine the anthropogenic contribution of Cu, Zn, Pb and Hg to surface sediments along the length of the Charles River.

2. Evaluate the trends and probable sources of Cu, Zn, Pb and Hg to sediments in the Charles River.

3. Assess the potential for toxicity to aquatic organisms that may occur as well as outline the implications for the future management of sediments in the Charles River and similar rivers.

The Charles River was selected for this research because it is representative of streams in other urban settings, it is popularly used for recreation, has been the focus of cleanup efforts, and contains high concentrations of metals (Breault et al. 2000). The US Geological Survey (USGS) included the Charles River in its National Water Quality

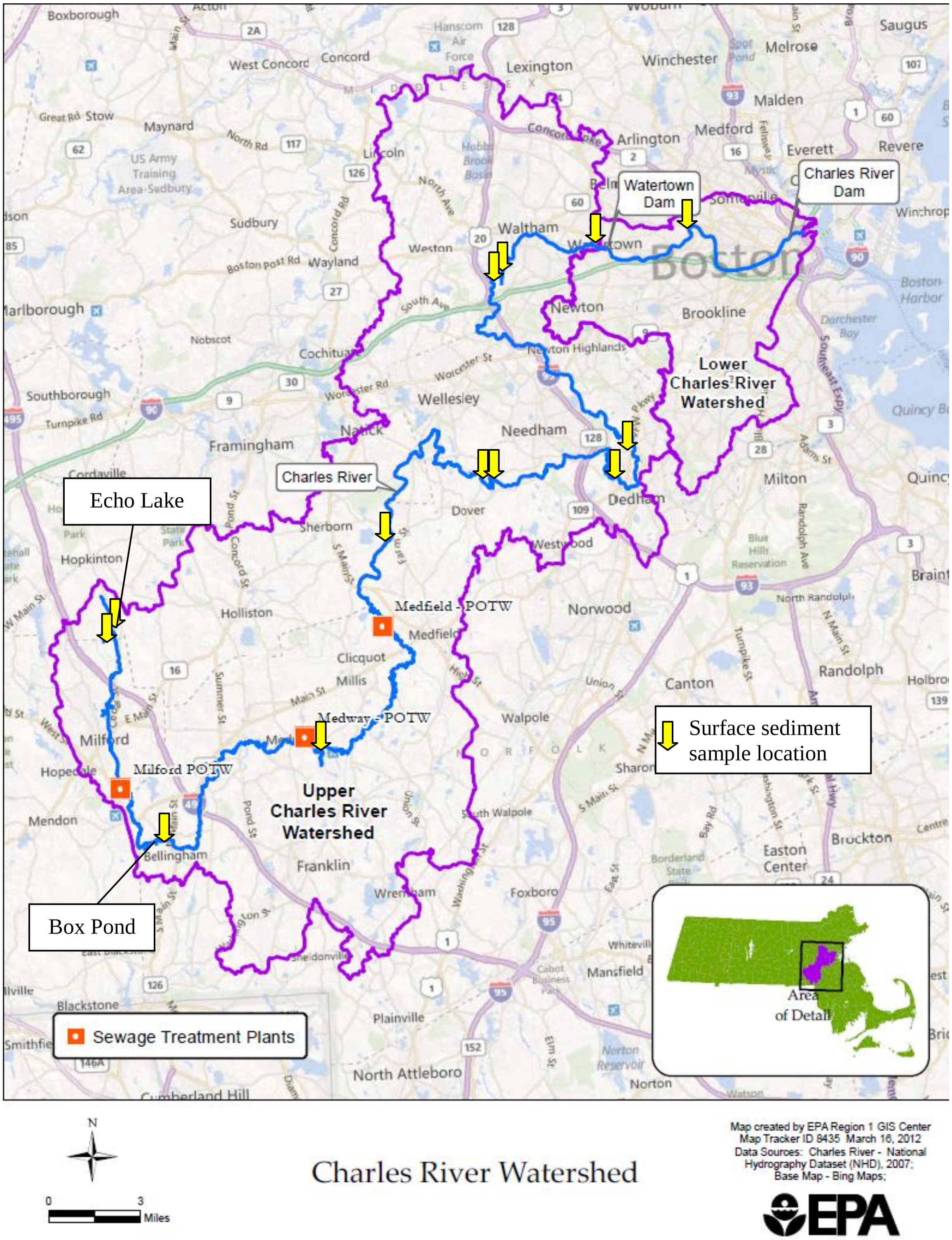
Assessment (NAWQA) program that evaluated 35 urban water bodies throughout the nation (Mahler et al. 2006). In 1995 the EPA began the Clean Charles 2005 program to restore the river for public use (U.S. Environmental Protection Agency 2005). The Charles River is important as a drinking water resource in the upper portions of the watershed and a recreational resource for many of the more than 1 million residents of the watershed (Charles River Watershed Association 2005).

5.1.1. Setting

The Charles River is approximately 125 km in length and the watershed covers 767 km^2. The Charles River lies entirely within the border of Massachusetts and is bound to the west and south by the 1400 km^2 Blackstone River watershed, to the east by the Taunton and Neponset River watersheds, and to the west and north by watersheds of tributaries of the Merrimack River which include the Sudbury, Concord, Assabet, and Mystic Rivers. The Charles River flows generally northward from its headwaters at Echo Lake in Hopkinton, Massachusetts, to the Charles River Basin (CRB) in Boston. The CRB is separated from Boston Harbor by a dam that creates the pool of water that forms the more familiar portion of the Charles River that is a Boston landmark (Charles River Watershed Association 2005).

Despite its wide expanse in the CRB in Boston, the Charles River is actually a small stream with an average annual flow into Boston Harbor of 20 $m^3\ s^{-1}$. The Charles River was one of the first industrialized rivers in the United States, but the industrial use of the river declined through the 1970’s and the primary use of the river has since become recreational (Charles River Watershed Association 2000). The Charles River was notorious for its poor water quality through the mid-20th century (Standells 1966). Cleanup efforts began in the 1970's and continue to the present (Hill 1975; U.S. Environmental Protection Agency 2005).

There are two main divisions of the Charles River watershed, the Upper and the Lower Charles River Watershed. The Upper Charles River extends from Echo Lake to the edge of the Boston Basin in Dedham, dropping at a gradient of 1.1 m km^{-1}. The bedrock geology underlying the Upper Charles River is comprised largely of metamorphosed granites and volcanic materials (Zen 1983). The Lower Charles River watershed encompasses Boston and surrounding communities depicted on Figure 5.1. The bedrock geology of the Lower Charles River watershed consists primarily of flat, easily eroded sedimentary rocks such as the Cambridge Slate and the Roxbury conglomerate, the gradient of the Lower Charles River is less than 0.5 m km^{-1} (Zen 1983). The location of the Charles River watershed, important features, and location of the sampling points are shown on Figure 5.1.



Map created by EPA Region 1 GIS Center
Map Tracker ID 8435 March 16, 2012
Data Sources: Charles River - National Hydrography Dataset (NHD), 2007;
Base Map - Bing Maps;

Figure 5.1. The Charles River Watershed and surface sediment sampling locations. The Charles River may be divided into Upper and Lower Charles River Watersheds as shown.

5.1.2. Land Use and Sources of Anthropogenic Metals

To assess the land use within the Charles River watershed the primary metrics examined were population density and percentage of Commercial, Industrial, and Transportation (%CIT) land use (Commonwealth of Massachusetts 2012). Both population density and %CIT are frequently used and easily obtainable metrics to estimate the degree of land use in a watershed (Coles et al. 2004; Coles et al. 2010). Generally, %CIT is a measure of impervious surfaces and is commonly derived from Geographic Information System analysis (Commonwealth of Massachusetts 2012). Both population density and %CIT are gross measures of land use, but are easily applied and have been demonstrated to work in other watersheds (Coles et al. 2004; Chalmers et al. 2007). The population and %CIT data used to examine the behavior of Cu, Pb, Zn and Hg are listed in Table 5.1.

Table 5.1. Population density and % Commercial, Industrial and Transportation in communities that border the Charles River. Listed from upstream (Commonwealth of Massachusetts 2012).

Community	Population Density (People/km^2)	Commercial, Industrial & Transportation (%)
Hopkinton (Echo Lake)	185	5%
Milford	690	11%
Bellingham	313	7%
Franklin	423	6%
Medway	411	3%
Norfolk	262	3%
Millis	248	3%
Medfield	325	2%
Sherborn	101	0.4%
Natick	776	10%
Dover	139	0.4%
Needham	872	8%
Dedham	847	14%
Wellesley	978	5%
Weston	256	4%
Newton	1778	9%
Watertown	3106	22%
Cambridge	5435	29%
Boston	4603	30%

The association between population density and %CIT is not entirely parallel. The correlation coefficient of the two metrics for each metal was 0.9, indicating that some differences are present. The differences may be type of residential land use, high density in urban areas and low density in suburban areas. Population density may also provide a measure of the metals supplied to the watershed in addition to atmospheric fallout. That includes abrasion from objects, such as Cu from automobile brakes, as well as direct discharges (Davis et al. 2001). The %CIT is a measure of collection area and all metals from atmospheric fallout and abrasion from man-made materials that are collected on the impervious surfaces and then quickly conveyed to water bodies in storm water. The difference between the two metrics may be that parking lots and transportation networks may displace population. This analysis examined the association of each of these metrics.

The contribution of land use through the population density and %CIT may be obscured by a number of anthropogenic sources and mechanisms. Echo Lake in Hopkinton, Massachusetts is the headwaters of the Charles River and the background location for the metal concentrations. It was determined in Chapter 3 that Echo Lake metal concentrations were affected by storm water from residential areas. Additional sources of increased concentrations of Cu, Zn, Pb, Hg and TOC downstream of Echo Lake may include: the bedrock geology, industrial discharges, POTWs, historically-contaminated sediments that are re-suspended, and storm water runoff from urban areas.

The bedrock geology is a source of natural metals. The contribution of the geology at Echo Lake, representative of much of the Upper Charles River watershed, was described in Chapter 3. There is a change of rock type in the Lower Charles River watershed but that change is located just upstream of Watertown Dam, Station #13. Therefore, it is unlikely that geology would be the source of increases in sediment metal concentrations through Station #13.

Industrial discharges at Box Pond have contributed many metals to sediments in the past (U.S. Environmental Protection Agency 1993; U.S. Environmental Protection Agency 1997; Chi et al. 2009). During the period the surface sediment samples were believed to be deposited in the Charles River, 1990 to 2000, industrial discharges were regulated under State and Federal laws and therefore perhaps not a direct contributor to sediment metal concentrations. Industries with metal-containing discharges had pre-treatment programs at the facility that lowered the concentrations of waste streams prior to discharge to sewage treatment plants or Publically-owned treatment works (POTWs) (U.S. Environmental Protection Agency 1999).

Focusing on POTWs as potential sources, the Upper Charles River has three sewage treatment plants in Milford, Medway and Medfield shown on Figure 5.1. The communities below Medfield either have individual septic systems or are connected to the Deer Island Facility on Boston Harbor and therefore do not contribute sewage directly to the Charles River (Charles River Watershed Association 2005). The combined average daily flow of all three treatment plants to the Charles River in 1998 was 42 million liters per day or approximately 0.5 $m^3 s^{-1}$ (Charles River Watershed Association 2000). The Milford POTW is a tertiary treatment plant that treats and discharges residential and industrial sewage to the Charles River.

Another potential source of metals to waterways and sediments are deposits of historically-contaminated sediments that are re-suspended (Simpson et al. 1998). The concentrations of several metals in surface sediments of Box Pond are elevated above regulatory guidelines for aquatic life in sediments, especially Hg (Ingersoll et al. 1996; U.S. Department of Commerce 2012). In Chapter 4, it was determined that relict sediments, perhaps containing metals from a woolen mill abandoned in the mid-19th century or metals from paint manufacturing, may be the source of continued high concentrations of metals in the upper 3 cm of Box Pond sediments. High concentrations of Hg, Zn and Pb and some portion of the Cu in sediments that post-date 1970 are believed to be due to historic sediments that were eroded from upstream locations contaminated by the paint industry.

Another source of metals, only recognized in the past 20 years, is storm water runoff. As described in Chapter 1, storm water conveys metals from natural sources, atmospheric fallout, and abrasion of man-made surfaces. Impervious areas collect atmospheric fallout and direct it to waterways where the metals may be incorporated into sediments (Van Metre and Mahler 2003; Wallace et al. 2004). The population density and %CIT were examined with respect to the concentrations of metals in sediment. This relationship was found to be significant in Chapter 3 for the Echo Lake watershed, and has been shown to be relevant in other watersheds (Coles et al. 2004; Chalmers et al. 2007).

5.1.3. Sample Collection

Sediment collection occurred during three periods: sediment cores were collected from Echo Lake in August 1999 and Box Pond in January 2001, and eleven sediment surface samples were collected in June 2001. The upper 3 cm of the sediments were examined based on sediment core dates from Echo Lake and Box Pond, two of the 13 stations, using radionuclide techniques. The general goal was to examine the previous 10 years of deposition, 1990 to 2000, because environmental regulations should have reduced or eliminated direct discharges, and therefore improvements in water quality and hence, sediment quality, were expected. The upper 3 cm of the Echo Lake and Box Pond sediment cores were dated at 21 and 30 years of sediment, respectively (Luce and

Wallace, in preparation). The Box Pond location was similar to the other 11 locations and therefore that value was selected.

The concentrations of the metals and TOC in the upper 3 cm of the sediment cores from Echo Lake and Box Pond, described in Chapters 3 and 4, respectively, were averaged to supply a single value for these locations and serve as representative surface sediment samples. The eleven sediment surface samples were collected at locations selected on the basis of having the least potential for local road runoff and other recent disturbances.

Ten of the eleven surface sediment sampling locations were selected to obtain a fine-grained sample from the upper 3 cm of sediment from that location. A coarse-grained surface sediment, believed to have a low total organic carbon (TOC) content, was collected at the background location, Echo Lake. Metal binding is associated with the concentration of TOC in sediments (Mantoura et al. 1978; DiToro 2001). Obtaining both high and low TOC sediments from the background location facilitated comparison to sediment further downstream that may have low TOC concentrations.

Sediment cores of 9 and 12 cm were collected at two stations that had fine grained sediments and were located near points that may show long-term trends of deposition. Sediments were sectioned at 3 cm intervals in the eleven surface samples unless there was a composition change in the sediment and in which case the section was shortened to collect only that stratum. The sample stations were designated by the distance upstream from the Charles River dam. For instance, the Echo Lake core was taken approximately 125 km upstream of the Charles River dam and is thus named Station #125.

The thirteen total sediment stations beginning at the headwaters of the Charles River, and proceeding downstream, are described below as to conditions and pertinent features. Echo Lake is a protected drinking water reservoir and the two sediment samples taken at this location are considered the background, affected primarily by atmospheric deposition. A coarse-grained low TOC sediment sample was collected near the bank of Echo Lake, Station #125.1, and a sediment core, containing fine-grained sediment, was collected at the deepest portion of the lake, Station #125.

Downstream of Echo Lake, the Charles River passes Milford, Massachusetts, a large urban and industrial area that has been active since the 19th century. The water that was taken from Echo Lake is returned to the Charles River a short distance downstream from Milford, after treatment, by the Milford POTW. A sediment core was collected downstream of Milford and the Milford POTW, at an impoundment on the Charles River, Box Pond, Station #111, to assess the impact of an urban, industrial watershed on the concentrations of metals and TOC. Similar to Station 125, the concentrations of metals and TOC in sediments for Station #111 are an average of sediment concentrations over 3 cm.

After Box Pond, the Charles River flows approximately 60 km through an area that has a lower population density and lower %CIT. Within this run of the river are Stations #95, #70, #53, #52.9. The sampling locations at Stations #95, #70, which are Walker Street and Bridge Street, respectively, are not behind dams, but are in narrow channels with coarser sediments. These stations are a short distance downstream of POTWs in Medway and Medfield, Massachusetts, respectively.

Sediment samples were collected from a near-shore area above Cocharan Dam, Station #53, and above the USGS gauging station, Station #52.9, which was a concrete weir across the river. The samples from these four locations, Stations #95, #70, #53 and #52.9, were selected to represent a stretch of the river flowing through a rural area with a population density below 400 people km^{-2}.

The character of the river changes at the Ames Street sampling point, Station #42. Upstream of Station #42 urban areas become more prevalent and the population density increases to over 800 people km^{-2} (Commonwealth of Massachusetts 2012). Through this area the Charles River widens and flows more slowly. At Station #41 there is a structure that is used to attenuate flooding by diverting water into the Neponset River watershed, hence this station is designated “Neponset River.” A 9 cm core was collected at this location and sectioned at 3 cm intervals to determine if changes had occurred over time due to the proximity of a major roadway, Route 1. The 9 cm core would indicate any trends, potentially over 30 years.

The area of Stations #23 and #22.4 is an impoundment and no flow was evident. The population density decreases in this area primarily due to the intersection of a major transportation network, Interstate Routes 90 and 95 meet upstream of this area. Route 90 is a turnpike with additional impervious associated with the toll plazas and interchanges. The increase in transportation network greatly increases the amount of storm water issued to the river in this area.

At Station #23, the Charles River Watershed Association (CRWA) maintains a recreational area with a dock and boat rental. The sediment sample at Station #23 was obtained with a Ponar grab sample device operated from the dock. A 12 cm core was collected at Station #23 and sectioned at 3 cm intervals to assess the long-term effects of storm water from the roadways. Station # 22.4 was taken from the bank of the Charles River approximately 0.6 km downstream of the CRWA dock to further gauge the effect of storm water runoff from the highway system in a location less likely to be disturbed by boat traffic.

The sediment sample obtained at the Watertown Dam, Station #13, was taken approximately 100 m upstream of the dam. At the time of collection, the river was flowing rapidly through this area and over the dam. The current slowed in the sample area due to trees and debris deposited just upstream. It is likely that these sediments may be younger than 10 years. The watershed surrounding the Charles River at Station #13 is highly urban with a population density greater than 2,000 people km^{-2} (Commonwealth of Massachusetts 2012).

Once the river flows over Watertown Dam the river enters the CRB, the standing pool of water held back by the dam at Boston Harbor, 13 km further downstream. During periods of low flow in the summer, a saline wedge has been known to penetrate as far as the Watertown Dam from Boston Harbor (Breault et al. 2000). The last downstream sampling point was in the CRB, off the dock at Elliott Bridge, Station #9. The area surrounding Station #9 is highly urban. It is likely that the sediments in this area are frequently disturbed by boat traffic and may be periodically affected by saline conditions.

The locations of the sampling points, with respect to latitude and longitude, are listed in Table II.10 in Appendix II. The sample processing and analysis, as well as quality assurance and quality control, are described in Chapter 2. Briefly, the concentrations of Cu, Pb and Zn were determined with a Perkin-Elmer Inductively Coupled Plasma – Mass Spectrometer, the concentration of Hg was determined by Cold Vapor Atomic Adsorption, and TOC was determined with a Perkin-Elmer 2400 CHN analyzer.

5.2. Results and Discussion

The results of analysis for Cu, Zn, Pb, Hg and TOC are shown below in Table 5.2.

Table 5.2: Surface sediment concentrations of Cu, Zn, Pb , Hg and TOC from the Charles River.

Station	Station (km)[1]	Strata Type[2]	Depth (cm)	Cu (μg/g)	Zn (μg/g)	Pb (μg/g)	Hg (ng/g)	TOC %
Echo Lake[3]	125	Muck	0-3	58	188	125	182	7.1
Echo Lake	125.1	Sand	0-3	8	39	26	209	1.0
Box Pond[3]	111	Muck	0-3	400	471	188	1471	13.0
Walker St	95	Silt	0-2	68	184	79	73	2.4
		Sand	2 – 5	16	146	67	94	1.9
Bridge St – Sherborn	70	Gravel	0-3	43	185	53	133	2.6
Cocharan Dam	53	Fine sand	0-3	22	154	76	176	3.0
USGS station	52.9	Sand	0-3	7	63	19	33	0.6
Ames Street	42	Muck	0 – 3	78	544	131	387	8.9
			3 – 6	85	376	120	385	10.0
Neponset River	41	Silt	0 – 3	17	92	58	157	8.8
			3 – 6	13	83	16	126	20.0
			6 – 9	17	163	5	198	27.0
CRWA	23	Muck	0 – 3	104	696	283	678	13.2
			3 – 6	103	695	284	650	9.8
			6 – 9	105	662	343	738	9.3
			9 – 12	109	672	426	1150	9.6
CRWA	22.4	Silt	0-3	84	645	251	896	10.7
Watertown Dam	13	Silt	0-3	72	308	244	323	1.6
Elliott Bridge	9	Silt	0 – 2	44	432	171	253	2.8
		Clay	2 – 6	11	92	21	138	2.1

[1] The distance (km) of the sampling station upstream from the dam separating the Charles River Basin from Boston Harbor.

[2] The designation of the type of material was based on observation of the collected material. Muck had no observable particles. Silt had observable particles on smearing.

[3] The Echo Lake (Muck) and Box Pond samples are the average concentrations of the upper 3 cm determined from the sediment cores analyzed at 5 mm intervals.

The concentrations of Cu, Zn, Pb, Hg and TOC for the top 3 cm of sediment are plotted in Figure 5.2. The Station numbers for the sampling points cited in Table 5.2 coincide with the distance scale on the abscissa of Figure 5.2.

