

Metals in Mashapaug Pond: An interdisciplinary approach to understanding the industrial history of Providence, RI

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*A thesis submitted in partial fulfillment of the requirements for the degree of
Bachelor of Science with Honors in Geology-Biology.*

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Brown University
May, 2017



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Acknowledgements

This work would not have been possible without the dedication of my two advisors, Dave Murray and Tim Whitfeld, who supported my interest in this project from its inception as a summer Undergraduate Research and Teaching Award. Additionally I am grateful for the stellar advising of Jim Russell and Jan Tullis, and the support of my professors throughout my undergraduate career. Thank you to everyone who patiently helped me with the research itself: Joe Orchado, Will Daniels, Laura Messier, Lynn Carlson, Martha Cooper, Scott Frickel, and Michael Murphy; and to my family, friends, and fellow students for their encouragement and support. Finally, I would like to thank Holly Ewald, the Urban Pond Procession, the students and teachers of Alvarez High School, and the members of the Mashapaug Pond community at large. You have made this project an honor and joy to work on.

Abstract

Due to its history of industrial pollution and its importance to the communities who have lived nearby, Mashapaug Pond has been the focal point of environmental activism, artwork, and sociological research. The pond, located within the city of Providence, RI, and with a documented history of metalworking and other industrial activity, provides a case study for understanding how industrialization affected urban ecologies. By combining GIS land use mapping, sediment core analysis, and herbarium specimen sampling this work explores this history from three previously unexamined perspectives. Sedimentary accumulation in Mashapaug Pond records the concentration of heavy metals input to the pond, as well as recording other changes to land use, such as deforestation, in the watershed. The sedimentary record demonstrates that heavy metal pollution of the pond began around 1850, and that the period of peak industrial pollution occurred in the early 20th century. Chromium (Cr) provides the most direct record of industrial activity within the watershed itself, and does not begin to increase until around 1880. Present day concentrations of industrial metals, including mercury (Hg) and lead (Pb), in the pond have remain above the pre-industrial baseline, and have not declined relative to terrigenous materials. Herbarium specimens provide additional insights into biological uptake and incorporation of metals from the past and present. In particular, comparing metal concentration in plants and soil collected from the same site highlights that plant contamination is largely dependent on soil concentration, which can be extremely localized from sources such as parking lots. Heavy metal pollution in the Mashapaug Pond watershed is an ongoing problem, and further investigation into remediation strategies should be pursued.

Introduction

Motivation

The American Industrial Revolution is widely considered to have begun in 1790 when William Slater established a textile mill on the Blackstone River, upstream of the city of Providence, Rhode Island (Rose 2008; Marlow 2016; Nixon 1991; Salacup 2014). Providence rapidly grew into an industrial hub, and a production center of cotton and wool textiles. The metal working industry in Providence was born of the need for metal machinery, such as steam engines, to use in textile production, and later evolved to include wire pulling and jewelry manufacture (Kulik & Bonham 1978). As Nixon (1991) puts it, between 1850 and 1925 “*the development of railroads, the mechanization of agriculture, the invention and spread of electrical distribution systems, the telegraph, the telephone, the introduction of canning and skyscrapers and automobiles, all contributed to the exponential growth in metal manufacturing.*” Providence, with its early start, became one of the most industrialized cities in the country.

The legacy of industrialization continues to affect Rhode Island. This small state has 200 sites that are suspected to be hazardous waste disposal sites, and 12 hazardous waste sites on the National Priorities List, the list of sites eligible to receive remediation financing through the federal Superfund program (EPA 2017; Rose 2008). Heavy metal contamination, along with poor air quality, is widely known to be a human health risk (Ho & El-Khaiary 2009), and Rhode Island’s asthma and cancer rates, both of which can be linked to environmental pollution, are among of the highest in the country (CDC 2008; CDC 2016). Within the state, Providence has the highest concentration of hazardous waste sites, manufacturing sites, and power plants (Kulik & Bonham 1978; Rose 2008). Urban centers such as Providence experience the compounding risk factors of close proximity to multiple pollution sources, concentrated population, and higher rates of poverty. Understanding both the historical and present levels of heavy metal pollution in cities highlights the importance of environmental regulation in preserving public safety.