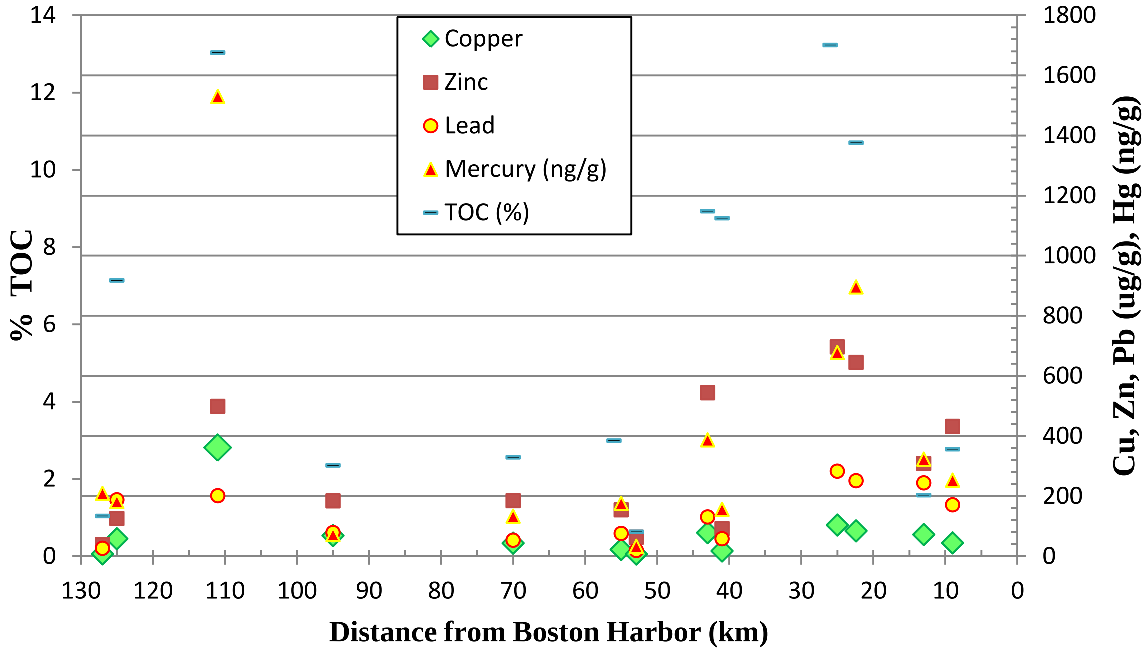


Figure 5.2. Concentrations of Cu, Zn, Pb, Hg and TOC in the upper 3 cm of Charles River sediments.

Table 5.1 and Figure 5.2 show that the concentrations of Cu, Zn, Pb and Hg increase downstream from Echo Lake. These high concentrations also coincide with urban areas and high concentrations of TOC indicating that either the metals are anthropogenic in origin, or that TOC is the controlling ligand for the metals, or that TOC as well as the metals are a function of population. TOC was measured during this research because of its known association with many metals including Cu, Pb, Zn and Hg (Wallace et al. 1991). Figure 5.2 shows two peaks of metal concentration corresponding to the industrial source at Box Pond, Station #111, and a broader peak beginning at Station #42 and continuing to Station #22.4. The concentrations of metals in sediment decline in the two stations downstream of Station #22.4, which is an area of intense urbanization. The relationship between the concentrations of each of the metals, TOC, and land use metrics is better examined on an individual basis.

5.2.1. Copper in the Charles River

An examination of the concentrations of Cu in the Charles River finds generally low concentrations in sediments, except for Box Pond. Compared to other urban rivers, Cu concentrations in Charles River sediments are higher in concentration. The National Water Quality Assessment (NAWQA) determined that the median concentration for Cu in 34 other urban waterways was 48 $\mu g\ g^{-1}$ with upper and lower quartile values of 85 and 35 $\mu g\ g^{-1}$, respectively (Breault et al. 2000; Mahler et al. 2006). Table 5.2 and Figure 5.2 show that downstream of Box Pond (#111) sediment sample concentrations of Cu decrease and, at stations #70, #53, and #52.9, are comparable to the background concentration. The concentration of Cu in Charles River sediments begins to rise with the increase in population density and %CIT land use, especially at Station #23 near a major transportation network.

The linear regression of Cu with TOC concentration found an association (R^2 = 0.38). Because TOC is an important ligand binding some metals, the Cu concentrations were normalized by dividing the concentration of Cu in sediment by the TOC present. The results were then compared to the population density and the %CIT in the communities that border the Charles River as shown in Figure 5.3.

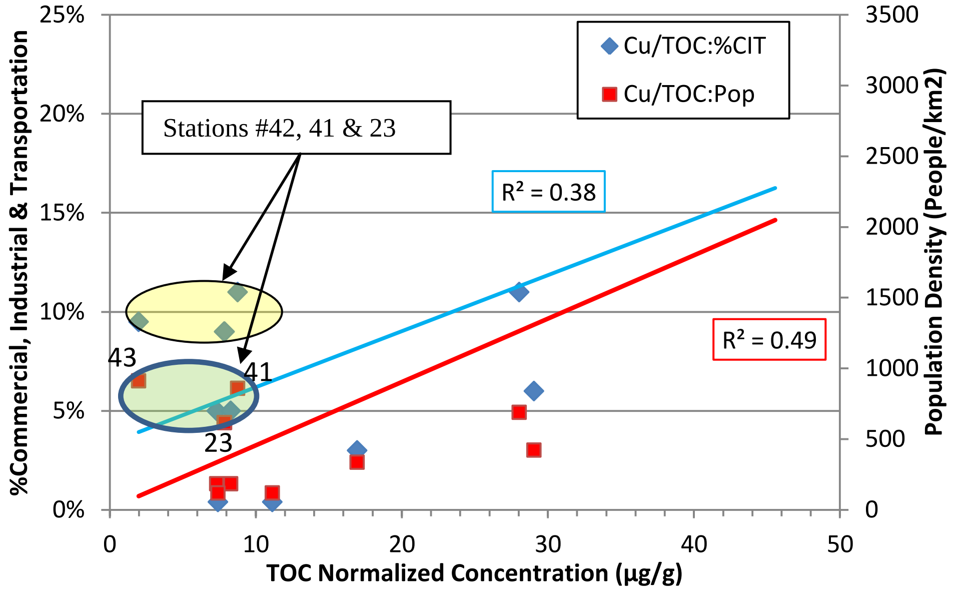
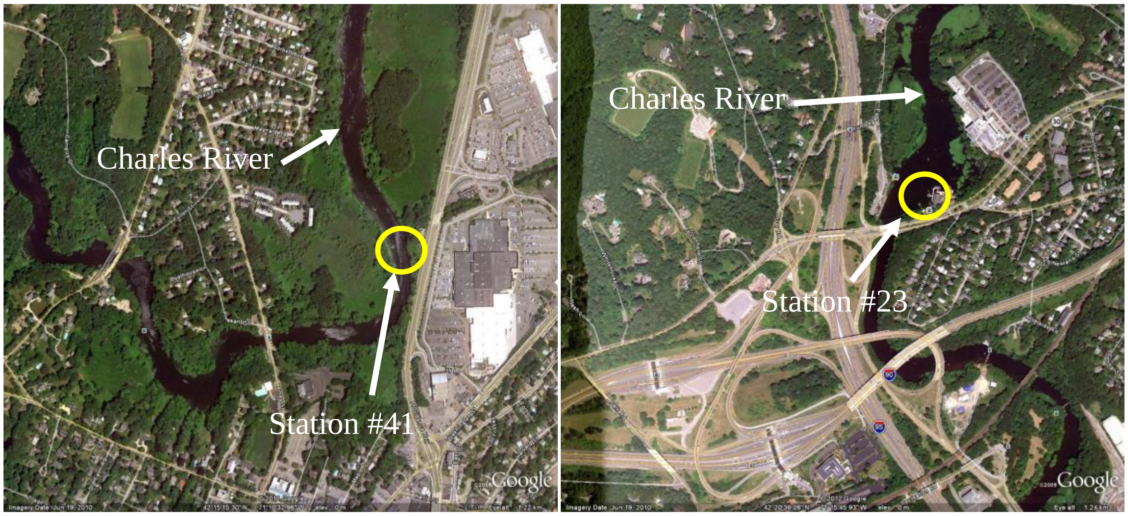


Figure 5.3. Normalized Cu compared to the population density and the %Commercial, Industrial and Transportation network in the communities that border the Charles River.

Figure 5.3 was adjusted by removing the Elliott Bridge Station (#9), which may be affected by periodic saline conditions (Breault et al. 2000). Population density and %CIT are broad indicators of contribution, and in this instance show relatively good agreement. The relationship appears stronger with population (R^2 = 0.49). A primary source of Cu is automobile brakes (Davis et al. 2001). The values for the stations at Ames Street, Neponset River, and CRWA, with respect to %CIT, are highlighted in yellow and the same stations relative to population are highlighted in green. These stations, 42, 41, and 23 are adjacent to areas with large storm water discharges.

However, these three stations underscore a weakness in evaluating concentration based on the broad indicators of population and %CIT. With respect to population, a regression line through just stations #43, #41, and #23, which are highlighted in green and labeled in Figure 5.3, shows that these points would have a negative slope (lower concentrations with higher population). The %CIT parameter appears to be more robust in that higher %CIT yields higher concentrations of Cu.

The reason for the failure to predict the higher concentrations for more populous sites is perhaps the effects of local discharges of storm water. Station #23 is immediately adjacent to a major transportation network where Interstate 90 and Interstate 95/Route 128, a highly traveled route around Boston, intersect. Storm water from this area is considerable. Examining the long-term concentrations evident in Table 5.2, CRWA #23, shows that the concentrations have been consistent, approximately 105 μg g^{-1}, since perhaps the 1960s. The nature of each sampling location is shown in Figure 5.4.



a. Station #41, Neponset River. b. Station #23, CRWA.

Figure 5.4. Locations of the Neponset River Station (#41) and the Charles River Watershed Authority Station (#23).

Although station #41, Figure 5.4a, is adjacent to a highly developed site, much of the storm water runoff is discharged downstream of Station #41. The immediate watershed upstream of Station #41 has a wide natural buffer. By contrast, the storm water from the transportation network shown in Figure 5.4 b. is introduced upstream of Station #23. This signals the importance of local discharges of storm water.

To develop a predictive model for Cu concentrations would require additional investigations as to sources and sorption onto a wide number of ligands. However, a simple model can be constructed using the equation of the regression line for the comparison of normalized Cu/TOC to %CIT inserting the appropriate values in equation 5.1.

$$\%CIT = 0.0028(Cu/TOC) + 0.0336 \qquad \text{Equation 5.1}$$

Applying this equation generically found that for sediment with a TOC concentration of 3%, every 1% increase in %CIT increased the concentration of Cu by 10 μg g^{-1}. To obtain model concentrations the background from Echo Lake is added. Figure 5.5 shows the values predicted using this model as compared to actual values.

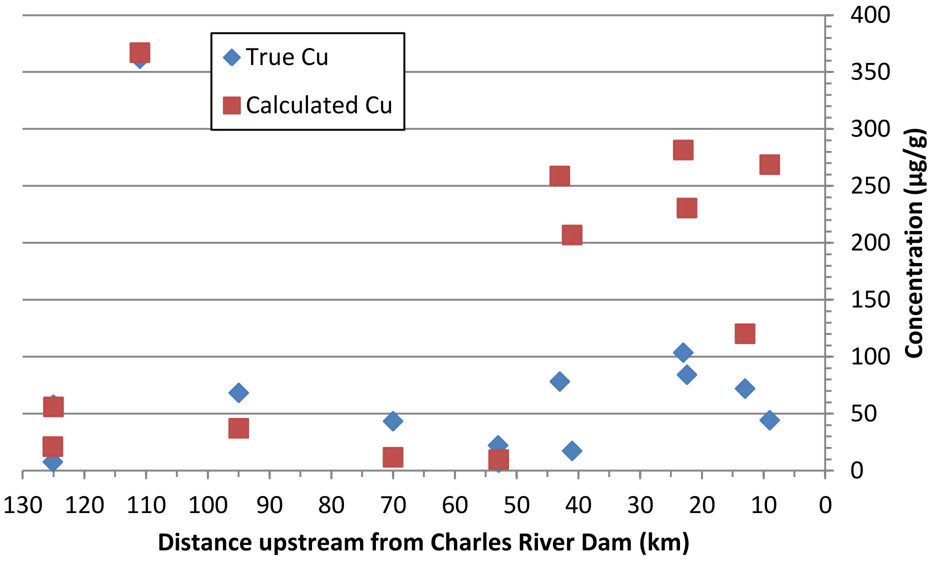


Figure 5.5. Comparison of Cu concentrations from the model results to the actual concentrations.

Figure 5.5 shows good agreement (a correlation coefficient of 0.65) with stations in the upper portion of the watershed. The model over-predicts in the lower stations indicating that perhaps the association with Cu is non-linear or that other factors are critical in binding Cu to sediment. Based on TOC and %CIT the sediments below Station #42 are shown to be under-saturated with respect to Cu by this simple model.

5.2.2. Zinc in the Charles River

The concentrations of Zn shown in Table 5.2 and Figure 5.2 are much greater than Cu with 6 of the 13 stations exceeding the NAWQA median value of 200 µg g^{-1}. The average concentration of Zn in all surface sediments (137 µg g^{-1}) exceeds the ERL concentration of 110 µg g^{-1}.

The correlation of Zn to TOC was better than Cu ($R^2 = 0.51$), but the regression of Zn normalized to TOC against either the %CIT or population density had a negative correlation and a poor R^2 (< 0.2) for each regression as well. The disagreement of the TOC normalized Zn may be due to the nature of the particulate Zn. If the source of Zn is tire wear as described in literature, it is possible that the TOC is ineffective as a measure of Zn and another factor such as grain size becomes important (Davis et al. 2001). Instead, the surface concentrations in Table 5.2 were plotted relative to the %CIT and population density in Figure 5.6 instead of TOC normalized values.

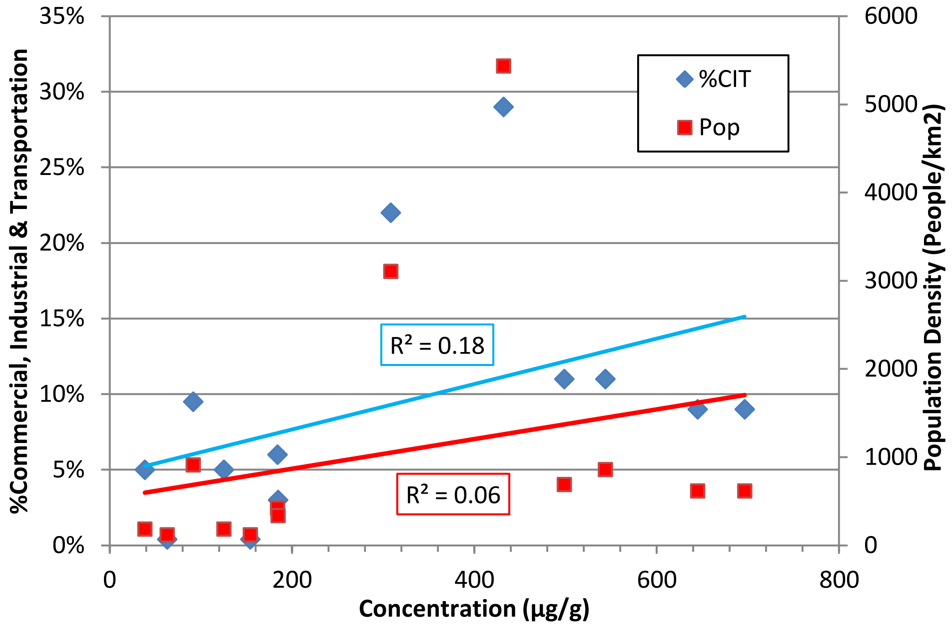


Figure 5.6. Comparison of Zn concentrations in the upper 3 cm of sediment relative to the %Commercial, Industrial, and Transportation land use and Population Density in the communities that border the Charles River.

Although the R^2 values are poor: 0.18 and 0.06, for %CIT and population density, respectively, the slope of the correlations are positive. Like Cu, Zn has consistent concentrations from the 1960's until 2000 at Station #23. Zn also shows the same relationship with respect to lower concentrations at Station #41 where the watershed is less disturbed compared to Station #23. A comparison of Zn concentrations relative to the location of each station indicates that a relationship with %CIT may exist as shown in Figure 5.7.

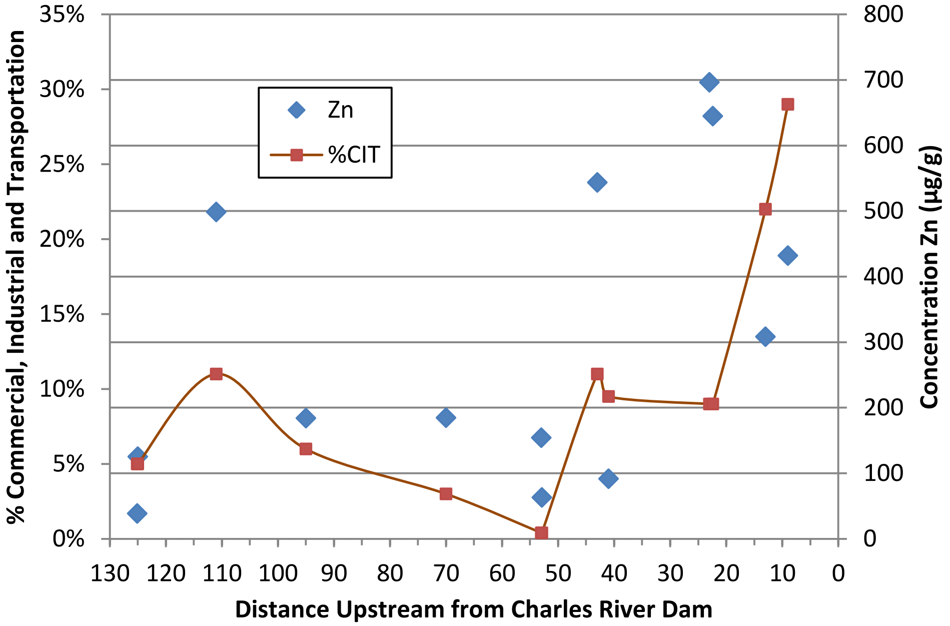


Figure 5.7. Concentration of Zn in Charles River sediment is compared to the % Commercial, Industrial and Transportation network of the communities that border the river.

Figure 5.7 demonstrates parallels between %CIT and the concentration of Zn. The %CIT is shown as a continuous line although it is recognized that the effects are more likely to be more pronounced at the discharge points and trend to the average further downstream from each discharge point. The correlation of Zn concentrations with %CIT, the better result between %CIT and population density, yielded a correlation coefficient of 0.42, but eliminating stations #13 and #9 improved the coefficient to 0.68. Station #13 is Watertown Dam, the flow of water at the time of collection was vigorous, TOC was just 1.6% and it is possible that either the grain-size or the potentially younger age of the sediments at Station #13 create the difference between Zn and %CIT. Station #9 was eliminated due to the periodic saline influence. The relationship improved on a spatial scale rather than a linear scale in the regression perhaps because the relationship is not linear, that particle density or grain size is an important factor in Zn concentration which would require focused investigation into the nature of the Zn particles and binding (Coles et al. 2004). The simple model shown to work for Cu does not work with Zn. Applying the same form of equation to the %CIT and %TOC did yield synthetic values that had a high correlation coefficient (0.81). The regression and the modeled concentrations are shown in Figure 5.8.

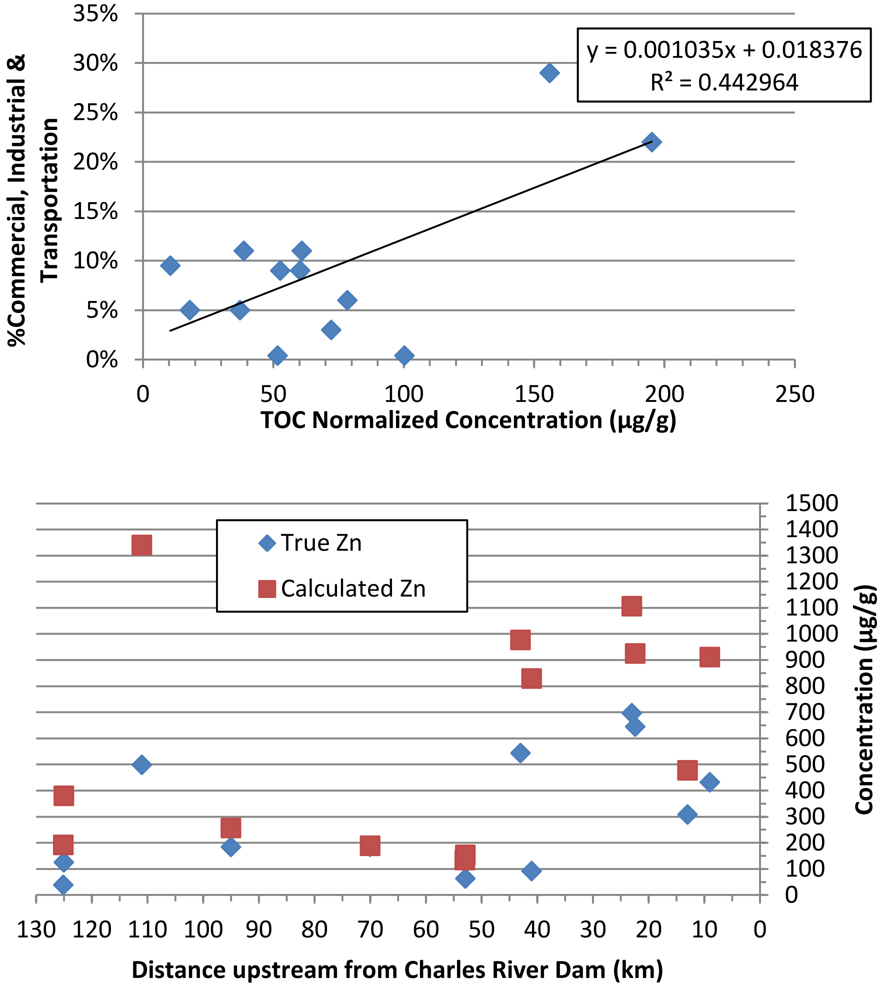


Figure 5.8. Association of Zn concentrations, normalized to TOC, with % Commercial, Industrial and Transportation land use (upper graph) and the modeled results from that association (lower graph).

A problem with this result is that the regression coefficient is greatly improved by two outliers that if removed, yield a negative slope and poor regression coefficient. Therefore, although Zn concentrations appear to be associated with %CIT in the Charles River based on TOC, the confidence in that association is weak. Other factors that govern the concentration of Zn, principally grain size and sorption, must be examined more closely to build a better model.

5.2.3. Lead in the Charles River

The concentration of Pb throughout the Charles River is pervasive. It exceeds the ERL in all but three stations and the ERM in 7 of the 13 stations. Its average concentration, 137 µg g^{-1}, exceeds the ERM and the upper quartile concentration for the NAWQA water bodies (130 µg g^{-1}).

A comparison of the high TOC and low TOC Echo Lake Pb concentrations indicates a dependence on TOC concentration. Yet the regression of Pb through the entire Charles River against TOC values found the lowest R^2 (0.38) of all four metals. Comparing the concentrations of Pb normalized to TOC found consistently poor regression coefficients indicating that Pb shared the character of Zn in that other factors were important to the concentration of Pb relative to land use as expressed by %CIT. In Figure 5.9 the concentration of Pb is plotted relative to the Station location.