Framing the Approach

Through industrialization, human activity has drastically altered the geochemical cycling of heavy metals. Increased concentrations of contaminants such as lead (Pb), chromium (Cr), arsenic (As), and mercury (Hg) in the environment are of critical importance to both human and ecologic health. Sediment cores taken from a body of water provide a continuous history of heavy metal input to that watershed, and herbarium specimens, plant specimens collected in the past and preserved, provide an indication of how heavy metals were historically incorporated into terrigenous biological systems. Together, these two records preserve an ecological timeline for a given site. Although both sediment cores and herbarium specimens have been widely used to study past environmental conditions (Lavoie 2013; Valette-Silver 1993), to the best of my knowledge the two techniques have never been used in conjunction to understand the history of a single site from both perspectives. Sedimentary analysis provides a continuous record, which contextualizes the discontinuous plant record, and herbarium

specimens provide a measure of the bioavailability of contaminants passive sedimentary accumulation does not.

The goal of this research is to relate observed fluctuations of heavy metal concentration in sediment cores and old and new herbarium specimens to changes in land use as documented by historical maps, archival documents, and oral histories. Botanical and sedimentary timelines are expected to reflect historical industrialization, providing valuable insights into the impact of industrialization on urban ecological systems. In order to develop a detailed ecological history based on multiple data sources, it is necessary to limit the geographic scope of the research. Mashapaug Pond, the largest freshwater body in Providence was selected as a case study. In the following sections I will discuss: (1) the reasons for focusing on Mashapaug Pond; (2) the historical and socioeconomic context of Mashapaug Pond; (3) the metals of interest and their sources; (4) the investigative approaches I will employ, including (4a) land use mapping, (4b) sediment core analysis, and (4c) plant and soil analysis.

1. Mashapaug Pond, a Case Study

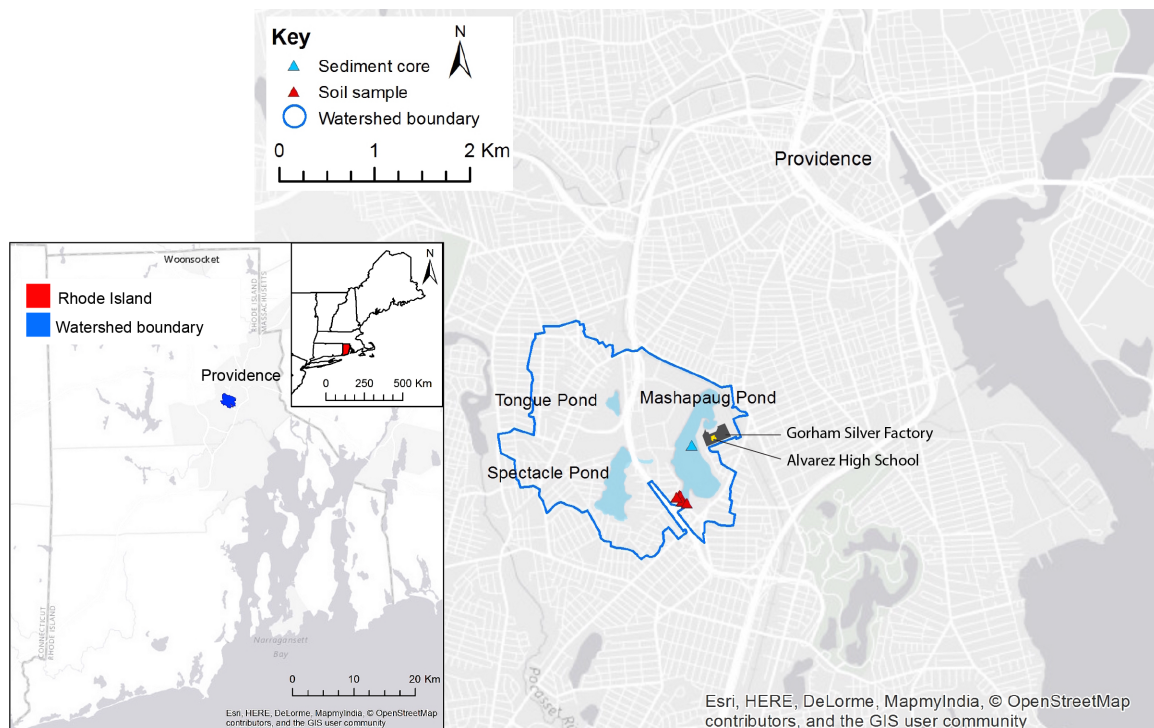


Figure 1: Located in Providence, RI, on the Northeastern coast of the United States, the study site is the watershed of Mashapaug Pond (4 km²). Tongue Pond and Spectacle Pond drain into Mashapaug Pond and are labeled, as are the former Gorham Silver Factory site (dark grey) and Alvarez High School (yellow). The locations of the sediment core (blue triangle) and soil samples (red triangles) collected are also indicated.

Mashapaug Pond, located in south Providence provides a suitable case study. The kettle pond, located at 41°47'37.9"N, 71°26'00.9"W, has an area of 36.8 ha and maximum depth of 5 m. The pond itself is located in Providence, and the 4 km² watershed stretches into the neighboring town of Cranston (Fig. 1). Part of the Pawtuxet

River Watershed, it is fed by Tongue Pond and Spectacle Pond to the west, and drains into the Roger Williams Park ponds to the southeast, which eventually drain into Narragansett Bay (RIDEM 2007).

Historically, Mashapaug Pond has been a center for indigenous people, part of a residential neighborhood, and host to a variety of commercial and industrial sites. In particular, the Gorham Manufacturing Company silver factory was located directly on the shore of the pond, along with several other industries, including the American Enamel Company (Anon 1899). Given this documented industrial history, Mashapaug Pond may serve as a proxy for understanding the ecological impact of industrialization throughout Rhode Island and the northeastern United States.

The history of Mashapaug Pond has been recorded in several different ways, making it a strong candidate for a case study of this kind. First, the watershed area has been included on detailed fire insurance maps dating back to 1889, and aerial images of the area have been collected beginning in 1939. Second, sediment cores have previously been collected from Mashapaug Pond and used for analysis of pollen percentages, indicating that the sediment provides a continuous and undisturbed accumulation record (Bernabo 1977). Third, a total of 84 plant specimens from the Brown University Herbarium are labeled as being collected from Mashapaug Pond, with dates of collection ranging from 1871 to 1935. Heavy metal analysis on a subset of these plants has been shown to be a viable method of studying past environmental conditions (Rudin et al. 2017). Fourth, the watershed has been the focus of research on indigenous history (Simmons 2010), socioeconomic and cultural history of a racially diverse neighborhood (Boltz 2013), and urban succession (Marlow 2016), all of which provide historical context for the site. Fifth, the watershed is the site of ongoing environmental justice activism surrounding the construction of Dr. Jorge Alvarez High School (Fig. 1) on a former industrial site (EJLRI n.d.; Hauptman n.d.), and the legacy of environmental racism (Lin-Sommer 2016).

It is my hope that the research described in the following pages can augment the existing body knowledge about Mashapaug Pond, and serve as a resource for understanding the multifaceted impacts of industrialization on this beloved ecosystem.