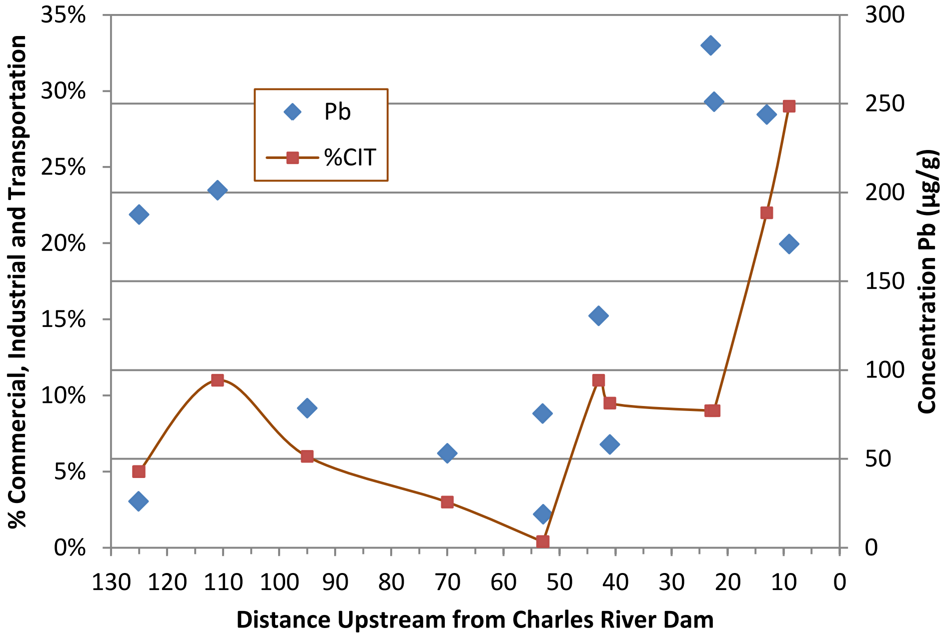


Figure 5.9. Concentration of Pb at each of the sampling stations compared to the %Commercial, Industrial, and Transportation land use in communities that border the Charles River.

Figure 5.9 shows a similar pattern to that of Zn, the correlation coefficient for Pb sediment concentration relative to %CIT was 0.51. The high concentration of Pb at Station #125 compared to downstream stations was unexpected, but may be due to the ratio of open water to the watershed and the presence of municipal trash incineration nearby (Massachusetts Department of Environmental Protection 2011). The open water of Echo Lake comprises 10% of its watershed while open water in the entire Charles River watershed is 2.6%. The Pb that is delivered through the atmosphere may be incorporated into the Echo Lake sediments with less attenuation from soils and other materials in the watershed than the remaining river.

If the direct fallout of Pb onto open water at Echo Lake is the difference, this indicates that watershed soils are an important surface in absorbing and increasing the residence time of Pb in the watershed soils, delaying the increase in sediments. The importance of this attenuation factor is shown by the rise in concentration beginning at Station #23 where storm water from a major highway network enters the river.

Station #23 is greatly affected by the nearby interstate system. Table 5.2 also shows that the lower 3 cm horizons collected at Station #23 parallel the lowering in concentration of Pb due to the leaded gas ban, with the lowest interval (9 to 12 cm deep) nearly twice the value (426 µg g^{-1}) than the top 3 cm (283 µg g^{-1}).

Attempts to obtain a predictive model similar to Cu did not work for Pb for the same reasons they did not work for Zn. The regression of Pb normalized to TOC against the %CIT was affected by two outliers which, if removed yield a negative correlation. This indicates that the concentration of Pb is dependent on factors that govern its sorption and perhaps the proximity of any discharges. The modeled results did show fair agreement for some of the stations in the upper watershed, but no agreement for Stations #42, #41, #23, and #22.4. Figure 5.10 compares the modeled to the true concentrations of Pb in the Charles River.

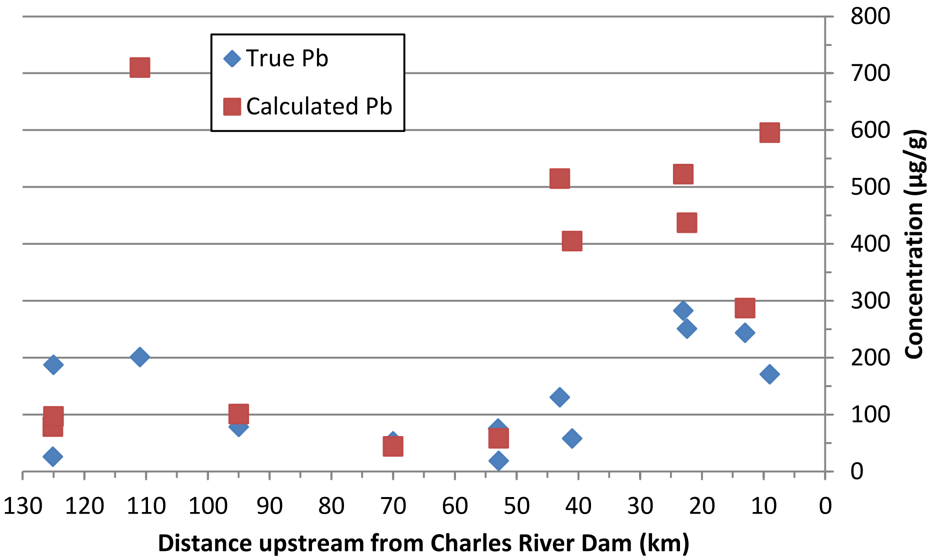


Figure 5.10. Comparison of modeled concentrations to the true concentrations of Pb at each of the sampling stations.

Similar to Zn, although some model results were close to the true values, confidence in applying those results to other locations is weak. Additional work is needed to determine causative factors that sequester Pb in sediments. Due to the declining concentrations of Pb following the ban on leaded gasoline, the assumption that all the sediments are from the same period (1990 to 2000) may affect this analysis.

5.2.4. Mercury in the Charles River

The supply of Hg to Eastern Massachusetts is primarily from atmospheric fallout from industry and power plants (Wallace et al. 2004). Anthropogenic uses of Hg have dwindled from the 1970s until the 1990s with perhaps the largest use as a fungicide and disposal of dental fillings (Hawley 1977; Wallace et al. 2004). The average concentration of Hg in the Charles River, similar to Cu, Zn and Pb, is higher than the

NAWQA median value (0.180 µg g^{-1}) which is also the ERL. Eight of the 13 Charles River stations exceed the ERL for Hg and two of those have concentrations that exceed the ERM.

Although the best regression coefficient was obtained comparing the concentration of Hg to TOC ($R^2 = 0.58$), Hg concentration also had a poor correlation between %CIT and Hg normalized to TOC. Hg concentration was negatively correlated with population density, but had its best correlation coefficient of 0.64 between the concentration of Hg and the %CIT when the values for Stations #13 and #9 are removed. Figure 5.11 displays the concentration of Hg in the upper 3 cm of sediments in the Charles River, compared to the %CIT.

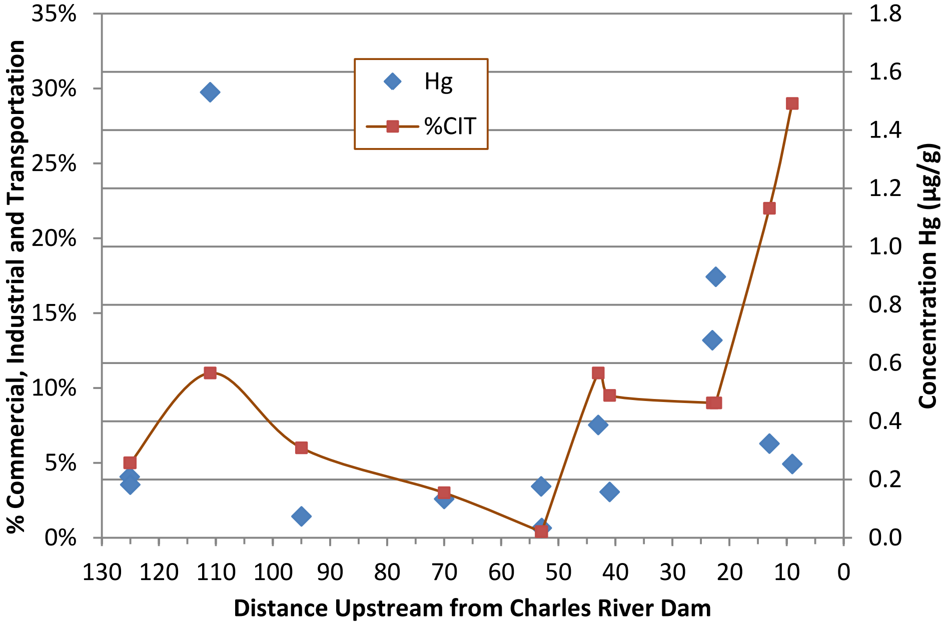


Figure 5.11. Concentration of Hg in Charles River sediment compared to the % Commercial, Industrial, and Transportation land use in the communities that border the river.

The Hg concentration at Station #111 is likely due to the erosion of sediments tainted by disposal of Hg in the paint manufacturing process that may have lasted until 1991 (Hawley 1977; U.S. Environmental Protection Agency 2012). Examining the results of Station #23 in Table 5.2 finds higher concentrations in deeper, older sediments. Concentrations in the sediment column taken at Station #41 are much lower than even the present concentrations at Station #23. Both Pb and Hg are highly regulated metals in industry and both metals have been slowly eliminated from regular consumer use since the mid-1970's (Chillrud et al. 1999; U.S. Environmental Protection Agency 2012). Because the top 3 cm are estimated to have been deposited since 1990, it would be expected that concentrations of Pb and Hg would be restricted to atmospheric fallout (Van Metre and Mahler 2003; Wallace et al. 2004). Because the concentration of Hg is low at Station #41 while downstream at Station #23 it is elevated it must be assumed that the source is atmospheric fallout.

Although the regression value was poor ($R^2 = 0.15$), the association of TOC normalized Hg to %CIT appeared to not be affected by outliers. Similar to Cu, a simple model was constructed using the equation of the regression line for the comparison of normalized Hg/TOC to %CIT inserting the appropriate values in equation 5.2 and adding the background concentration developed in Chapter 3 for Echo Lake, 0.115 µg g^{-1}.

$$\%CIT = 0.5072(Hg/TOC) + 0.0523 \qquad \text{Equation 5.2}$$

Applying this equation found that for sediment with a TOC concentration of 3%, every 1% increase in %CIT increased the concentration of Hg by approximately 0.060 µg g^{-1}. Figure 5.12 shows the values predicted using this model compared to actual values.

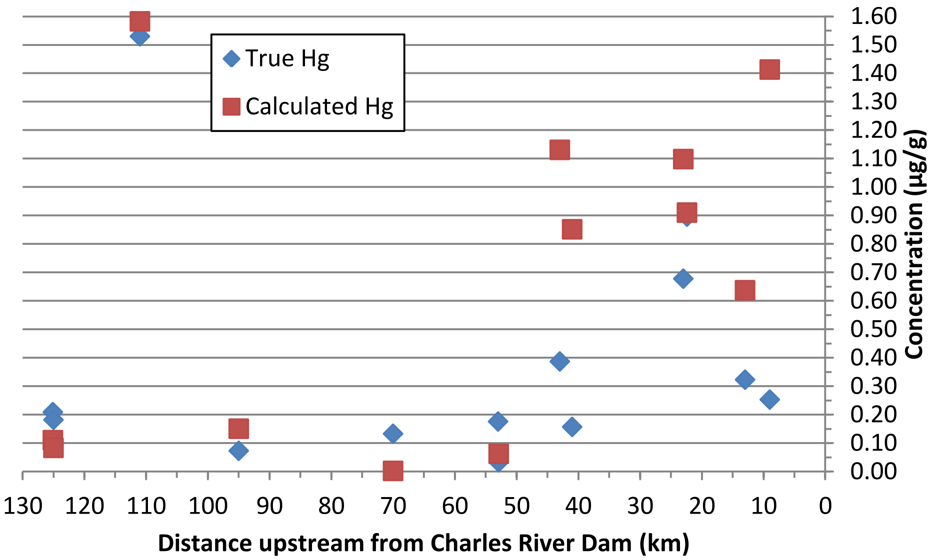


Figure 5.12. Comparison of Hg concentrations from the model results to the actual concentrations.

The modeled results, similar to Pb, over-predict the concentrations in the stations downstream of Station #42. The reason may again be different sorption properties. The reasoning that sorption may play a role is that at Station #22.4 the agreement was very good (0.896 µg g^{-1} true: 0.910 µg g^{-1} predicted) yet at Station #23 the model over-predicts. Whereas the sediment as Station #22.4 was natural, Station #23 had an oily, altered appearance. Both equation 5.1 and 5.2 are dependent upon the content of TOC. The model result for Station #23 overestimated the concentration of Hg by 62% (0.678 µg g^{-1} true, 1.098 µg g^{-1} model). Decreasing the TOC at Station #23 to 7.5% from 13.23% found excellent agreement with the model (< 1%).

Although such sensitivity lends some circumspection in the utility of the model it none-the-less indicates the importance of the substrate. Equation 5.2 was also sensitive to the %CIT. For instance, dropping %CIT from 9% to 5% at Station #23 predicted a sediment concentration below the background concentration in Echo Lake. This highlights either an inaccuracy in the model or that drainage improvements can have a significant impact on metal concentrations. Regardless, for all the metals a greater understanding of the processes that bind the metals to soils and sediment in the watershed is necessary to resolve the differences found.

5.3 Toxicity, Trends and Implications of Metals in Sediments

The concentrations of Cu, Pb, Zn and Hg exceeded toxicity standards established by regulatory agencies at many of the stations established in the Charles River. In fact, no sediment sampling point was below the regulatory standards for all metals. Table 5.3 highlights the metals that exceed regulatory standards.

Table 5.3. Surface sediment sampling points and the concentrations of Cu, Pb, Zn, Hg and TOC.

Surface Sediment Sampling Point	Station #	Cu µg/g	Pb µg/g	Zn µg/g	Hg µg/g	TOC %
Echo Lake	125	57.9	**187.6**	125.4	0.2	7.1
Echo Lake	125.1	7.6	26.1	38.7	0.2	1.0
Box Pond	111	**361.6**	**201.3**	**498.6**	**1.5**	13.0
Walker St	95	68.3	78.6	184.2	0.1	2.4
Bridge St - Sherborn	70	43.4	53.2	184.7	0.1	2.6
Cocharan Dam	53	22.1	75.6	154.3	0.2	3.0
USGS station	52.9	7.0	18.9	63.2	0.0	0.6
Ames Street 0-3	43	78.2	**130.6**	**543.7**	**0.4**	8.9
Neponset River	41	17.3	58.2	91.7	0.2	8.8
CRWA	23	**103.6**	**282.8**	**696.5**	0.7	13.2
CRWA	22.4	84.1	**251.1**	**644.9**	**0.9**	10.7
Watertown Dam	13	72.0	**243.9**	**308.4**	**0.3**	1.6
Elliott Bridge	9	44.2	**171.0**	**432.1**	0.3	2.8
ERL		41	55	110	0.180	
ERM		190	99	550	1.060	
NAWQA Range High		85	130	350	0.27	

Exceeds ERL	🟨	
Exceeds ERM	🟪	
Exceeds NAWQA Range High Concentration	**187.6**	(outlined & bold)
High TOC Station	7.1	

Table 5.3 would appear to indicate that the Charles River is highly toxic to aquatic life. Yet, toxicity testing of sediments by EPA in 1996 determined that sediments in several locations near those collected as part of this research were not toxic because the mineral form of the metal was not bio-available (U.S. Environmental Protection Agency 1997). However, the potential for the re-suspension of these sediments may introduce them into environments where the mineral form is altered to a more bio-available form

and toxicity may occur (U.S. Environmental Protection Agency 1997; Rogers et al. 2002).

The presence of high concentrations of metals in the Charles River sediments can pose hazards to aquatic life and present a future management problem. Determining the sources of continued metal deposition to sediments must be considered in restoring the river.

Although testing has found the high concentrations of metals in the Charles River do not pose a threat of toxicity to test organisms, the paradigm of exposure of aquatic organisms may have flaws. Other research has found that the fine veneer of sediments associated with vegetation may create an environment where sediment metals were less likely to be bound by sulfides and therefore more bio-available (Rogers et al. 2002). The important aspect of the above, to this research, is that there exists a reservoir of sediments in Box Pond and other downstream locations that contain metals that may be suspended and create conditions downstream that are toxic to aquatic life and degrade water quality.

Since 1995 EPA has spent considerable amounts of money and effort to make the Charles River safe for boating and swimming, with respect to bacterial counts, 100% of the time. That goal was to be achieved by 2005, but has not yet been attained (U.S. Environmental Protection Agency 2005). EPA has since addressed other parameters to restore the general health of the river. One such effort is reducing phosphorus to minimize blue-green algae blooms (U.S. Environmental Protection Agency 2008). However, the approach taken thus far has not examined the interplay of sediments with water quality. Excess metal concentrations have been shown to impact the diversity of bacterial colonies (Singleton and Guthrie 1977). The sorption characteristics of the river sediments may control the concentration of metals nearly as much as the inputs into the river. Therefore, examining the behavior of metals and the sorption properties of sediments in the Charles River may assist in its restoration.

Another consideration is that as many of the dams along the Charles River fill with sediment, the need to manage or dispose of these sediments during dredging or dam removal projects must be considered (Doyle et al. 2003). Many of the dams along the Charles River are the remains of former mills and are therefore sometimes greater than 100 years old (McAdow 1992). For instance, the average depth of Box Pond was estimated to be 1.5 meters in depth in January 2001. At a sedimentation rate of 0.3 cm yr^{-1}, determined in Chapter 4, more than half the existing water column of Box Pond will be lost by 2035 without dredging. Dredging may be conducted if conditions deteriorate in the stream and sufficient money is available. If dredging occurs the sediment will certainly contain high concentrations of metals and potentially other contaminants that will require special handing in their disposal.

5.4 CONCLUSIONS

The concentrations of Cu, Zn, Pb, and Hg in Charles River sediments deposited in the last ten years were determined to exceed the range of concentrations for those metals in other, similar urban water bodies and exceed regulatory guidelines established to assess toxicity to aquatic organisms in much of the river.

The concentrations of Cu, Zn, Pb and Hg were a function of both population density and %CIT. The better associations were found with %CIT and, using TOC concentrations, simple regression models were developed to predict Cu and Hg concentrations in sediment. Disagreements between the modeled results and the actual results appear to be a function of sorption characteristics. The association with %CIT and the sensitivity of the model with respect to %CIT signals the importance of storm water and its flow into surface waters such as the Charles River. The model indicates that minimizing storm water runoff in the area of the intersection of Interstate Routes 90 and 95 may improve conditions in the Charles River.

CHAPTER 6

THE CHARLES RIVER, SUMMARY AND CONSIDERATIONS

Abstract

The analysis of dated sediment cores and surface sediment samples taken in the Charles River found that changing land use in the Charles River watershed increased the concentration of metals in sediments. Land use, measured as the percentage of Commercial, Industrial and Transportation network, resulted in increases of storm water flow which decreased the residence time of metals in the upland areas of the watershed. The impoundments created along the river received these metals, sorbed to sediments, and deposited them behind the dam thus increasing their residence time within the Charles River. Simple models indicated that improvements in storm water management may reduce the concentrations of metals that may cause toxicity in aquatic organisms. Restoring the Charles River and other similar, urban rivers is desirable as these water ways are increasingly used for recreation. To design cleanup efforts for urban rivers will require different monitoring and analysis strategies to determine sediment inventories and the present fluxes of metals into water ways. Understanding the sources and fluxes of metals to the storm water is needed to restore the Charles River.

6.1 Introduction

The Charles River is a signature element of Boston, but historically was one of the more polluted waterways in the nation (Breault et al. 2000; Haglund 2003). As such, EPA and other regulatory agencies have been attempting to restore it for public use (Hill 1975; U.S. Environmental Protection Agency 2005).

The cleanup effort intensified in 1995 with creation of the Clean Charles 2005 program. The goal of the program was to make boating and swimming in the Charles River Basin in Boston safe 100% of the time, with respect to surface water concentrations of *Escherichia coli* bacteria, by 2005. In 1995, the first year of monitoring, the river was safe for boating 39% and swimming 19% of the time. Steady progress occurred but reached an asymptote short of that goal and as of 2009 the river was safe for boating 92% and swimming 62% of the time (U.S. Environmental Protection Agency 2005).

EPA has worked to eliminate discharges to the Charles River, but has since determined that other factors are partly responsible for the continued poor water quality. EPA expanded efforts to achieve the 100% safe goal by increasing storm water regulations and focusing on nutrients in the upper watershed to address cyanobacteria (blue-green algae) (Tetra-Tech Inc. 2009; U.S. Environmental Protection Agency 2010; U.S. Environmental Protection Agency 2011).

EPA's assessment of the Charles River has been primarily through surface water monitoring of a narrow range of parameters (U.S. Environmental Protection Agency 2005). Surface water sampling has utility, but provides only a snapshot of a dynamic system and does not allow for a discrimination of contaminant sources. Determining the sources of impairment and addressing them will allow a more efficient means of restoring the river. Sediments are the primary substrate in contact with surface water and therefore have the greatest capacity to affect long-term water quality (Boudreau and Jorgensen 2001; Ren and Packman 2004). Although there are few links between sediment quality with respect to metals and microbial communities, some impairment of microbial diversity due to high concentrations of metals has been demonstrated (Singleton and Guthrie 1977). Metals may also influence the aquatic communities and water quality (Luoma and Carter 1991; Peeters et al. 2000). Therefore, a more thorough characterization of sediments may better address problems with water quality in the Charles River.

Because of the particle-reactive nature of metals and their tendency to be incorporated into sediments, sediments provide a means of assessing changes and trends of metal concentrations in waterways (Olsen 1979; Olsen et al. 1982). Dated sediment cores allow the connection of historical land use changes to changes in metal concentrations in sediment.