2. Historical Context of the Mashapaug Pond Watershed

Indigenous people have lived in the Northeastern United States since approximately 13,000 BC (Dove & Ewald 2012), and the earliest human remains yet found near Narragansett Bay were dated to be 3,300 years old (Nixon 1991). Prior to European colonization, a Narragansett village called Mashapaug was located on the shores of the pond (Simmons 2010; Weeden 2011). This village is thought to have been occupied year-round, with agricultural fields for corn, beans, squash, cucumbers, and melons located nearby (Dove & Ewald 2012). Although much of the landscape was likely forested at this time, Native American land use practices included small-scale burning of forested land to clear it for agricultural use and aid the growth of forage plants for deer (Bernabo 1977; Nixon 1991; Salacup 2014). When Giovanni Verrazzano arrived in Narragansett Bay in 1542, the only metal that the Narragansett possessed were copper sheets that they had likely acquired through trade with tribes in the Great Lakes region (Nixon 1991).

Beginning with European settlers' arrival and seizure of land from Narragansett and other southern New England tribes, population density and land clearing increased dramatically. In 1636, Roger Williams signed a deal with Narragansett chief sachems Canticonus and Miantunnomi, gaining control of "...*those lands from the river and fields at Pawtucket the Great Hill of Neutaconkanut on the northwest and the town of Mashapaug to the west* (Dove & Ewald 2012)." European diseases and warfare, such as King Philip's War of 1675, killed many indigenous people throughout Rhode Island (Lin-Sommer 2016; Bernabo 1977). However, members of the Narragansett tribe, along with other indigenous people, have continued to live in the West Elmwood and Reservoir neighborhoods (Simmons 2010; Weeden 2011).

Beginning in the late 17th century, farms were established in the area by John Sayles and others (Elorza n.d.). Until the middle of the 19th century the area surrounding Mashapaug Pond was predominantly agricultural, and Mashapaug Pond was used for wealthy society parties (Deller 2010). In 1814, William Potter constructed a water-powered cotton mill on his farmland, the earliest evidence of industrial activity in the watershed (Bagnall 1893; Stone 1857). Several other industrial operations were soon built on the shores of Mashapaug Pond, including Earl Carpenter's icehouses (1849), the American Enamel Company, and John Hope and Sons' Company fabric engraving (1882). Elsewhere in the Mashapaug Pond watershed, early industries included What Cheer Brewery, Narragansett Brewing Company, Metropolitan Facing Works, and railroad infrastructure of the Union Railroad Company (Kulik & Bonham 1978; Anon 1916; Anon 1889).

The most noteworthy industrial development was the construction of the 37-acre silver factory built on the northeastern side of Mashapaug Pond by the Gorham Manufacturing Company between 1888 and 1890 (Deller 2010). Founded in 1831, Gorham had become the world's leading producer of silverware by 1860 (Soules n.d.). The company continued to grow, and in 1890 a factory was established on the banks of Mashapaug Pond, which included a bronze foundry where notable statues were produced, including the statue of George Washington in the U.S. Capitol Rotunda. In the early 20th century, the demand for silver flatware declined, and the Great Depression significantly reduced the buying capacity of the American public. During World War II, Gorham shifted to producing small arms parts, tank bearings, torpedo components, and millions of 40mm shell casings (Soules n.d.). Following the war, Gorham never fully recovered. The factory was purchased by Textron in 1967 and ceased production entirely in 1985 (Textron 2012).

Along with industrial development, residential neighborhoods grew around the pond, particularly following the construction of major roads leading to central Providence, including Greenwich Road now Reservoir Ave., and Middle Road now Elmwood Ave. (Deller 2010). One testament to the residential growth in the early 19th century was the establishment of the Hebrew Cemetery in 1849 just south of Mashapaug Pond at 375 Reservoir Ave (Anon 1916). Soon after, in 1865, the Union Railroad Company ran its first streetcars along Westminster Street, Cranston Street, and Elmwood Avenue, increasing the ease of transportation to downtown (Deller 2010). With the addition of these services, residential construction occurred throughout much of the Reservoir neighborhood in the late 1800s and early 1900s. By the time the first aerial photographs were taken in 1939, nearly the entire watershed was developed.

In oral history interviews, residents of the West End neighborhood in the 1940s and 50s describe using the pond for hockey games, baptisms, fishing, boating, and swimming (Campbell 2011; Hooks 2012; Montiero 2013). Some recall eating crayfish and snapping turtles from the nearby creek, although others remember being warned not to drink or touch the water in Mashapaug Pond because, “*it was always on the green side*” (Campbell 2011). The neighborhood they describe was a vibrant and close-knit community, and it was one of the few neighborhoods where people of color were able to own property (Boltz 2016; Weeden 2011).

However, city records describe the neighborhood declining financially. Citing vacant properties, deterioration of housing, and high “indices of social breakdown,” such as welfare cases, venereal disease, and juvenile delinquency, the Providence Redevelopment Agency decided that the cost of updating infrastructure for the neighborhood was prohibitive (Malley 1960). Instead, beginning in 1961, the city demolished a swath of the West Elmwood neighborhood on the western side of Mashapaug Pond to build the Huntington Expressway section of Route 10. As part of a multi-million dollar urban renewal plan, the area was rezoned to allow for the construction of the Huntington Expressway Industrial Park (Building Officials Conference of America 1962). The industrial park was home to several electrotyping and electroplating facilities (Korwin n.d.).

Oral histories describe how the demolition of the neighborhood west of Mashapaug Pond disproportionately harmed Black and Native American residents (Boltz 2013). Pervasive redlining prevented people of color from obtaining mortgages or renting in many parts of Providence, making it difficult for Black and Native American residents to relocate. Furthermore, homeowners were offered only \$5000 as compensation for relocating, which was insufficient to buy a home in other parts of the city (Montiero 2013). Cliff Montiero, a resident and lifelong civil rights activist describes the impact of redlining:

The banks redlined and wouldn't give mortgages to people of color. Many neighborhoods, they classified as white. People of color could not get mortgages in those areas. So when the urban renewal went in, it was really Negro removal without doing anything to improve their life. Many people used to be homeowners. After losing their home ownership in the Mashapaug Pond area became renters. So finding renting was difficult... But I thought it was a nice recreational area, a nice neighborhood. And I think it's nice that they developed an Industrial Park, but at what expense and whose expense? It was the expense of the people of color... I guess the acquisition of the most inexpensive land is the way we grow in America (Montiero 2013).

One theme that is evident in the history of Mashapaug Pond is that the harm caused by land seizure and pollution fall disproportionately on communities of color. This theme continues to the present day, as highlighted by the story of Dr. Jorge Alvarez High School. The student body is 78% Hispanic, 9% African American, 9% Asian, 2% Native American, 2% White. The school has a large immigrant population, with 32% of students receiving ESL or bilingual education, and a high poverty rate, with 72% of student receiving subsidized meals. Statewide rates are 7% and 47% respectively (RIDE 2017).

The school was built on the former Gorham Manufacturing Company site (Fig. 1). The factory itself traded hands multiple times and ceased operation in 1986. In 1990 the owners, the Seamen Equity Group, defaulted on their taxes and the city of Providence foreclosed (Carini, 2010). The factory was demolished in 2001, and in 2007 the school building was built on Parcel B, although the soil and groundwater remained contaminated. A major concern for the school site is vapor intrusion of trichloroethylene (TCE) and perchloroethylene (PCE), which were used to clean machine parts and are known carcinogens (Carini, 2010; Martí et al, 2012).