This dissertation determined the concentration trends of metals in sediments with respect to certain land uses. Chapters 3 and 4 discussed the analytical results of two sediment cores collected in the headwaters of the Charles River. These chapters described the effect of different land uses and sources, as well as the processes that affected sediment metal concentrations. The land use types evaluated included residential development, established urban areas, and industrial and commercial activities. Chapter 5 extended the conclusions drawn from Chapters 3 and 4 and determined relationships between land use and metal concentrations in sediments throughout the river in a more limited time frame using surface sediments.

Because the Charles River and other rivers in urban areas are increasingly looked upon as recreational resources, characterizing all components of a waterway become important (Haglund 2003). A better understanding of the relationship between land use, population density and the concentration of metals in sediments will enable more effective regulation and management of discharges to all rivers.

Taken together, Chapters 3, 4, and 5 of this dissertation suggest new approaches to monitoring and managing urban rivers. Sediment sampling, and in particular the analysis of dated cores, is a missing component of the Charles River monitoring program. Properly assessed, sediment cores can be used to set regulatory standards and plan restoration efforts. Increased monitoring of other sources and discharges to the river to determine the fluxes of metals and other contaminants can also clarify the sources of impairment. This research can be used as a case study of the Charles River Watershed, a typical urban watershed, to suggest the use of dated sediment cores in the assessment of watershed health.

6.2 Sampling and Analysis

The samples for this dissertation consisted of two sediment cores and 11 surface sediment grab samples. The sediment cores were collected in two impoundments on the Charles River, Echo Lake and Box Pond, and were 35 and 30 cm in length, respectively. Each sediment core was sectioned at 5 mm intervals and absolute dates were assigned to those intervals through radiometric dating techniques using ^{210}Pb, ^{214}Pb and ^{137}Cs. The surface sediment samples consisted of the upper 3 cm of sediment and were collected at various intervals along the Charles River. The 5 mm sediment core intervals and the 3 cm thick surface sediment samples were processed and analyzed for TOC, Al, Fe, Mn, Hg, Pb, Cd, Cu, Zn, Ag, Sc, Sr, As, Cd, Sn, Cr and Co. Techniques and quality assurance and quality control are discussed in Chapter 2.

Weighing into each evaluation was consideration of the physical and chemical factors that may affect metal concentration and deposition rates as those metals traverse the watershed, enter the waterways and are then deposited. Physical factors considered included alterations to waterways such as dams and storm water management. Chemical factors included the addition of metals through atmospheric fallout, direct discharges, and the concentration of TOC as well as the potential chemical changes imparted by the physical changes listed in Chapter 1.

Federal and State agencies begin their assessment of sediment metal concentrations based on their potential for toxicity. These guidelines include the Effects Range Low (ERL) and Effects Range Median (ERM). Within this research seven of the analyzed metals have established values to assess toxicity: Hg, Pb, Cd, As, Zn, Cu, and Cr. The general application is that concentrations of these metals that are below the ERL rarely exhibit toxicity, while concentrations exceeding the ERM usually have toxic effects and additional sampling and other assessments are performed (Ingersoll et al. 1996; National Oceanic and Atmospheric Administration 1999). In this dissertation the ERL and ERM concentrations were used as a benchmark to evaluate the severity of metal contamination and the importance of any concentration trends.

6.3 Echo Lake Sediment Core

Echo Lake, the headwaters of the Charles River, is a drinking water reservoir that has been protected for more than 100 years. Yet, analysis of the Echo Lake sediment core found metal concentrations increased by anthropogenic activities. Concentrations of Pb and Hg determined in Echo Lake sediments deposited during the 19th century demonstrated the importance of atmospheric fallout. The concentrations of Pb from 1860 to 1880 were increased by emissions from an industrial area outside of the Echo Lake watershed. Increases in Hg concentrations during three separate intervals: 1872, 1887 to 1889, and 1903, appeared to be the result of local atmospheric discharges during construction of a railroad line and two dams. The concentrations of both metals in these specific intervals of sediments exceed the modern-day ERL. This result not only demonstrates the impact of atmospheric deposition, but also that older sediments are not necessarily free of anthropogenic effects even in remote water bodies.

The Echo Lake watershed transitioned from a rural, undeveloped area, to a residential area beginning in 1969. Atmospheric deposition remained an important source for metals in Echo Lake sediments, but the residential development was also found to impact the concentrations of metals in sediment despite a 500 m unaltered buffer zone surrounding the lake.

Analysis of the Echo Lake sediment core determined that despite a 500 m buffer zone, residential development in the watershed since 1970 had increased the concentration of several metals to exceed regulatory standards for aquatic life and altered the lake ecology. The deposition rate of sediments increased four-fold over natural conditions after 1969, perhaps due to poor erosion control during construction of the roadways for the subdivisions, and appears to be responsible for the elimination of rooted aquatic plants in 1984 that had populated the lake bottom since 1882. The excess sedimentation may have also increased the supply of other nutrients that created a bloom of floating nuisance aquatic vegetation in 1990 that required treatment with copper sulfate.

The source of anthropogenic Hg, Pb, and Cd in Echo Lake appears to be atmospheric fallout that is collected by storm water and directed to the lake. The implications of these findings in Chapter 3 are that although changes in land use may introduce additional allochthonous metals, one of the primary changes is the alteration of the residence time of metals that are delivered by atmospheric fallout. Hg, Pb and Cd that would otherwise be retained in watershed soils are gathered on impermeable surfaces and directed to Echo Lake. The residence time of each metal is decreased in the upland portions of the watershed, but increased in Echo Lake by incorporation into sediment.

Once incorporated into the sediment these metals may become exposed to the environment through desorption during redox changes or resuspension (Simpson et al. 1998; Morford and Emerson 1999). Retaining these metals behind an impoundment increases the opportunity for these metals to affect aquatic organisms and sediment quality (Luoma and Carter 1991; Rogers et al. 2002).

6.4 Box Pond Sediment Core

Although Box Pond is a short distance downstream from Echo Lake, it received industrial discharges, storm water runoff from a large urban area, and treated sewage from the Milford publically-owned treatment works (POTW) over a century. The result is that Box Pond contains sediments that have significantly higher concentrations of metals in sediments than the sediments deposited in Echo Lake at the same time.

The largest impact to metal concentrations in the Box Pond sediments was from paint manufacturing. Beginning in the 1940’s Hg, Pb, Cd, and As increase in concentration, peak in 1970, and then begin to decrease in concentration. The reason for the decrease in concentration is unknown, but the concentrations of Pb and Cd exceed the ERL and the concentration of Hg exceeds its ERM in all sediments deposited after the 1970 peak in concentration.

The Milford POTW also exerted some influence on sediment metal concentrations. One of the horizons in the Box Pond sediment core, 1987, was identified as having the highest concentrations for the majority of the metals analyzed during this research. That date corresponded to work performed at the Milford POTW. The source of these metals was either discharge materials from the POTW or re-suspension of older sediments when the discharge was re-directed.

Despite the cessation of the industrial discharges, compared to the background location in Echo Lake, sediment concentrations of Hg, Pb, Cr, Sn, and several other metals remained higher than would be expected. It was concluded that the source of these concentrations was likely relict sediments deposited in the Charles River and eroded or re-suspended and deposited in Box Pond.

6.5 Charles River Surface Sediment Samples

The results of the analysis of the Box Pond sediment core led to the hypothesis that sediments downstream of Box Pond may be influenced by the high concentrations found in Box Pond. The sampling of surface sediments throughout the remainder of the Charles River focused on the concentrations of Hg, Pb, Cu and Zn in the upper 3 cm of sediment that were assumed to represent sediments deposited between 1990 and 2000. Deeper samples were obtained at two stations that were believed to be diagnostic of conditions over the long-term.

It was determined that the high concentrations of Hg, Pb, Cu and Zn found in the Box Pond sediment core decreased dramatically downstream of that location. This indicated that impoundments serve as effective sediment reservoirs and increase the residence time of metals in a river.

The concentrations of the surface sediment metals were found to be a function of the percentage of Commercial, Industrial, and Transportation network land use (%CIT) or roughly an estimate of impermeable coverage in a community. The %CIT and population density were chosen as the variables to examine because they are readily available statistics and have been shown to have a significant correlation with the health of aquatic organisms in other water bodies (Chalmers et al. 2007; Coles et al. 2010). Simple regression models were constructed for Cu and Hg that indicated that the concentration of TOC and the %CIT were good predictors of the concentration of those metals. The models also indicated that the concentrations of those metals were sensitive to the %CIT implying that improvements to storm water management may reduce the concentration of those metals.

The association of Zn and Pb with TOC and %CIT appeared favorable, but the distribution of the data did not allow for a model to be constructed that would lend any confidence to the results. None-the-less, the association shown by Zn and Pb with %CIT indicates that they share a similar relationship and that improved storm water management would likely yield improvements to sediment metal concentrations.

The regression models also demonstrated that the sorption properties of metals need better characterization in such systems. Further examination of the effects on grain size, TOC, and other ligands in areas that receive storm water would further refine the models presented for Cu and Hg.

6.6 Considerations and Future Efforts

The relationship between land use and the effects on metal concentration has been determined to be relevant with respect to stream health in several other water bodies (Coles et al. 2004; Chalmers et al. 2007). What is novel in this research are the demonstrated advantages of collecting dated sediment cores to compare the concentration trends of metals to changes in land use. The sediment cores provided an indication of which metals to focus on during an examination of downstream surface sediments. The results of sediment coring also suggest strategies in sampling: examine flowing portions of the river likely to be eroded and historic deposits of sediment. The observations made during this work suggest methods that regulatory agencies could employ to improve the assessments of urban rivers and may provide future lines of research.

The goal of monitoring and regulation is to assess and prevent contamination. The data can assist in the restoration of a contaminated river, such as the Charles River, to conditions safe for human health and the environment. Sediments reflect the long-term conditions in a surface water body and can influence water quality (Olsen et al. 1982; National Oceanic and Atmospheric Administration 1999; DiToro 2001). Quantifying the relationship between activities in a watershed and the sediment quality in the river is dependent upon understanding the character of the existing sediments, atmospheric contributions of contaminants, the collection and management of storm water, and the fluxes of metals and other contaminants.

Environmental monitoring conducted by regulatory agencies, such as the EPA's monitoring of the Charles River, has examined a narrow range of contaminants from current sources, but rarely determines the historical inputs to the river that sediment may contribute. Pond and lake sediments provide a record of the past and a legacy for the future if the sediment is remobilized or needs to be managed such as during dredging or dam removal. Dated cores from impoundments on a river, such as those in this research, can help determine the inventory of contaminants in a river and how past changes have affected concentrations of contaminants or the conditions in a water body.

For instance, the Echo Lake sediment core demonstrated that an understanding of the effects of poor erosion control and storm water could have prevented the extirpation of the natural aquatic vegetation and a bloom of nuisance vegetation which necessitated treatment of a lake with copper sulfate. The weed treatment caused Cu to exceed the ERL in the sediments in a drinking water reservoir.

A dated sediment core can also supply detailed information about the inventory of sediments and the rate of deposition of metals and other contaminants in the past. In managing a watershed, regulatory agencies should determine the contaminants that exist in the current sediments, the flux of natural and anthropogenic metals to sediments, and be able to attribute portions of that flux to different sources. The purpose would be to create plans to address the largest contributions of metals and contaminants to sediments.

Collection and analysis of sediments requires a viable dating scale that ties the results to knowledge of the historic activities. The history of activities in the Box Pond watershed proved to be critical to understanding the sources of metals in those sediments. Knowledge of past waste disposal and manufacturing processes is needed to better focus sampling efforts. The history of many industries, some now abandoned and forgotten, along with their waste stream and discharge histories on the remainder of the Charles River are unknown.

Targeted grab samples can support the conclusions drawn from the sediment cores or reinforce those results. Sampling of discrete sources such as atmospheric fallout, POTWs and storm water infrastructure should be performed in detail to determine sources and the contribution of those sources. For instance, POTWs receive wastes from residential users and industrial sources that have a pre-treatment program prior to the discharge to the POTW. Moreover, significant fractions of the discharge from a POTW, such as total suspended solids, are not analyzed. The largely unknown contribution of a POTW with respect to metals may be very significant.

The critical factor for many of the metals in the Charles River, especially Hg and Cu, was storm water. But storm water is only a conveyance. The sources of anthropogenic metals include atmospheric fallout and the abrasion of man-made surfaces that contain metal. The %CIT, or impermeable surface, alters the residence time of anthropogenic metals in the watershed. As soils that collect metals and slowly release them over time are replaced by impervious surfaces, as represented through %CIT, the residence time of those metals are decreased in the upland reservoir. These metals are then conveyed quickly to surface water.

If the river is free-flowing the grain size is increased and the TOC content generally decreased. But with the Charles River and other rivers in the eastern United States containing many dams, the impoundments retain fine-grained, high TOC sediments that contain high concentrations of metals. The residence time of metals entrained in storm water is increased behind those dams and therefore available over a greater time to affect aquatic life and stream health in general. Because dam removal has become more common to address impaired (sediment-filled) or old and unsound dams, an opportunity exists to determine the effects of metal concentrations and stream health as more of the these sites become available (Doyle et al. 2003).

Therefore, to decrease the concentrations of metals in sediments three avenues appear to be available: reduce the sources, increase the residence time of metals in the upland portion of the watershed, or reduce the residence time of fine-grained, high TOC sediments in the river. A combination of the above would further address the problem.

This research examined the behavior of metals in one reservoir of metals in the Charles River watershed, the sediment column, against the changes in another reservoir, the upland portions of the watershed. Further characterization of this interaction could focus on the supply of metals, how they are retained in the upland reservoir, and the sorption properties in the sediment reservoir. For instance, a focus on Hg could examine the rate of emission by industries, the fallout flux, the retention in soil and on impermeable surfaces, and its conveyance to surface water. Chapter 5 found that in sediment the sorption of Hg needed further characterization to refine the predictive model. Determining the inventory and flux of metals or other contaminants in the atmosphere, soil, groundwater, surface water, and sediments moving through a watershed would assist regulatory agencies in assessing the impacts to waterways and be a logical extension of this research.

APPENDIX I

TOTAL ORGANIC CARBON ANALYSIS

Table I.1. Total Organic Carbon and Nitrogen for the Echo Lake Core. This table further describes TOC on a mole basis and as a ratio with Nitrogen .

Echo Lake Sample	Total Organic Carbon			Molality (moles/kg)		Mole Ratio
Depth	**%C**	**±**	**%N**	**C**	**N**	**C:N**
upper floc	9.51	0.11	0.97	7.92	0.69	11.43
lower floc	8.72	0.15	0.8	7.26	0.57	12.71
0	7.67	0.16	0.64	6.39	0.46	13.98
0.5	7.48	0.16	0.61	6.23	0.44	14.30
1	6.92	0.08	0.55	5.76	0.39	14.67
1.5	5.22	0.08	0.43	4.35	0.31	14.16
2	6.93	0.11	0.56	5.77	0.40	14.43
2.5	8.61	0.11	0.69	7.17	0.49	14.55
3	6.26	0.08	0.44	5.21	0.31	16.59
3.5	6.8	0.10	0.48	5.66	0.34	16.52
4	7.08	0.09	0.48	5.89	0.34	17.20
4.5	6.36	0.11	0.46	5.30	0.33	16.12
5	6.58	0.08	0.47	5.48	0.34	16.33
5.5	6.34	0.10	0.44	5.28	0.31	16.80
6	6.52	0.11	0.44	5.43	0.31	17.28
6.5	6.46	0.11	0.45	5.38	0.32	16.74
7	6.55	0.08	0.44	5.45	0.31	17.36
7.5	7.1	0.13	0.51	5.91	0.36	16.23
8	6.11	0.06	0.4	5.09	0.29	17.81
8.5	6.11	0.11	0.42	5.09	0.30	16.96
9	6.26	0.11	0.41	5.21	0.29	17.81
9.5	6.14	0.11	0.41	5.11	0.29	17.46
10	5.95	0.13	0.41	4.95	0.29	16.92
10.5	5.77	0.08	0.38	4.80	0.27	17.71
11	5.92	0.07	0.36	4.93	0.26	19.18
11.5	5.75	0.09	0.35	4.79	0.25	19.16
12	6.07	0.12	0.42	5.05	0.30	16.85
12.5	5.85	0.09	0.35	4.87	0.25	19.49
13	5.81	0.11	0.36	4.84	0.26	18.82
13.5	6.88	0.07	0.37	5.73	0.26	21.68
14	7.3	0.12	0.42	6.08	0.30	20.27
14.5	7.47	0.12	0.46	6.22	0.33	18.94
15	8.36	0.09	0.48	6.96	0.34	20.31
15.5	9.51	0.12	0.57	7.92	0.41	19.46
16	9.26	0.16	0.6	7.71	0.43	18.00
16.5	9.71	0.20	0.64	8.08	0.46	17.69

Echo Lake Sample	Total Organic Carbon			Molality (moles/kg)		Mole Ratio
Depth	%C	±	%N	C	N	C:N
17	10.89	0.09	0.68	9.07	0.49	18.68
17.8	11.66	0.16	0.76	9.71	0.54	17.89
18.3	11.51	0.16	0.75	9.58	0.54	17.90
18.8	12.33	0.20	0.76	10.27	0.54	18.92
19.3	12.25	0.24	0.78	10.20	0.56	18.31
19.8	12.16	0.30	0.83	10.12	0.59	17.08
20.3	13.6	0.26	0.86	11.32	0.61	18.44
20.8	16.88	0.35	1.17	14.05	0.84	16.82
21.3	20.59	0.50	1.43	17.14	1.02	16.79
21.8	23.76	0.45	1.66	19.78	1.19	16.69
22.3	25.16	0.31	1.56	20.95	1.11	18.81
22.8	29.93	0.38	1.53	24.92	1.09	22.81
23.3	27.16	0.43	1.51	22.61	1.08	20.98
23.8	25.95	0.33	1.74	21.61	1.24	17.39
24.3	25.22	0.32	1.78	21.00	1.27	16.52
24.8	26.92	0.41	1.98	22.41	1.41	15.86
25.3	23.5	0.32	1.65	19.57	1.18	16.61
25.8	26.32	0.31	1.77	21.91	1.26	17.34
26.7	24.54	0.32	1.71	20.43	1.22	16.74
27.2	30.01	0.43	1.96	24.99	1.40	17.86
27.7	26.3	0.28	1.71	21.90	1.22	17.94
28.2	25.04	0.30	1.67	20.85	1.19	17.49
28.7	26.48	0.48	1.93	22.05	1.38	16.00
29.2	27.08	0.35	1.85	22.55	1.32	17.07
29.7	28.58	0.38	1.83	23.79	1.31	18.21
30.2	27.77	0.53	1.84	23.12	1.31	17.60
30.7	30.16	0.31	1.64	25.11	1.17	21.45
31.2	27.26	0.41	1.75	22.70	1.25	18.17
31.7	26.36	0.42	1.67	21.95	1.19	18.41
32.2	24.44	0.29	1.54	20.35	1.10	18.51
32.7	24.66	0.25	1.53	20.53	1.09	18.80
33.2	25.21	0.38	1.67	20.99	1.19	17.60
33.7	26.84	0.36	1.72	22.35	1.23	18.20
34.2	26.73	0.39	1.68	22.25	1.20	18.55
34.7	27.65	0.53	1.82	23.02	1.30	17.72
35.2	29.4	0.50	1.99	24.48	1.42	17.23

Table I.2. Total Organic Carbon and Nitrogen from the Box Pond Core.

Box Pond Sample	**Total Organic Carbon**			**molality (moles/kg)**		**Mole Ratio**
Depth	**%C**	**±**	**%N**	**C**	**N**	**C:N**
0 to 1 cm	13.01	0.22	1.07	10.83	0.76	14.18
2	13.12	0.09	1.13	10.92	0.81	13.54
3	12.97	0.11	1.22	10.80	0.87	12.40
4	12.57	0.11	1.15	10.47	0.82	12.75
5	12.29	0.11	1.21	10.23	0.86	11.84
6	12.82	0.14	1.23	10.67	0.88	12.15
7	8.19	0.14	0.81	6.82	0.58	11.79
8	13.54	0.15	1.3	11.27	0.93	12.15
9	15.29	0.21	1.24	12.73	0.89	14.38
10	13.72	0.21	1.09	11.42	0.78	14.68
11	15.4	0.15	1.34	12.82	0.96	13.40
12	13.92	0.17	1.2	11.59	0.86	13.53
13	14.75	0.96	0.91	12.28	0.65	18.90
14	15.34	0.21	0.96	12.77	0.69	18.63
15	14.01	0.15	0.92	11.66	0.66	17.76
16	14.08	0.24	0.91	11.72	0.65	18.04
17	12.37	0.16	0.84	10.30	0.60	17.17
18	11.34	0.13	0.72	9.44	0.51	18.37
19	10.33	0.14	0.72	8.60	0.51	16.73
20	8.76	0.10	0.5	7.29	0.36	20.43
21	7.82	0.14	0.57	6.51	0.41	16.00
22	8.17	0.14	0.55	6.80	0.39	17.32
23	8.8	0.13	0.45	7.33	0.32	22.80
24	6.28	0.12	0.39	5.23	0.28	18.78
25	4.81	0.09	0.3	4.00	0.21	18.70
26	4.51	0.08	0.27	3.75	0.19	19.48
27	5.06	0.05	0.23	4.21	0.16	25.66
28	0.93	0.02	0.04	0.77	0.03	27.11
29	0.27	0.00	-0.04	0.22	0.00	
30	0.75	0.01	-0.05	0.62	0.00	

Table I.3. Organic Carbon and Nitrogen Analysis, Charles River, Eastern Massachusetts.

Station	River (km)	Strata Type	Depth (cm)	TOC %	N %
Echo Lake	0	Sand	0-3	1.04	0.05
Walker St	30	Silt	0-2	2.35	0.12
			2 - 5	1.86	0.09
Bridge St - Sherborn	55	Gravel	0-3	2.56	0.16
Cocharan Dam	72	fine sand	0-3	2.99	0.19
USGS station	72.1	Sand	0-3	0.63	0.00
Ames Street	82	Muck	0 - 3	8.93	0.55
			3 - 6	9.99	0.49
Neponset River	84	Silt	0 - 3	8.75	0.47
			3 - 6	19.95	0.97
			6 - 9	27.02	1.24
Charles River Watershed Association (CRWA), boat dock	102	Silt	0 - 3	13.23	0.92
			3 - 6	9.76	0.63
			6 - 9	9.34	0.55
			9 - 12	9.57	0.47
CRWA	102.6	Silt	0-3	10.70	0.72
Watertown Dam	112	Silt	0-3	1.58	0.05
Elliott Bridge	116	Silt	0 - 2	2.77	0.12
		Clay	2 - 6	2.13	0.05

Table I.4. Calibration Blanks

Time	Carbon %	Nitrogen %
1127	0.020	0.100
1158	0.010	-0.030
1323	0.210	0.130
Avg	0.080	
SD	0.11	
n =	3	

Table I.5. Analytical Blanks

Time	Carbon %	Nitrogen %
1220	-0.460	-0.080
1225	0.090	-0.230
1415	0.230	-0.390
1518	0.320	-0.200
1626	0.000	0.000
1218	0.160	-0.600
1454	0.470	-0.520
1119	0.590	-0.590
1221	0.030	-0.110
1332	-0.67	-0.2
1528	0.03	-0.55
1640	0.030	0.470
0	0.250	-0.310
1718	0.550	-0.080
1754	1.380	0.120
1440	-0.050	0.190
0	0.090	-0.590
33	0.380	-0.750
130	0.140	-0.630
232	-0.040	-0.710
Avg	0.176	SD 0.41

Table 1.6. Difference from Standard Reference Material

Time	Carbon	Nitrogen
1153	0.9%	1.3%
1230	-0.2%	-0.3%
1420	0.8%	0.9%
1523	-0.1%	-0.9%
1631	-0.3%	-0.7%
1223	-0.1%	0.0%
1500	4.0%	2.6%
0	0.2%	-0.5%
1226	0.4%	-0.2%
1645	0.1%	0.8%
1621	1.3%	0.9%
1723	1.9%	1.6%
1759	1.4%	-0.2%
1445	0.4%	-8.6%
2047	-1.1%	0.6%
2208	-0.6%	-1.0%
38	-0.9%	1.7%
135	0.0%	0.2%
237	0.7%	1.1%
Avg	0.005	
SD	0.01	

Table I.7. Comparison of Duplicates

	%C	%N	%H	% Diff OC
e17d	2.852	6.1	0.31	-6.87%
e17	2.561	6.55	0.44	
e31d	3.38	8.01	0.39	9.73%
e31	3.283	7.3	0.42	
e43d	3.035	13.06	0.73	-3.97%
e43	3.762	13.6	0.86	
e55d	2.197	24.58	1.64	0.16%
e55	2.595	24.54	1.71	
e66d	2.29	26.09	1.51	6.75%
e66	2.3358	24.44	1.54	

APPENDIX II

METAL ANALYSIS

II.1. Inductively Coupled Plasma – Mass Spectrometer

Metals, with the exception of mercury, were analyzed on an Inductively Coupled Plasma-Mass Spectrometer ICP-MS. For each run, the standard calibration curves were checked to ensure that the standard recoveries were sufficient for both the initial and final curves. The net intensity values were blank adjusted and then adjusted according to the calibration curve that provided the best fit to standards, the QC check standards that were placed at every tenth analysis, and the standard reference materials. Matrix effects were checked via samples spiked with known concentrations of prepared aqueous standards. Analytical accuracy was further ensured by comparison of digestion duplicates and analytical replicates. The concentration of each metal is reported below.

Table II.1. Box Pond limits of detection, average recovery for the SRMs, and the average of the analytical and digestion duplicates.

	LOD[1]	**Avg. BCSS-1 SRM Recovery**	**Avg. PACS-1 SRM Recovery**	**Average of Analytical Replicates**	**Average Difference of Digestion Duplicates**
^{27}Al	0.12 mg/g	103.2%	100.2%	1.50%	6.68%
^{57}Fe	0.01 mg/g	111.3%	108.7%	-4.07%	0.80%
^{55}Mn	11.10 ng/g	125.73%	102.08%	0.88%	-6.24%
^{65}Cu	0.25 ng/g	106.51%	101.58%	-1.02%	-9.41%
^{64}Zn	0.86 ng/g	119.19%	95.44%	-1.66%	2.95%
^{206}Pb	0.04 ng/g	115.73%	98.52%	-2.05%	9.11%
^{75}As	0.27 ng/g	106.00%	87.20%	-4.53%	1.24%
^{110}Cd	0.01 ng/g	104.59%	110.37%	11.36%	-7.44%
^{120}Sn	0.9 ng/g	95.79%	109.92%	1.32%	-3.73%
^{52}Cr	5.4 ng/g	113.21%	106.12%	0.40%	-25.03%
^{59}Co	0.59 ng/g	105.08%	92.25%	0.42%	11.18%
^{109}Ag	0.002ng/g	No SRM		-0.94%	-2.64%
^{88}Sr	2.76 ng/g	No SRM		-2.36%	15.21%
^{45}Sc	3.14 ng/g	No SRM		-3.06%	-13.74%

[1] Based on 0.2 g of sample material.

Table II.2. Box Pond sediments, the range of values, and a comparison to the SRM certified values.

	Units	**Max**	**Min**	**BCSS-1**	**PACS-1**
^{27}Al	mg/mL	67.79	32.40	62.6 ± 2.17	64.7 ± 1.16
^{57}Fe	mg/mL	42.27	4.87	32.9 ± 0.98	48.8 ± 0.84
^{55}Mn	µg/mL	596.88	71.56	229 ± 15	470 ± 12
^{65}Cu	µg/mL	467.12	-2.08	18.5 ± 2.7	452 ± 16
^{64}Zn	µg/mL	682.69	13.01	119 ± 12	824 ± 22
^{206}Pb	µg/mL	270.20	8.15	22.7 ± 3.4	404 ± 20
^{75}As	µg/mL	39.97	-0.25	11.1 ± 1.4	211 ± 11
^{110}Cd	µg/mL	5.30	0.13	0.25 ± 0.04	2.38 ± 0.2
^{120}Sn	µg/mL	257.32	-0.21	1.85 ± 0.2	41.1 ± 3.1
^{52}Cr	µg/mL	246.65	4.31	123 ± 14	113 ± 8
^{59}Co	µg/mL	14.20	0.67	11.4 ± 2.1	17.5 ± 1.1
^{109}Ag	µg/mL	11.82	0.03	No SRM Available	
^{88}Sr	µg/mL	163.83	51.78		
^{45}Sc	µg/mL	12.22	2.37		

Table II.3. Echo Lake limits of detection, average recovery for the SRMs, and the average of the analytical and digestion duplicates.

	LOD[1]	**Avg. BCSS-1 SRM Recovery**	**Avg. PACS-1 SRM Recovery**	**Average Difference of Analytical Replicates**	**Average Difference of Digestion Duplicates**
^{27}Al	0.12 mg/g	97.50%	102.44%	0.82%	4.24%
^{57}Fe	0.03 mg/g	101.39%	96.64%	-1.62%	-3.46%
^{55}Mn	2.06 mg/g	110.70%	104.52%	1.69%	4.45%
^{63}Cu	1.7 ug/g	110.50%	100.60%	5.20%	4.71%
^{64}Zn	41 ug/g	109.87%	102.52%	0.00%	2.47%
^{208}Pb	0.80 ug/g	113.03%	103.96%	-0.61%	2.68%
^{75}As	5.23 ug/g	105.99%	91.23%	-3.38%	0.03%
^{114}Cd	0.36 ug/g	97.20%	104.07%	2.02%	-1.30%
^{120}Sn	6.21 ug/g	61.30%	110.39%	1.32%	-3.73%
^{52}Cr	5.26 ug/g	93.52%	91.02%	-2.48%	1.39%
^{59}Co	0.28 ug/g	110.14%	112.32%	-0.88%	1.52%
^{107}Ag	0.04 ug/g	No SRM		2.35%	6.01%
^{88}Sr	1.13 ug/g	No SRM		-1.25%	1.75%
^{45}Sc	1.76 ug/g	No SRM		3.71%	2.37%

[1] Based on 0.2 g of sample material.

Table II.4. Echo Lake sediments, the range of values, and a comparison to the SRM certified values.

	Units	**Max**	**Min**	**BCSS-1**	**PACS-1**
^{27}Al	mg/mL	76.49	8.22	62.6 ± 2.17	64.7 ± 1.16
^{57}Fe	mg/mL	90.40	4.49	32.955 ± 0.98	48.802 ± 0.84
^{55}Mn	µg/mL	952.33	162.34	229 ± 15	470 ± 12
^{63}Cu	µg/mL	70.15	4.56	18.5 ± 2.7	452 ± 16
^{64}Zn	µg/mL	278.93	3.58	119 ± 12	824 ± 22
^{208}Pb	µg/mL	134.63	4.80	22.7 ± 3.4	404 ± 20
^{75}As	µg/mL	18.65	1.27	11.1 ± 1.4	211 ± 11
^{114}Cd	µg/mL	1.43	0.10	0.25 ± 0.04	2.38 ± 0.2
^{120}Sn	µg/mL	15.06	0.00	1.85 ± 0.2	41.1 ± 3.1
^{52}Cr	µg/mL	58.48	3.50	123 ± 14	113 ± 8
^{59}Co	µg/mL	19.01	0.60	11.4 ± 2.1	17.5 ± 1.1
^{107}Ag	µg/mL	0.77	0.03	No SRM Available	
^{88}Sr	µg/mL	158.67	31.58		
^{45}Sc	µg/mL	47.26	16.98		

Analytical results for the Echo Lake and Box Pond cores are shown below in groups of figures. The Echo Lake results are followed by the Box Pond values. Within Echo Lake and Box Pond the metals are grouped by crustal indicator metals, Al, Sr, Sc and Co, by the redox indicators, Fe, Mn, Cr and Total Organic Carbon, by the anthropogenic metals, Cu, Zn, Ag, and Sn, and by the toxic metals Hg, Pb, As, and Cd. These are the values as detected by the ICP-MS except for Hg which was determined on the CETAC instrument and TOC on the Perkin-Elmer CHN detector. The y-axis in each case is the depth in cm of the core and the x-axis is the concentration. Each of these metal results will be discussed in the relevant chapters as they bear on the findings.

In examining the metal concentrations, for the bulk of the research, the values will be plotted against the year of deposition to derive a history of metal deposition in sediment. Where appropriate the metal results will be processed to remove the crustal contribution and derive a deposition rate, moles/m^2/year that will be plotted against the year of deposition.

The values that follow display the concentration against depth with the error bars. This format will enable the reader to more easily determine concentration ranges and trends. The actual data for each data set are contained in Excel sheets appended separately.

Figure II.1. Echo Lake sediment core crustal metals.

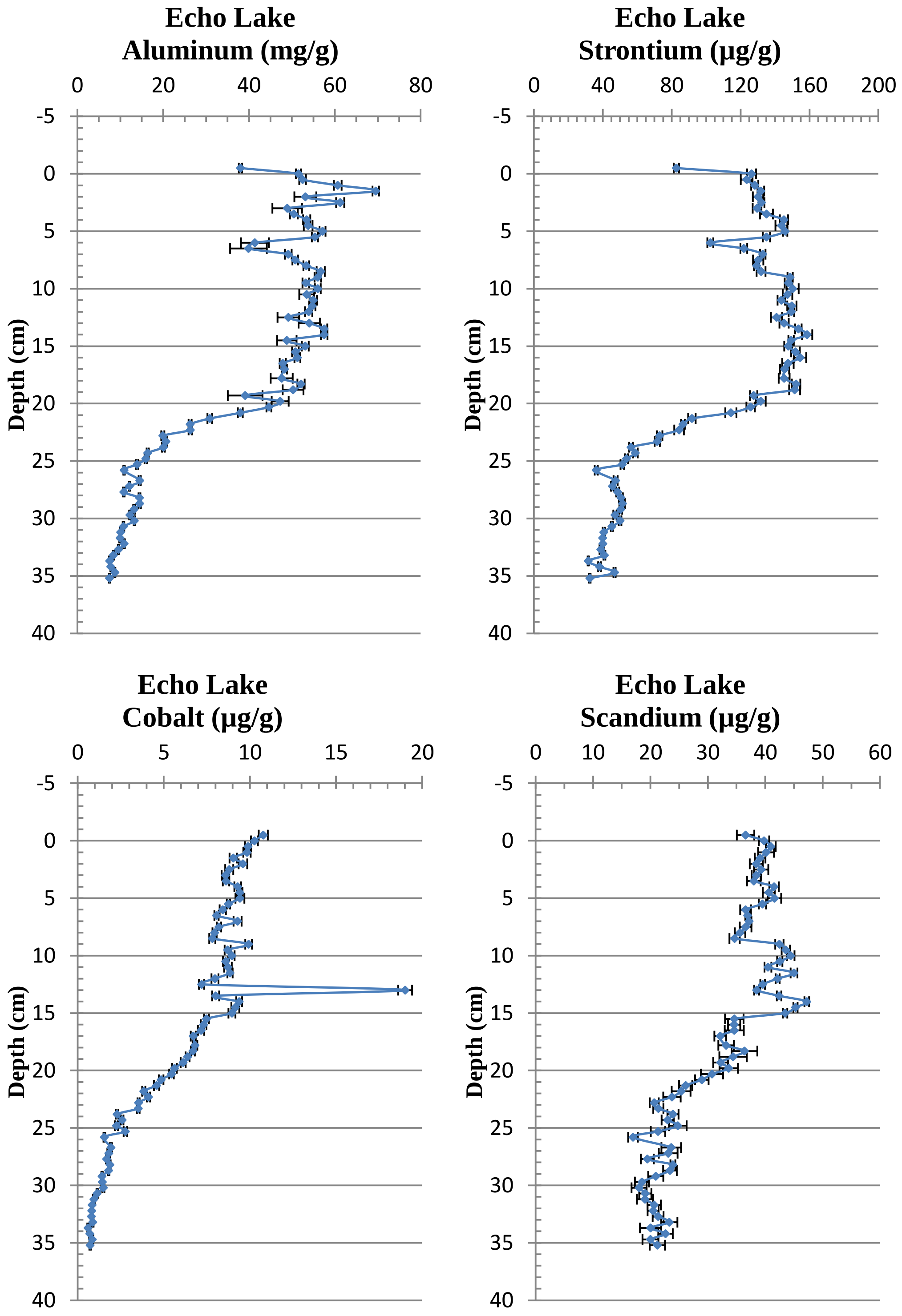


Figure II.2. Echo Lake sediment core redox indicator metals and total organic carbon.

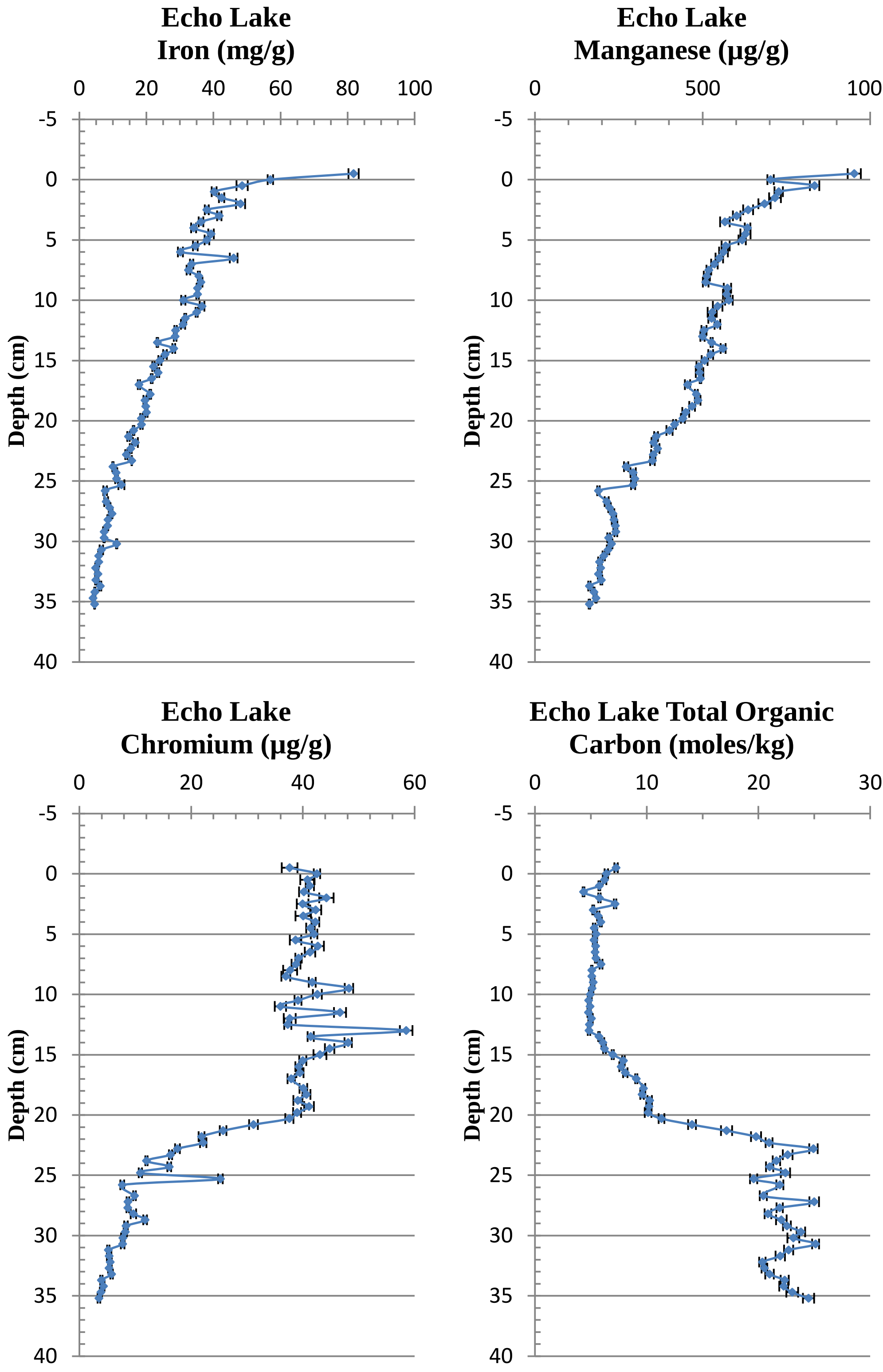


Figure II.3. Echo Lake sediment core anthropogenic metals.

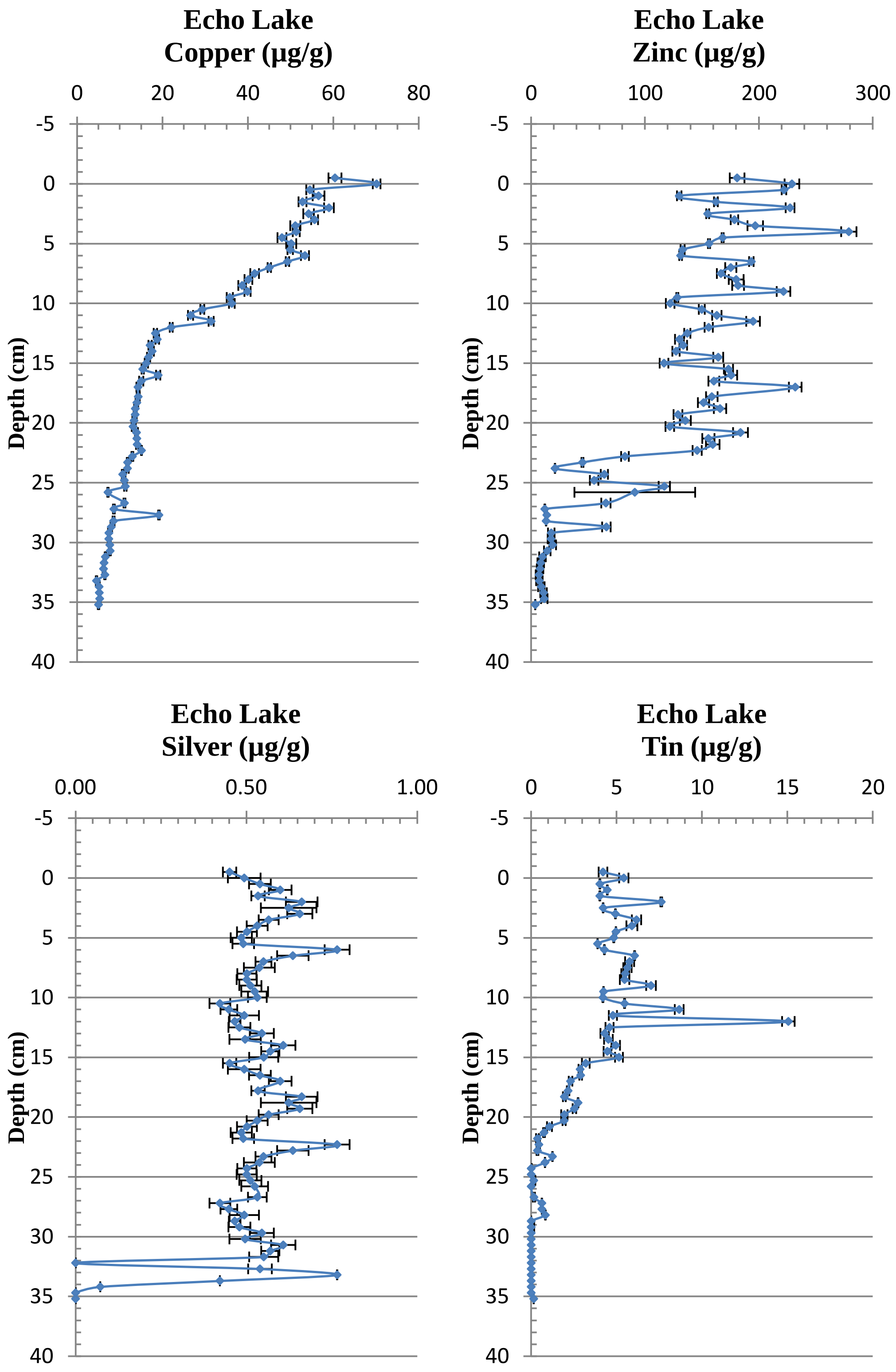


Figure II.4. Echo Lake sediment core toxic metals.