The danger of this situation, and insufficient transparency on the part of the Department of Environmental Management, sparked a wave of community organizing and activism (Carini, 2010; Rowan, 2012). The Environmental Justice League of Rhode Island and the Urban Pond Procession worked on a range of initiatives including: demanding accountability and community involvement in the Gorham site cleanup; addressing and mitigating stormwater pollution; and enacting the “Environmental Cleanup Objectives for Schools” or School Siting Bill (EJLRI n.d.). Thanks to these actions, parents and students are now fully informed about the risks and safety measures in place, and the space between the school in the pond has been capped and planted with grass, creating a valuable green space for neighborhood residents. Another recent activist push surrounding the pond is a lawsuit filed by Mashapaug Nahaganset leaders, a separate group from the Narragansett tribe, against the state of Rhode Island and the cities of Providence and Cranston for environmental racism (Lin-Sommer 2016). The claims of this lawsuit point to the long history of pollution that has affected the pond, which is of continued importance to the tribe.

3. Heavy Metals of Interest and their Sources

Industrial processes introduce heavy metals to the environment through metal extraction, smelting, processing, recycling and waste disposal (Han et al. 2002). Globally, since 1860 use of all the metals studied has grown consistently, except for Pb, which peaked in the 1980s (Han et al. 2003). Heavy metals are defined as the elements with a high atomic weight and a density at least 5 times greater than that of water (Tchounwou et al. 2012). Unlike more volatile organic pollutants, heavy metals accumulate in the environment (Han et al. 2002). Their persistent nature allows heavy metals to be used as indicator of past industrialization.

For the purposes of this study, seven heavy metals were selected for analysis: arsenic (As), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn). In the following paragraphs I will detail the health risks and potential sources of each element.

Arsenic (As) is a known carcinogen and poison that is detected in low concentrations worldwide. Emitted through smelting, refining of metallic ores, and semiconductor manufacturing, it is also used in insecticides, herbicides, fungicides, algicides, wood preservatives, and textile dyes (Tchounwou et al. 2012).

Chromium (Cr) is widely used to produce alloys when melted with other metals, particularly steel alloys, and for electroplating, or coating the surface of objects with metal. It is also used in tanning agents, dyes, and as a chemical catalyst (Naja & Volesky

2009). Cr exposure is of most concern in occupational settings, where inhalation poses a major risk.

Copper (Cu) was one of the first metals utilized by humans, and is produced at a rate of more than 13 million tons per year (Han et al. 2003). Cu is a biologically essential micronutrient, but becomes toxic at high concentrations (Norgate et al. 2007). It is used in a wide range of industrial activities, and the largest source of Cu in urban runoff was found to be car break wear, followed by painted house siding (Davis et al. 2001)

Mercury (Hg) is highly toxic, and can cause serious neurological and renal disorders. The primary source of Hg in the atmosphere is coal fired power plants (Nriagu & Pacyna 1988). Approximately 50% of Hg is used in the production of chlorine for bleaching paper pulp, and the next largest use (35%) is the production of batteries and switch gear (Naja & Volesky 2009). Other uses include dental preparations, thermometers, fluorescent and ultraviolet lamps, pharmaceuticals, and fungicides, particularly in paints.

Nickel (Ni), a toxin and carcinogen, is an inhalation risk in many industrial occupations, and can also be found in food and drinking water (Cempel & Nikel 2006). Ni is primarily used in the production of stainless steel and other alloys, and it is also used in catalysts and pigments, particularly in the chemical and food processing industries. Coal combustion also releases some Ni to the atmosphere.

Lead (Pb) has been widely studied because of the risk of neurological damage to children. Pb was commonly added to paint, which flakes as it deteriorates; unless painted over, the flaking paint can become dust, and is also eaten by young children (Tchounwou et al. 2012). Within homes, plumbing installed prior to 1945 utilized Pb pipes that cause drinking water contamination (Naja & Volesky 2009). Pb was added to gasoline in 1925 and, until banned in 1986, exhaust from leaded gasoline was a widely dispersed source of atmospheric pollution (Needleman 2004). In addition to these sources, industrial uses include batteries, construction materials, and ammunition (Naja & Volesky 2009).