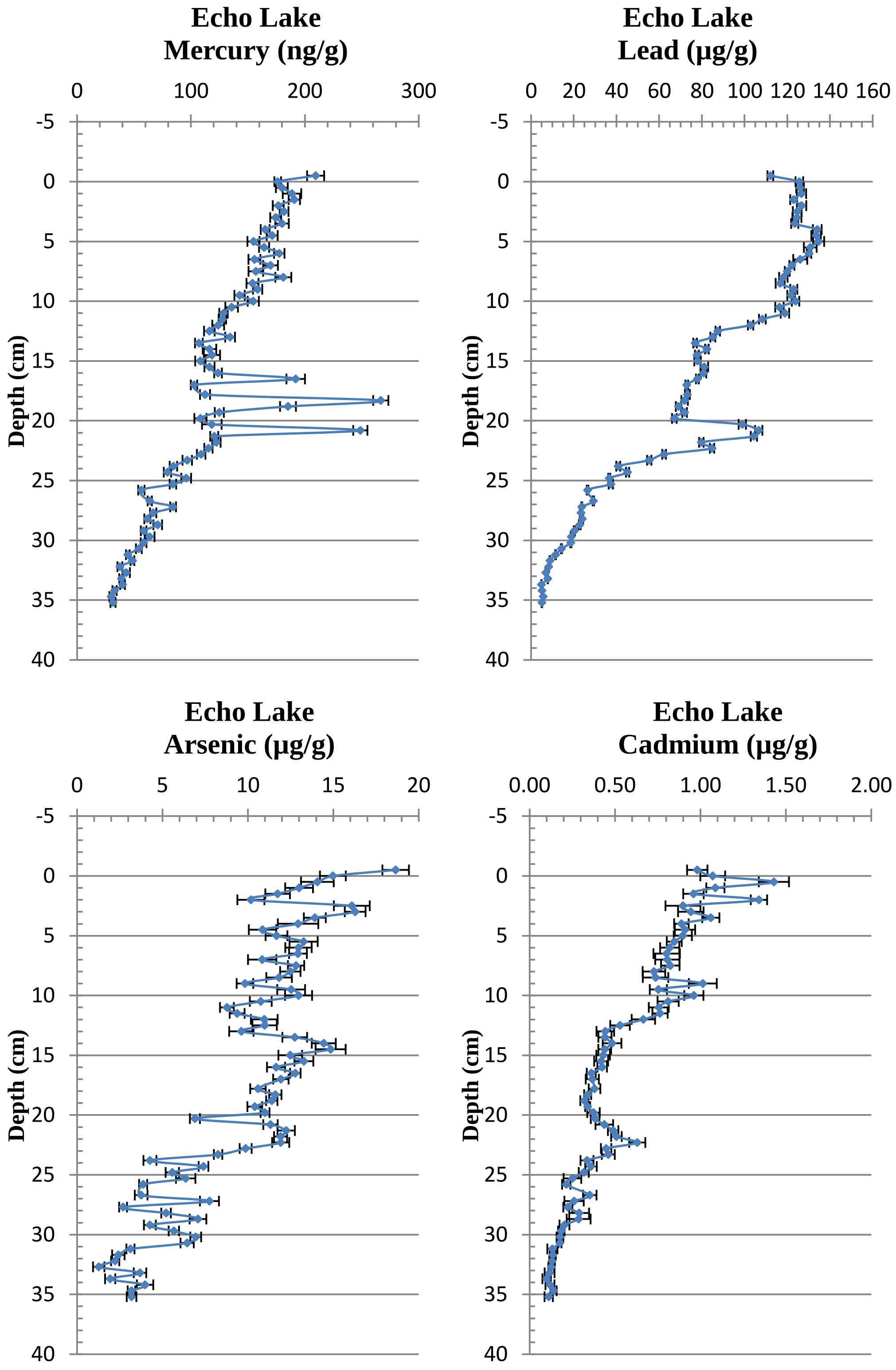


Figure II.5. Box Pond sediment core crustal indicator metals.

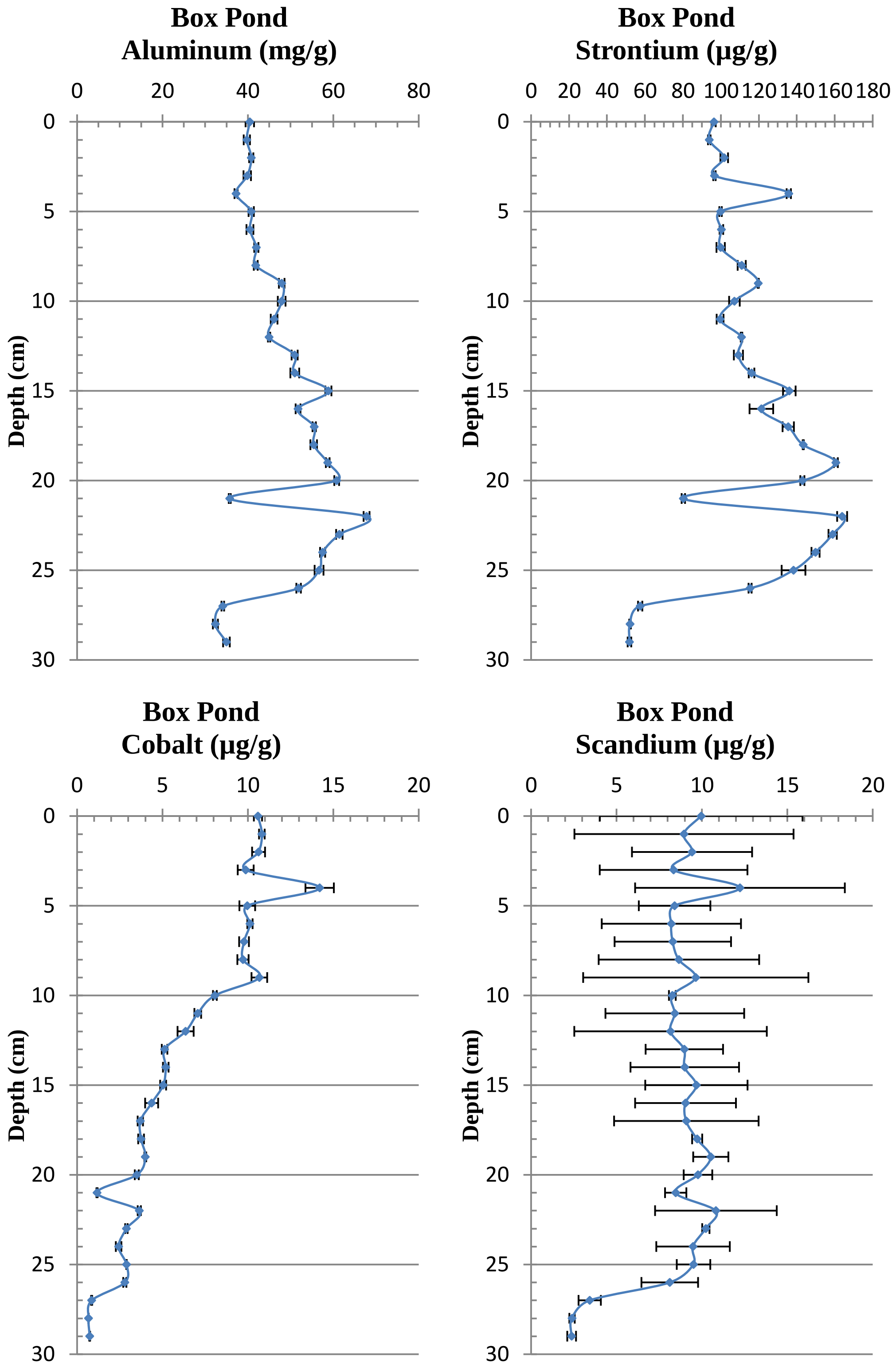
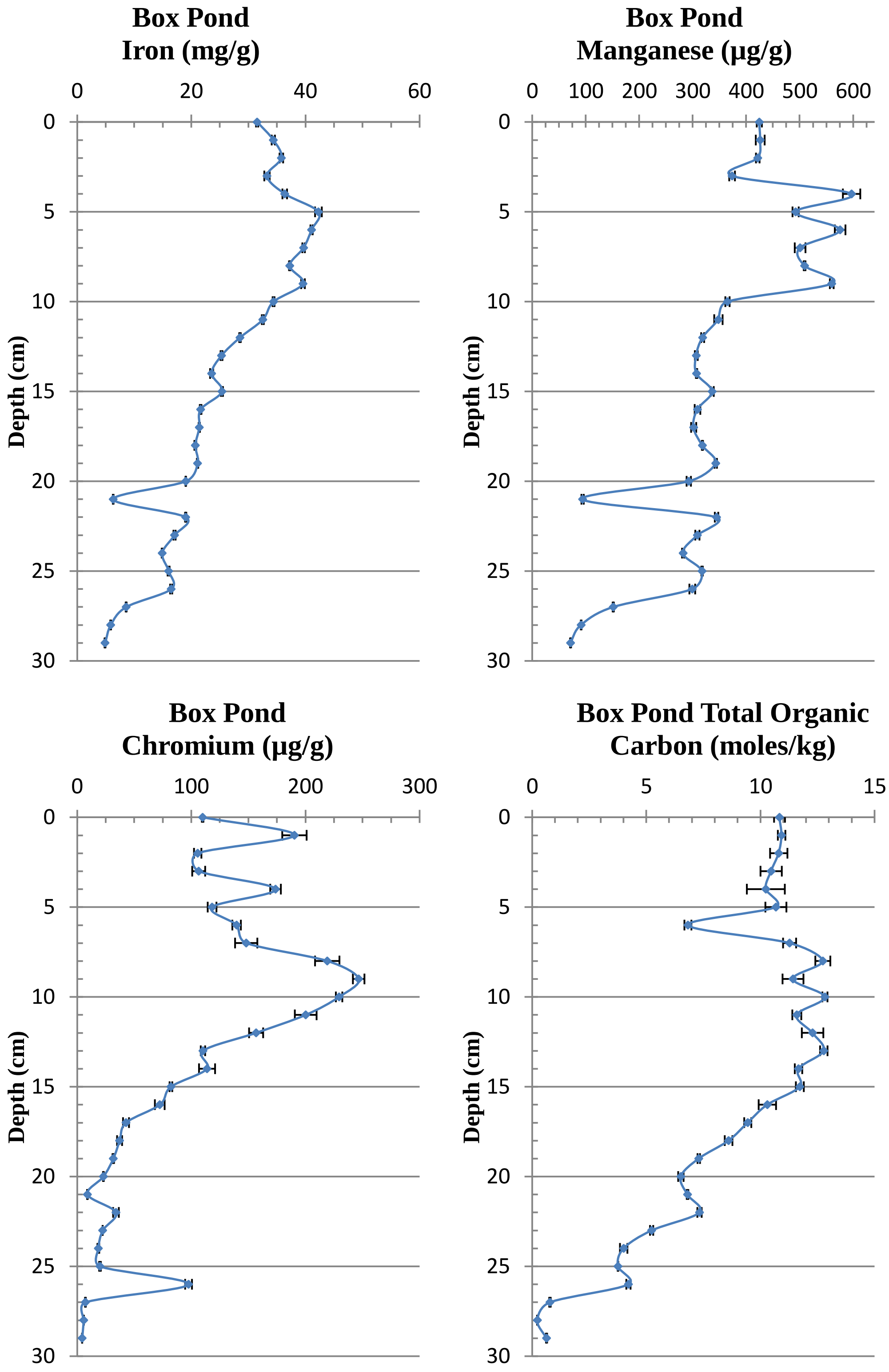


Figure II.6. Box Pond sediment core redox indicator metals and total organic carbon.


Box Pond Iron (mg/g)

Box Pond Manganese (µg/g)

Box Pond Chromium (µg/g)

Box Pond Total Organic Carbon (moles/kg)

Figure II.7. Box Pond sediment core anthropogenic metals.

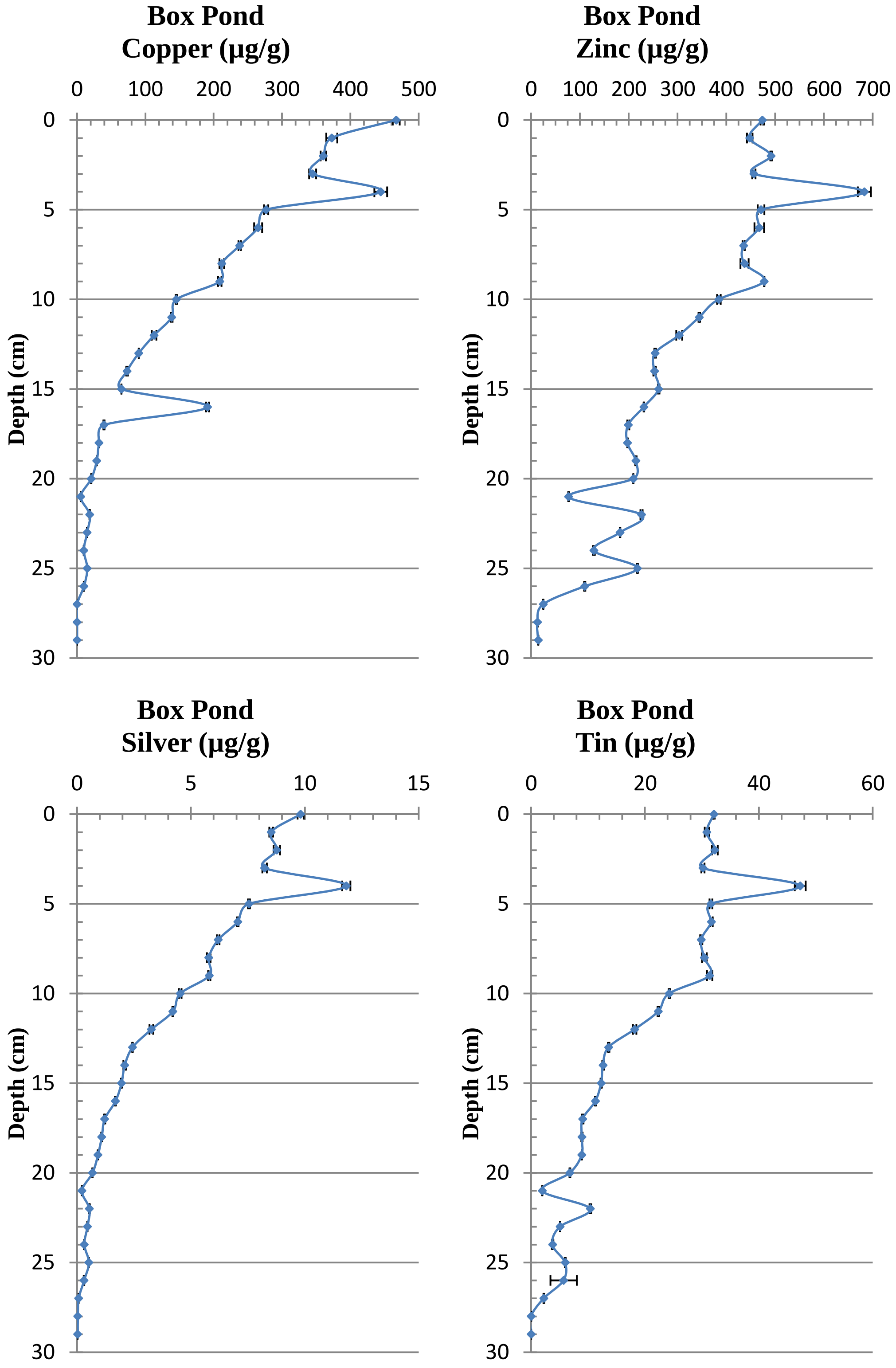
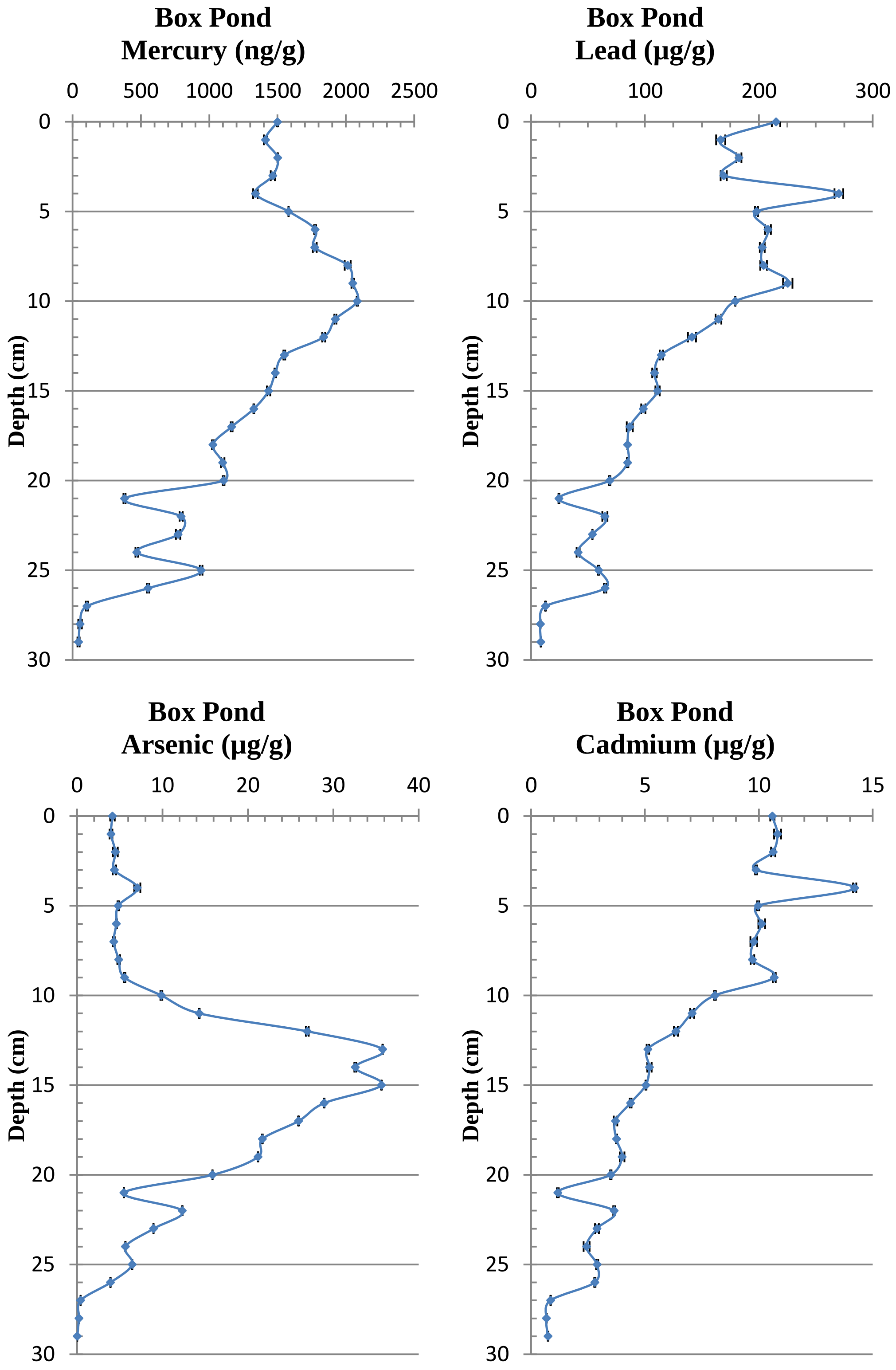


Figure II.8. Box Pond sediment core toxic metals.



II.2. Mercury Analysis

The data for mercury is displayed graphically in Section II.1., above. The QA/QC for mercury analysis is described below.

Table II.5. Mercury blank results.

Echo Lake Blank	Echo Lake Mercury ng/g
B1	5.92
B2	7.17
B3	2.22
B4	0.48
B5	1.29
B6	1.99
B7	3.71
B8	0.98
LOD	8.91
LOQ	29.71

Based on 0.2 g sample

Box Pond Blank	Box Pond Mercury ng/g
B1	2.28
B2	7.34
B3	2.64
B4	-2.63
B5	-1.02
B6	7.71
B7	2.55
B8	3.19
LOD	8.27
LOQ	27.57

Based on 0.2 g sample

Table II.6. Mercury Standard Reference Materials for Echo Lake

Echo Lake Reference Standard				
Sample_ID	**Corrected Concentration (ng/g)**	**Average Concentration (ng/g)**	**STDev Concentration (ng/g)**	**% Agreement with Certified Value**
STD1 PACS	3910.81	4140	330	90.59%
STD2 PACS	4629.43			
STD3 PACS	4024.34			
STD4 PACS	3995.62			
PACS-1	Certified Value		4570	±160

Table II.7. Mercury Standard Reference Materials for Box Pond.

Box Pond Reference Standard Sample_ID	Corrected Concentration (ng/g)	Average Concentration (ng/g)	STDev Concentration (ng/g)	% Agreement with Certified Value
Std2 Pacs1	4849.94	4724	257	103.36%
Std2 Pacs1-b	5011.62			
Std2 Pacs1-b	4784.13			
Std1(b)	4536.70			
Std1(b)	4661.82			
Std 2 Pacs1	4272.87			
Std 2 Pacs1	4948.48			
PACS-1	Certified Value		4570	±160

Table II.8. Analytical Replicates for Mercury, Echo Lake and Box Pond.

Echo Lake Analytical Replicates	Conc. (ng/g)	% Agreement
E'2	208.46	100.30%
E'2(R)	207.84	
E'10	182.20	103.82%
E'10(R)	175.48	
E'19	181.27	101.47%
E'19(R)	178.65	
E'27	122.99	99.76%
E'27(R)	123.28	
E'36	190.83	100.06%
E'36(R)	190.72	
E'43	115.71	96.88%
E'43(R)	119.44	
E'52	96.04	101.70%
E'52(R)	94.43	
E'59	69.98	98.81%
E'59(R)	70.82	
E'67	42.12	96.46%
E'67(R)	43.66	
E'72a	34.28	112.30%
E'72a(R)	30.53	
	Average	101.16%

Box Pond Analytical Replicates	Conc. (ng/g)	% Agreement
B59R	69.59	100.42%
B59R-b	69.31	
B43	415.65	103.20%
B43-b	402.75	
B27	1595.97	101.57%
B27-b	1571.23	
B9	1366.42	99.42%
B9-b	1374.41	
G7	52.94	84.10%
G7-b	62.95	
G17	584.06	91.96%
G17-b	635.11	
Std2 Pacs1-b	4716.07	96.77%
Std2 Pacs1-b	4873.28	
Std1(b)	4536.70	97.32%
Std1(b)	4661.82	
Std 2 Pacs1	4272.87	86.35%
Std 2 Pacs1	4948.48	
	Average	95.68%

Table II.9. Mercury digestion duplicates

Echo Lake Digestion Replicates		
Sample_ID	**(ng/g)**	**% Agreement**
E'5a	188.60	101.15%
E'5b	186.45	
E'38	113.25	102.91%
E'38a	110.06	
E'40	263.87	253.24%
E'40a	104.20	
E'52	95.24	136.61%
E'52a	69.72	
E'61	63.52	100.67%
E'61a	63.10	
E'67	42.89	97.41%
E'67a	44.03	
E'72	28.48	87.90%
E'72a	32.40	
	Average	125.7%
	Average w/o E40	104.4%

Box Pond Digestion Replicates		
Sample_ID	**(ng/g)**	**% Agreement**
B59R	188.60	101.15%
B59	186.45	
B35R	1290.50	107.59%
B35	1199.48	
B3R	1450.31	101.05%
B3	1435.21	
G6	46.49	104.11%
G6d	44.66	
	Average	103.47%

II.3. Surface Sediment Samples

Thirteen surface sediment samples were examined in Chapter 5. The analysis of the these samples, with respect to blanks, duplicates and methods were identical to those outlined in the above sections regarding the TOC, ICP-MS and CVAA analyses for the sediment cores. The location of the grab samples is shown in Table II.10.

Table II.10. Surface sediment sampling locations and the approximate distance from the Charles River dam.

Sample Location Town	Station (km)	Latitude	Longitude
Echo Lake[1]	125	42º 11' 33.18"	71º 30' 29.97"
Echo Lake, Hopkinton	125.1	42º 11' 34.91"	71º 30' 29.38"
Box Pond[2], Bellingham	111	42º 05' 41.35"	71º 29' 05.20"
Walker Street, Medway	95	42º 08' 24.01"	71º 23' 23.03"
Bridge Street, Sherborn	70	42º 13' 56.51"	71º 19' 49.51"
Cocharan Dam, Dover	53	42º 15' 30.17"	71º 15' 47.16"
USGS station, Dover	52.9	42º 15' 28.79"	71º 15' 46.24"
Ames Street, Dedham	43	42º 15' 09.21"	71º 10' 38.36"
Neponset River, Boston	41	42º 15' 15.87"	71º 10' 19.33"
CRWA Dock, Newton	23	42º 20' 41.11"	71º 15' 36.44"
CRWA Bank, Waltham	22.4	42º 20' 49.27"	71º 15' 34.53"
Watertown Dam, Watertown	13	42º 21' 54.57"	71º 11' 25.60"
Elliott Bridge, Cambridge	9	42º 21' 14.77"	71º 07' 57.43"

Table II.11. Community Data along the Charles River.

	Population Density (People/km^2)	**Residential Land use (%)**	**Commercial, industrial & transportation Land use (%)**
Hopkinton, Echo Lake	185	24%	5%
Milford, MA	690	37%	11%
Bellingham	313	27%	7%
Franklin	423	33%	6%
Medway	411	40%	3%
Norfolk	262	30%	3%
Millis	248	23%	3%
Medfield	325	32%	2%
Dover	139	28%	0%
Sherborn	101	22%	0%
Natick	776	47%	10%
Needham	872	50%	8%
Dedham	847	39%	14%
Wellesley	978	60%	5%
Weston	256	44%	4%
Newton	1778	63%	9%
Watertown	3106	50%	22%
Cambridge	5435	37%	29%
Boston	4603	41%	30%
Charles River Watershed	1286		

APPENDIX III

GEOCHRONOLOGY

III.1. Introduction

Radioisotope geochronology using non-destructive gamma detection of ^{210}Pb, ^{214}Pb and ^{137}Cs, was used to determine the absolute ages of each horizon of two sediment cores (Appleby and Oldfield 1978; Schell and Barnes 1986). The method of collection and preparation of the sediment cores are described in Chapter 2.

The natural radioisotope ^{210}Pb, an intermediate daughter product in the ^{238}U decay chain, was used to determine the date of deposition for each of the 5 mm sediment layers. The short-lived radioisotope ^{214}Pb was used to separate the *in situ* (supported) ^{210}Pb from that deposited from the atmosphere (excess). Radioisotope dating with ^{210}Pb is generally limited to 5 times the half-life, 22.3 years, which is approximately 110 years (Appleby and Oldfield 1978). Gamma emissions from ^{210}Pb and ^{214}Pb were detected at 46 keV and 295 keV, respectively, in this research.

The man-made isotope ^{137}Cs is produced by nuclear fission and serves as an excellent marker isotope in sediment, under optimal conditions this isotope shows the onset of above ground nuclear testing circa 1954 and the crescendo of U.S.-Soviet above ground atomic bomb testing in 1963. The gamma rays of ^{137}Cs were detected at energy levels of 661 keV.

Once the gamma emissions have been measured it is necessary to apply efficiency corrections to determine the true activity of each radioisotope. The necessary corrections are for branching, detector efficiency, geometry and self-adsorption. Branching efficiency is a measure of the number of decays that produce a gamma ray. Branching is a literature value that has been determined through other works (Schell and Barnes 1986). Detector efficiency is the percentage of gamma decays that pass through the detector that are counted. Because no detector can intercept all gamma ray emissions, and the detector used in this research was a planar detector, geometry corrections consider how many of the gamma decays pass through the detector. Both detector efficiency and geometry corrections were measured using Standard Reference Material 4350B, from the National Bureau of Standards with a known activity and a reference date of September 9, 1981. Pitchblende ore, Certified Reference Material CRM 101-A, was also used to determine efficiencies and was used in the construction of a button standard to determine self-adsorption in the sediment samples.

Self-absorption was measured by the use of a button source that was deployed on top of the sample using the method of Cutshall (Cutshall et al. 1983). Self-adsorption was determined for each sample by counting a sample to determine the activity in that sample and then placing a button standard on top of the sample and repeating the count.

The button standard was a plastic vial with a volume of 2.4 cm^3 and a wall thickness of 1mm containing a source material of 0.8 cm thickness and approximately 1.8 cm diameter. The button was weighed empty, packed only with a pitchblende ore, re-weighed on a Sartorius scale (1/10,000th g precision) and sealed with tape. The ore used inside the button consists of the CRM 101-A pitchblende ore - silica mixture from the U.S. Department of Energy New Brunswick Laboratory. The amount of uranium is certified as 1.007 ± 0.013 wt.% ($\alpha = 0.05$, df = 36).

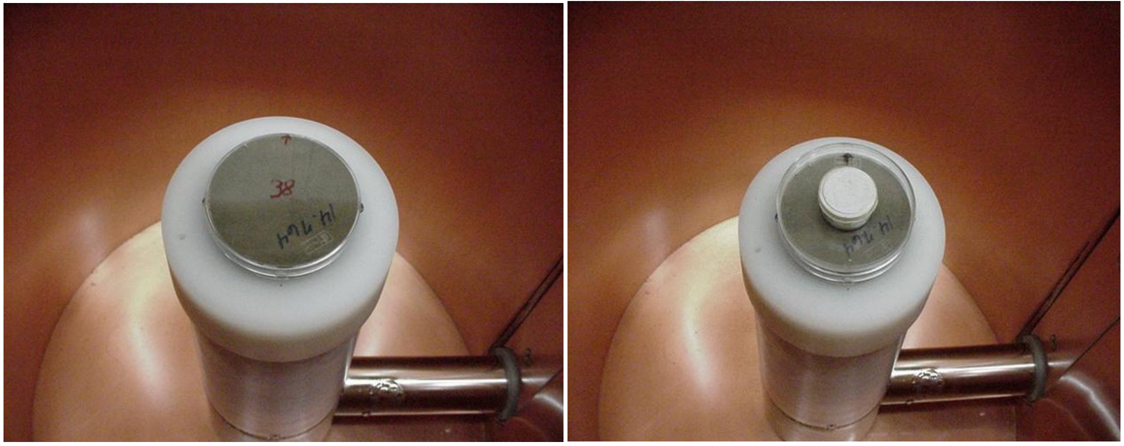
For the construction of the button standard the New Brunswick Laboratory Certificate of Analysis states that the Uranium content of the pitchblende ore - silica mixture is 1.007 " 0.013 Wt.% (" = 0.05, df = 36). Assuming secular equilibrium, the number of atoms of each species, and therefore the activities, of each of the parents and daughters are related through their decay constants at any one instant based on $A_{parent}N_{parent} = A_{daughter}N_{daughter}$. The amount of ore in the constructed button standard for this work is 2.7427 g. Based on the weight of the ore/silica mixture there should be 0.02762 g of uranium in the button. This translates to 0.0001152 moles of ^{238}U using the atomic weight of 238.029 g/mole. The number of atoms of ^{238}U in our button therefore is 6.938×10^{19}. Multiplying the decay constant of ^{238}U, $(0.6931/(4.468 \times 10^{9} \times 3.156 \times 10^{7}$sec/year)) the decay probability per second, by the number of atoms yields the number of decays per second:

$$4.915\text{x}10^{-18} \text{ x } 6.98805\text{x}10^{19} = 344.48 \text{ decays per second (dps)}$$

Equation 1

For secular equilibrium this number, 344.48 decays per second, or Becquerels (Bq), then cascades throughout the decay chain. The above calculation is for a button standard that weighs 2.7427 g. To get the decay per gram, one simply divides the decays per second by the grams in the button standard to arrive at the theoretical activity of 125.60 Bq/g. Figure III.1 depicts the measurement of a sample and measurement of the self-adsorption.

Figure III.1. Photographs of a sample measured on the LEGe detector (left) and the same sample with the button standard for determining self-adsorption (right).



For this work the following values were determined:

- ^{210}Pb at energy 46keV the combined branching, geometry and detector efficiency was determined to be 0.5114% and the value of self adsorption varied between the samples, but averaged 1.1160 for the Box Pond samples and 1.1247 for the Echo Lake samples.
- ^{214}Pb at energy 295keV the combined efficiency was determined to be 0.06835% and the value of self adsorption averaged 1.1076 for the Box Pond samples and 1.0087 for the Echo Lake samples.
- ^{137}Cs at energy 661keV the combined efficiency, including that for self adsorption, was determined using a 4350b standard and was determined to be 1.4%.

For each of the sediment cores, all error values were propagated from the original data. All data were also decay corrected to represent the activity present in the sample on the date of collection.

To determine the age dates of the various horizons in the sediment it is necessary to apply a model of the presumed deposition method of the sediment. The primary models used were the Constant Flux/Constant Sedimentation (CF/CS) model, the Constant Rate of Supply (CRS) model, and the Constant Initial Concentration (CIC) model. The use of these models is well described in the literature (Appleby and Oldfield 1992). For both sediment cores all models were used and compared to determine the sensitivity of the dating methods.

The models use the activity of the excess ^{210}Pb derived from the overall activity subtracting the activity of ^{214}Pb, assuming secular equilibrium. The plots of the resulting activities of excess ^{210}Pb and ^{137}Cs for the Box Pond and Echo Lake sediment cores, and the associated 1-σ error, are shown in Figures III.2 and III.3, respectively:

Figure III.2. Activity of excess ^{210}Pb data and ^{137}Cs in the Box Pond sediment core. The data are plotted against depth from the surface water/sediment interface. To make the data comparable, the ^{137}Cs activity was multiplied by 10.

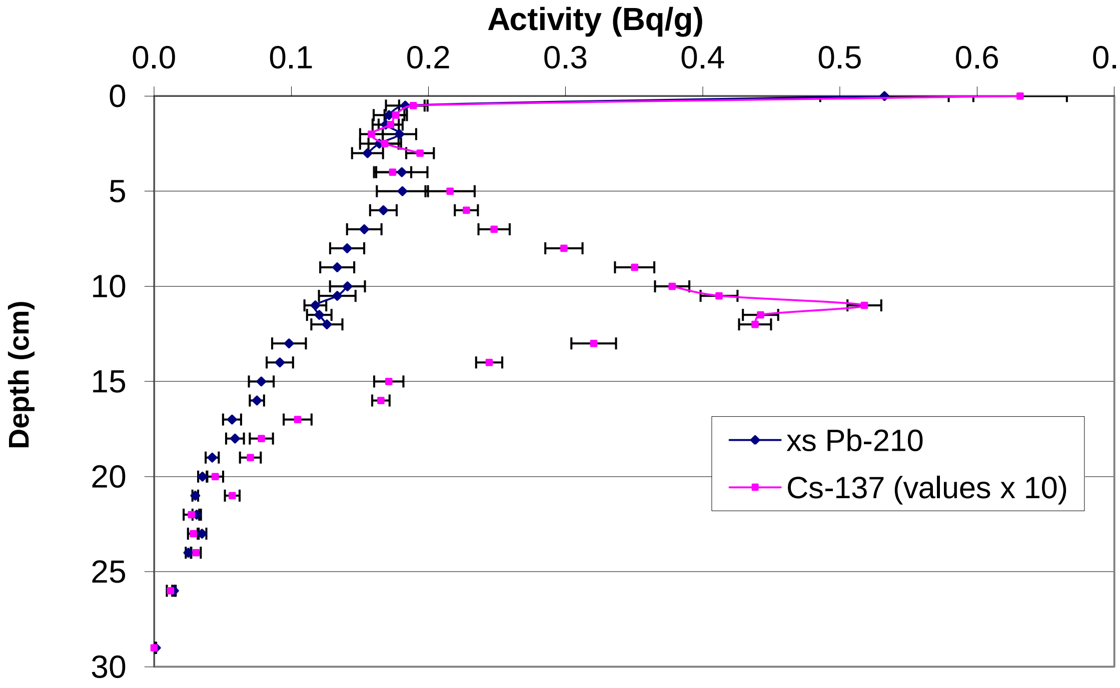
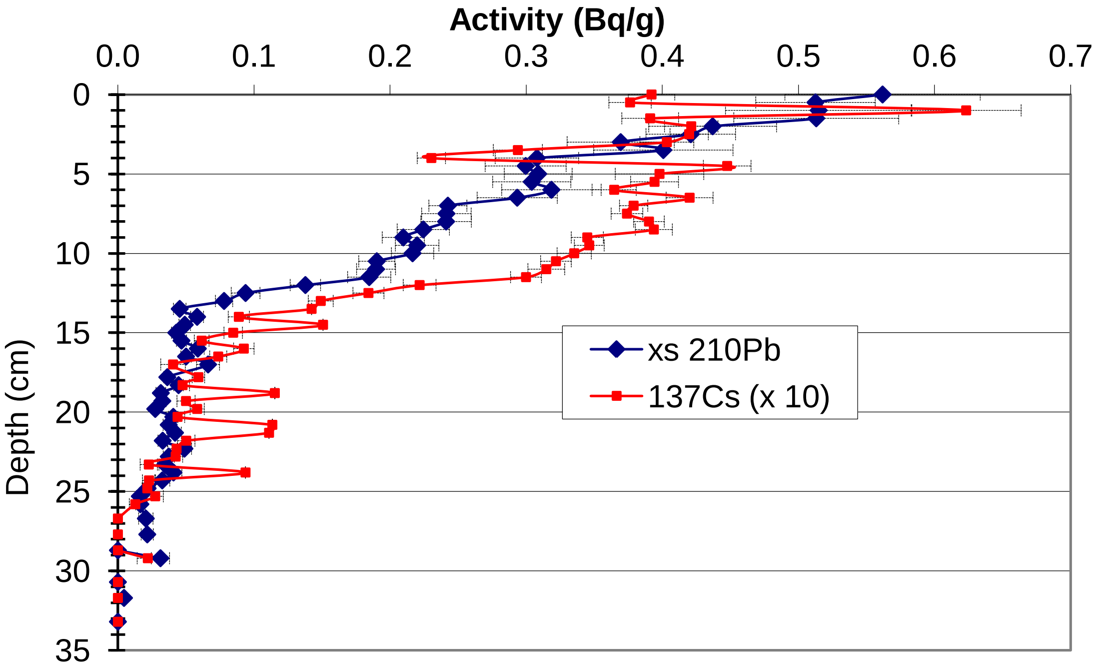


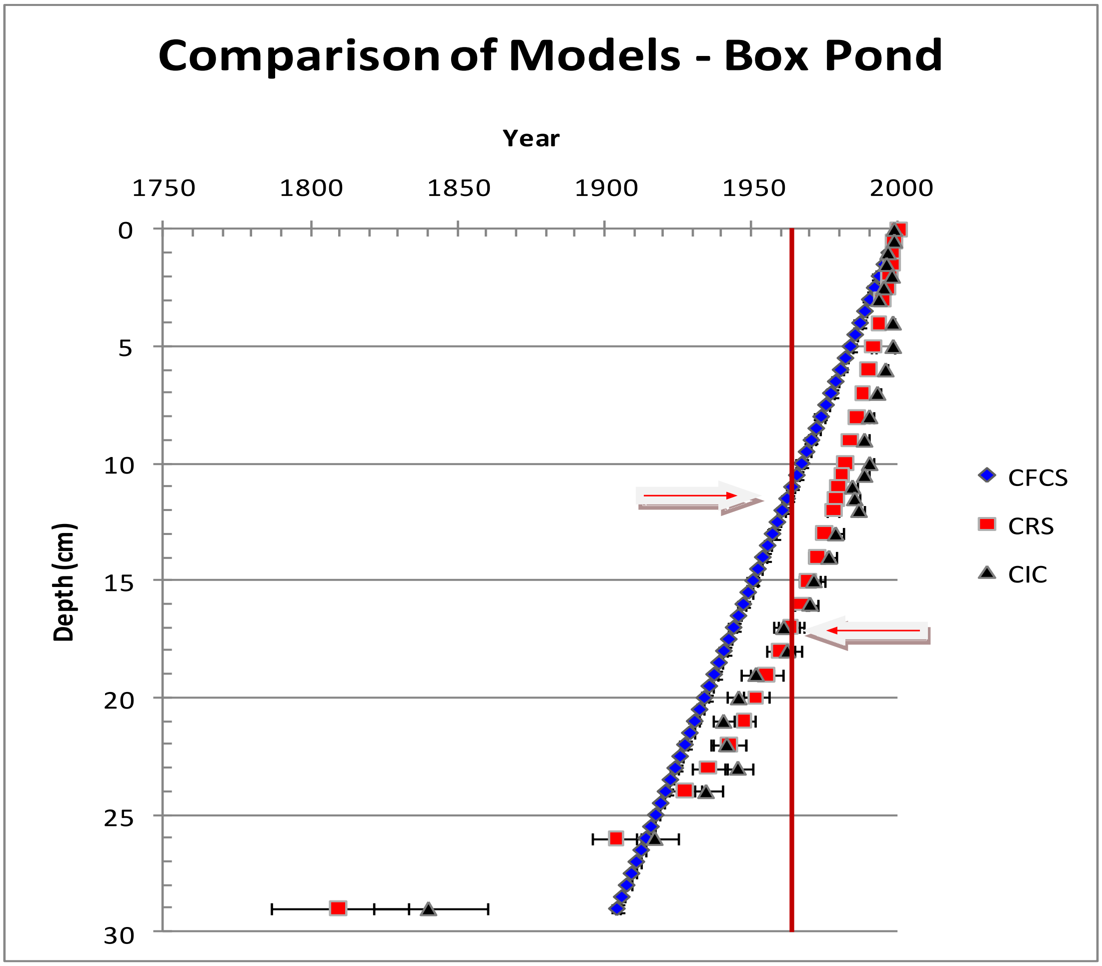
Figure III.3. Activity of excess ^{210}Pb data and ^{137}Cs in the Echo Lake sediment core. The data are plotted against depth from the surface water/sediment interface. To make the data comparable, the ^{137}Cs activity was multiplied by 10.



III.2. Box Pond

The Box Pond profile in Figure III.2 displays the typical excess ^{210}Pb decline with depth and ^{137}Cs peak at 1963. The three dating methods were in relatively good agreement at the top and bottom of the core. However, in the middle portion of the core a difference develops between the CF/CS method and the variable methods as shown in Figure III.4. Despite concurrence between the two variable methods, an examination of the data led to selection of the CF/CS method of dating as the more accurate by reason of the ^{137}Cs peak aligning with the 1963 date whereas the variable methods have the 1963 peak in the 1980s.

Figure III.4. Comparison of the dating models for the Box Pond sediment core.



In Figure III.4 a comparison of the results of running each of the models shows better agreement of the CF/CS to the data. This model was applied to the sediments with a sedimentation rate of 3 mm yr^{-1}. The red line in Figure III.4 represents the year 1963 and the arrows depict where in the sediment the CF/CS (upper) and CRS and CIC (both lower) represent the data. The accepted geochronology for the Box Pond core is shown below in Table III.1 the data and worksheets are in the attached Excel spreadsheets.

Table III.1. Stratigraphy and geochronology of Box Pond. Each depth interval has an assigned year and associated error.

Box Pond Geochronology

Description of Stratigraphy of Core	Depth, top of section (cm)	Accepted Date	
		Year	prop. Error 1-σ value (yrs)
liquid black gel	0	**2000**	**0.00**
Floc	0.5	**1998**	**0.13**
	1	**1997**	**0.11**
	1.5	**1995**	**0.09**
	2	**1993**	**0.11**
	2.5	**1992**	**0.14**
	3	**1990**	**0.12**
more cohesive	3.5	1988	
black	4	**1987**	**0.17**
	4.5	1985	
	5	**1984**	**0.17**
	5.5	1982	
	6	**1980**	**0.10**
lots of leaves	6.5	1979	
	7	**1977**	**0.14**
	7.5	1975	
	8	**1974**	**0.15**
	8.5	1972	
	9	**1970**	**0.15**
	9.5	1969	
	10	**1967**	**0.15**
	10.5	**1965**	**0.16**
	11	**1964**	**0.11**
	11.5	**1962**	**0.12**
	12	**1960**	**0.15**
big rock	12.5	1959	
	13	**1957**	**0.21**
	13.5	1956	
	14	**1954**	**0.17**
	14.5	1952	
black, clay-like	15	**1951**	**0.19**
	15.5	1949	
	16	**1947**	**0.11**
	16.5	1946	
	17	**1944**	**0.19**
	17.5	1942	
	18	**1941**	**0.18**
	18.5	1939	
	19	**1937**	**0.19**
	19.5	1936	
	20	**1934**	**0.15**
	20.5	1932	

Box Pond Geochronology

Description of Stratigraphy of Core	Depth, top of section (cm)	Accepted Date	
		Year	prop. Error 1-σ value (yrs)
■	21	**1931**	**0.11**
	21.5	1929	
	22	**1928**	**0.16**
	22.5	1926	
	23	**1924**	**0.15**
	23.5	1923	
	24	**1921**	**0.12**
	24.5	1919	
	25	1918	
	25.5	1916	
Coarse sand	26	**1914**	**0.14**
	26.5	1913	
	27	1911	
	27.5	1909	
	28	1908	
	28.5	1906	
	29	**1905**	**0.20**
	29.5	1903	

The bold dates with the 1-sigma values are derived from the CF:CS method of dating. The regular type dates without error are estimated from the surrounding values and used for plotting purposes.

III.3. Echo Lake

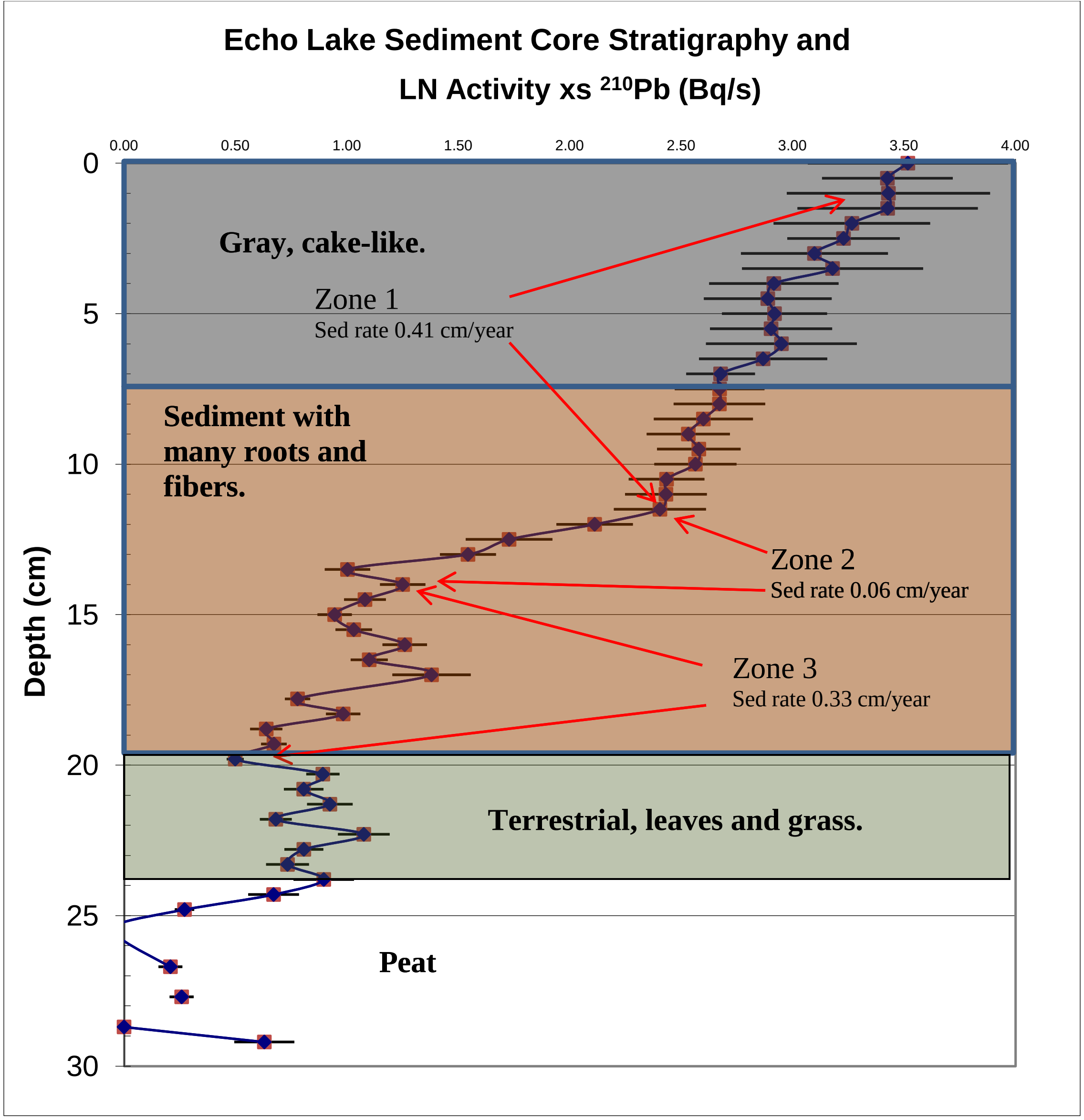
The Echo Lake sediment core activity profile for excess ^{210}Pb shown in Figure III-3 shows two anomalous features. First, the 1963 bomb peak of ^{137}Cs is absent and, second, applying the CF/CS method using excess ^{210}Pb in the 11.5 to 13.5 cm segment of the profile shows an unrealistic slow rate of sedimentation, approximately 0.06 cm yr^{-1} of sediment accumulation. By contrast the lower and upper sediments that bound this region have rates of 0.3 and 0.4 cm yr^{-1}, respectively.

Examining the inventories of both the Echo Lake and Box Pond cores proved diagnostic. The Box Pond core has an excess ^{210}Pb inventory of approximately 4000 Bq m^{-2}, 20% lower than the average for a similar impoundment in North Andover, 5200 Bq·m^{-2} (Wallace et al. 2004) and lower than the regional average of 5654 ± 3907 Bq·m^{-2} but within the range of error (Appleby and Oldfield 1992). The ^{137}Cs inventory in Box Pond is approximately 700 Bq·m^{-2} which yields a ratio of 5.6/1, ^{210}Pb/ ^{137}Cs, respectively.

By contrast, Echo Lake has a ^{210}Pb inventory of approximately 8200 Bq·m^{-2} and a ^{137}Cs inventory of approximately 1100 Bq·m^{-2} a ratio of 7.2/1, ^{210}Pb/ ^{137}Cs, respectively. The excess inventory of ^{210}Pb over that of the regional value and that found in a North Andover impoundment indicates that the Echo Lake location is likely a point sediment focusing. Yet, the apparent deficiency of ^{137}Cs relative to the ^{210}Pb indicates that some material is missing from the Echo Lake core.

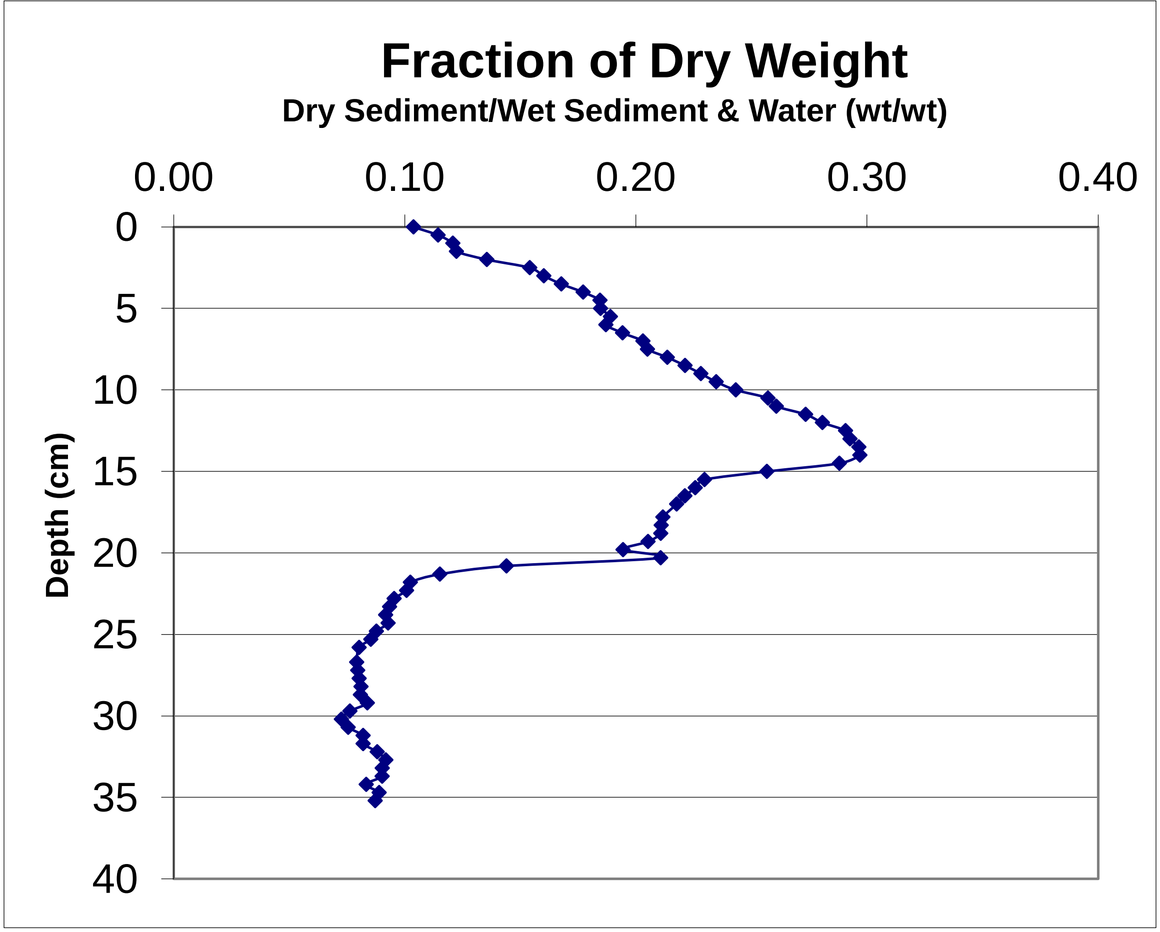
The morphology of Box Pond and Echo Lake are very different. Box Pond is narrow and shallow, while Echo Lake is wide and comparatively deep. The sediment core collection point for Box Pond, although in the deepest point near the dam, is less than 2 m deep and therefore subject to some of the effects of erosion at high energy flows in the river. High flows were witnessed during the sediment core collection in January 2000. Therefore, some loss of material is expected on a seasonal or episodic basis. The Echo Lake sediment core location has few erosive forces and during most times of the year is under more than 8 m of water. It is more likely that the location of the sediment core collection in Echo Lake is a site of sediment focusing (Davis and Ford (Jesse) 1982). Initially, the CF/CS model was applied to segments of the data. Those calculations are in the Excel spreadsheets, and the results are shown in Figure III.5, below:

Figure III.5: Natural log of activity of excess ^{210}Pb in the Echo Lake sediment core. The sedimentation rates for different segments of the profile are calculated. The stratigraphy of the Echo Lake sediment core is also described on the figure. Red arrows point to 3 of the 5 segments of differing deposition rates determined for the excess ^{210}Pb profile.



The key issue in Figure III.5 is that despite the consistent stratigraphy in the sediments with roots and fibers, there appear to be three separate deposition rates in the upper 20 cm of the sediment core. The interval between 11.5 and 13 cm, Zone 2, is not visually different from the interval above or below and it appears very coherent, despite it having a sedimentation rate that is five times lower than that above and below it. Taking this profile and dating the segments using the CF/CS model finds that the top of Zone 2 has a date of 1969 while 2 cm below it has a date of 1927, a span of nearly 40 years. The fraction of dry weight points to the significance of the 11.5 to 13 cm interval as shown on Figure III.6.

Figure III.6. Fraction dry weight of the Echo Lake sediments. This is a dimensionless number plotted against the depth and is calculated by dividing the dry weight for each 5 mm section by the weight of wet sediment.



Typical profiles of the fraction of dry weight show an increase with depth, which is what occurs in the upper 13 cm. At 13.5 cm to 19.8 cm, the density becomes less with depth, counter to the typical trend. There appeared to be no visual difference in the sediments from 7.5 to 19.8 cm. Below 19.8 cm, peat dominates the stratigraphy and maintains a consistent composition and density.

The slow rate of deposition and the apparent change in trend of fraction of dry weight in the interval between 11.5 and 13.5 cm point to a change in deposition when this interval was deposited. There are several possibilities for the deposition rate for this interval which may impact the radiometric dating and the overall observations in the sediment core regarding metal concentrations:

1. Loss of material that occurred either during coring or in 1968.
    a. The core was collected by a diver using a wide coring device. However, this seems unlikely.
    b. In 1968, eastern Massachusetts had extensive floods that impacted the Charles River and could have created an erosion event. However, an erosion event is unlikely as the watershed is quite small and the standing pool above the coring site in excess of 6 m.
    c. Also in 1968, the Milford water company installed a pipe in the bottom of the dam to pipe water to its treatment plant. The installation of that pipe, by a diver, may have impacted the sediment core site by removing material.
    d. Bioturbation, an organism could have removed some portion of the sediment for a redd (fish) or for hibernation (turtle).
    e. It is noted that this section has many roots indicating that plants grew profusely in this area. The plants could have been uprooted by some event, such as the preceding, and thus removed the sediment.

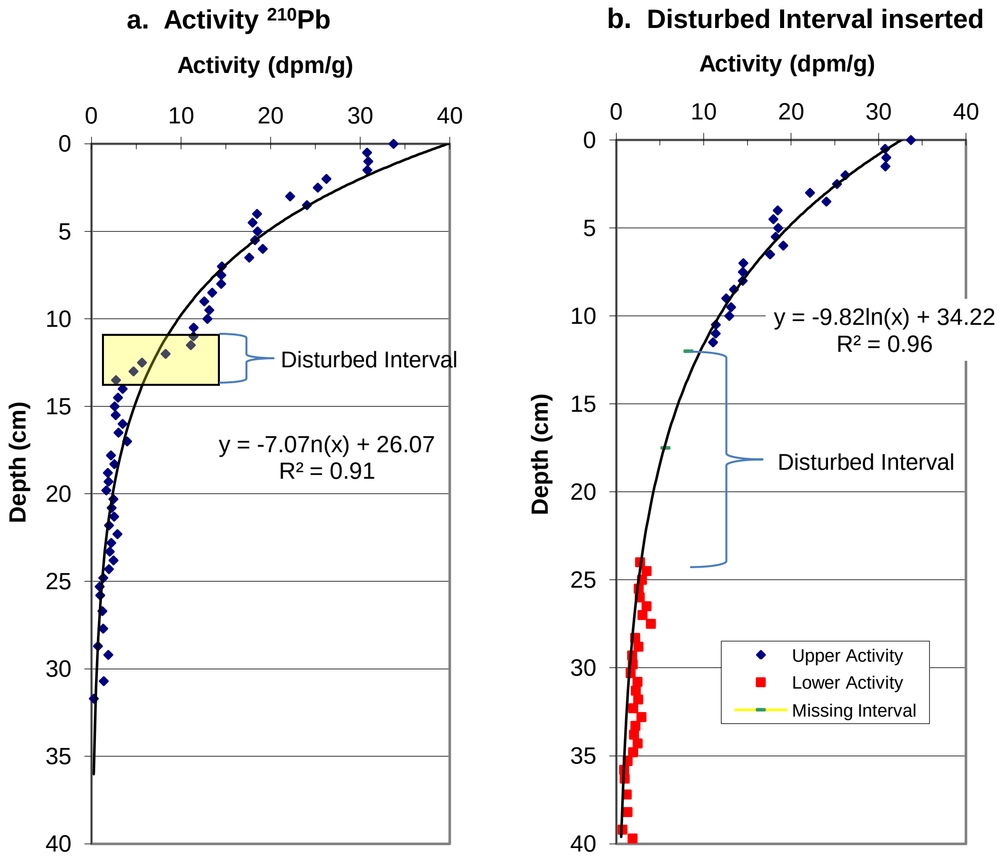
2. A plant or other material on the lake bottom may have created a sediment shade in the area of the core.

The low sedimentation rate, coupled with the apparent deficiency of ^{137}Cs in the core, indicated that some amount of material was removed from the sediment record in this location. This area is termed the “Disturbed interval” throughout this research.

One counter-argument to the removal of material might be that the Disturbed interval between 11.5 and 13 cm appears to have a trend in the activity of excess ^{210}Pb; however, that may be explained by the nature of the material. The hypothetical erosion event would suspend the sediment wherein some is removed, while some portion settles out of the turbidity cloud created after removal. The heavier particles, which would be less particle-reactive and therefore would contain less ^{210}Pb would settle first, and the finer material which would be more particle reactive would settle last.

Regardless of the mechanism, some portion of the sediment record from 11.5 to 13.5 cm is missing. To determine how much material was removed from the Echo Lake sediment record it was assumed that the missing material would have a logarithmic function similar to the sediments above and below the Disturbed interval (Appleby and Oldfield 1992). To determine the amount of missing material, the excess ^{210}Pb activity profile was graphically split into three segments: upper (0 to 11 cm), Disturbed interval (11.5 to 13 cm) and lower (13.5 to 34 cm). The upper segment remained stationary while the lower segment was moved downward and a logarithmic regression applied to the new configuration. The best-fit logarithmic regression was with 13 cm of separation between upper and lower segments as shown in Figure III.7:

Figure III.7. Analysis of the Disturbed interval: a) The activity of excess ^{210}Pb in the Echo Lake sediment core is shown with the problem interval, 11.5 to 13.5 cm highlighted. b) Separates the data into three segments: upper activity, Disturbed interval, and lower activity. The plot of the excess ^{210}Pb for the upper 11.5 cm remains as in (a) but moves the data below 13.5 cm downward until the best fit line was determined with a R^2 value of 0.96.



a. Activity ^{210}Pb

b. Disturbed Interval inserted

The Disturbed interval shown in Figure III.7b was stretched over the amount of material removed from the sediment record in this area. This work is shown in greater detail in the Excel sheet *Geochron Echo Lake.xlsx*. The conclusion of the analysis was that approximately 13 cm was removed from the sediment record between 11.5 and 13.5 cm.

The missing mass and activity, based on the sediment horizons above and below the Disturbed interval, was added back to the sediment core. Adding the missing ^{210}Pb inventory to the overall inventory yielded a total inventory of approximately 11,000 Bq m^{-2}. If 11,000 Bq m^{-2} were the total sediment core inventory, it would be approximately twice that of the expected inventory for this region indicating that the sediment focusing factor was approximately twice the typical rate (Davis and Ford (Jesse) 1982; Appleby and Oldfield 1992). The Box Pond ratio of the inventories of excess ^{210}Pb:^{137}Cs was 5.71:1. Using the Box Pond ratio, the expected inventory of Echo Lake ^{137}Cs based on the activity of ^{210}Pb, should be approximately 1900 Bq m^{-2}. The actual inventory of Echo Lake ^{137}Cs was 1100 Bq m^{-2}, a deficit of 800 Bq m^{-2} of what would be expected. The inventory of Box Pond ^{137}Cs over the period of the Disturbed interval, 1920 to 1969, is 436 Bq m^{-2}. If sediment focusing at Echo Lake is considered to be twice typical locations, the expected inventory of ^{137}Cs based on the ratio found at Box Pond, is 872 Bq m^{-2} similar to the calculated deficit of 800 Bq m^{-2}.

The CF/CS model was used to determine the dates of the Echo Lake sediment core in the upper segment. The dates of deposition for the metal concentrations in the Disturbed interval are assigned and if erosion was the source of the unconformity, would not be accurate, but if it were the product of shading may have some relevance to the dates shown. The lower segment was dated by inserting the missing inventory, and then using the CRS model to determine dates. All models were run and the CRS was chosen as it demonstrated the best agreement with stratigraphic breaks in the sediment core. At 19.3 cm the sediment transitioned from terrestrial debris to lake sediment. The 19.3 cm layer was believed to be when the dam filled in 1882. Although the 1850 date is beyond the accepted accuracy of the ^{210}Pb method, a local resident said that two sisters had maintained Echo Lake as a hayfield from the 1850's (Bowker 2005). Excel sheets provide an analysis of the data and the methods used.

The application of the ^{210}Pb geochronology dating methodology is typically for only 5 half-lives, 110 years, or approximately 1899 in this instance (Appleby and Oldfield 1978). The dating model's correspondence of 1882 with the known date of the lake's creation provided confidence in the model's accuracy. When the strata transitioned to peat, the model's results were extended downward based on the calculated accumulation rate of 8 yr cm^{-1}, which is comparable to other values in the literature. A similar peat bog in Switzerland had accumulation rates of approximately 10 yr cm^{-1} calculated using ^{14}C methods (Shotyk et al. 2000).

The final, accepted dates of the sediment core are shown in Table III.2. Error values are only supplied for the upper 11.5 cm because the uncertainty below that horizon is unknown.

Table III.2. Stratigraphy and geochronology of Echo Lake. Each depth interval has an assigned year and associated error. The dates 1959 to 1929 represent the result of a period of missing deposition and are speculative. No error was calculated for the intervals below the Disturbed interval. Summaries of observations regarding the sediment core are shown inside the stratigraphy.

Core Description	**Cored Depth (cm)**	**Accepted Year**	**Error Value Years**
Black soup.	0	1998	0.07
	0.5	1997	0.11
	1	1997	0.13
	1.5	1997	0.16
Black, but coherent.	2	1996	0.20
	2.5	1995	0.25
A little clay, black and very coherent.	3	1994	0.33
	3.5	1993	0.40
	4	1991	0.50
	4.5	1990	0.58
Less coherent than above.	5	1989	0.64
	5.5	1988	0.70
	6	1987	0.78
Clay, cake-like.	6.5	1986	0.86
	7	1984	1.00
Roots, fibers and vegetative matter.	7.5	1983	1.06
	8	1981	1.15
	8.5	1980	1.25
	9	1978	1.36
	9.5	1977	1.44
	10	1975	1.57
	10.5	1972	1.73
	11	1971	1.82
	11.5	1969	1.95
Same as above, but more coherent and very fibrous.	12	**1959**	
	12.5	**1949**	
	13	**1939**	
	13.5	**1929**	
	14	**1919**	
	14.5	**1915**	
Gray spots of clay present.	15	**1912**	
	15.5	**1908**	
	16	**1905**	
	16.5	**1903**	
	17	**1899**	
Fibrous and black.	17.8	**1892**	
	18.3	**1890**	
	18.8	**1887**	
	19.3	**1882**	
Cut grass stems.	19.8	**1879**	
	20.3	**1877**	

twigs too.	20.8	**1872**
	21.3	**1868**
	21.8	**1862**
	22.3	**1858**
	22.8	**1854**
Lots of leaves.	23.3	**1850**
Peat.	23.8	**1846**
	24.3	**1842**
	24.8	**1838**
	25.3	**1834**
	25.8	**1830**
	26.7	**1826**
	27.2	**1822**
	27.7	**1818**
	28.2	**1814**
	28.7	**1810**
	29.2	**1806**
	29.7	**1802**
	30.2	**1798**
	30.7	**1794**
	31.2	**1790**
	31.7	**1786**
	32.2	**1782**
	32.7	**1778**
	33.2	**1774**
	33.7	**1770**
	34.2	**1766**
	34.7	**1762**
	35.2	**1758**

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