Zinc (Zn) is a an essential micronutrient, a deficiency of which can cause a variety of diseases, and an excess of which can cause toxicity (Fosmire 1990). Much like Cu, Zn is used in a wide variety of industrial processes, including electrolytic process (Norgate et al. 2007). The primary sources of Zn in urban runoff were found to be brick walls and tire abrasion (Davis et al. 2001; Yousef et al. 1990).

4a. Land Use Analysis

Spatially quantifying land use change using GIS is a technique that has been widely used to study the ecological consequences of development. Satellite imagery has been used to track the growth of urban centers, and to study the development of industrial corridors (Liu & Yang 2015; Malik et al. 2013; Schneider et al. 2015). Land use mapping has also been approached on a watershed-scale, to specifically relate land use to watershed health (Bhaduri et al. 2000; LeBlanc & Fortin 2015). Historical maps have also been incorporated into watershed-based land use mapping, in order to precede satellite data (Garnier et al. 2013).

Previous studies of land use change using GIS have relied on data from between 2 and 6 years, typically spaced 10-20 years apart (Malik et al. 2013; Schneider et al. 2015). The categories used in analysis of land use change depend on the specifics of each

locality and the resolution of the data, but most studies have attempted to differentiate between natural, agricultural, residential, and commercial/industrial land use (Verburg et al. 2004).

This work employs similar techniques to build a land use dataset based on historical maps, aerial photographs, and satellite imagery of the Mashapaug Pond watershed. Residential and commercial/industrial development were of particular interest, as the watershed is completely developed and contains no agricultural or forested land aside from a few small parks. The construction of a highway through the watershed was also of significant interest. Industrial areas are expected to grow continuously throughout the time period studied. Residential development is expected to expand to a peak percentage prior to the construction of the highway, and then to decline.

4b. Sediment Core Analysis

Sediment cores provide a valuable historical record of the environmental input to a body of water, and have been used globally to study heavy metal pollution (Miller et al. 2014; Petit et al. 1984; Vaalgamaa & Conley 2008; Valette-Silver 1993). Cores from 31 lakes in Sweden showed that the earliest Pb pollution dates to the year 0, during the Roman Empire (Renberg et al. 2002). Cores from estuarine systems have been used to demonstrate that concentrations of heavy metals including As, Cr, Cu, Hg, Pb, Zn fluctuate in close association, and can be used to track industrialization through time (Fox et al. 1999). Both lake and estuarine cores have also been used to demonstrate the effectiveness of environmental regulation by showing the decline in heavy metals following the passage of regulatory laws (Hosono et al. 2010; Mahler et al. 2006).

The history of heavy metal pollution in Rhode Island, specifically, has been measured in sediment cores collected from Narragansett Bay (Goldberg et al. 1977). Concentrations of Pb and other metals were highest and began to increase earliest in cores collected closest to the industrial center of Providence, particularly in cores collected from the highly industrialized Seekonk River (Corbin 1989). Cores collected from salt marshes in Narragansett Bay show that the increase in Cu, Pb, and Zn began around 1850, and Zn peaked around 1920, while Cu and Pb peaked around 1940 (Bricker 1993). All three metals decreased from 1975 to 1990 (Bricker 1996). Given the close proximity of Mashapaug Pond to Narragansett Bay, the timing of heavy metal increases is expected to closely parallel the results described above.

In addition to recording the influx of heavy metals, sediment cores may provide a record of other anthropogenic changes to the watershed. Sediment cores from Lake Pleasant, located 100 miles northwest of Mashapaug Pond in Massachusetts, provided evidence that deforestation of the watershed began around 1780. The evidence supporting this conclusion were the co-occurring decrease in percent organic matter, decrease in tree pollen, increase in weedy species pollen, and increase in the ratio of carbon (C) to nitrogen (N) (Kaushal & Binford 1999). C increased relative to N because plants growing on land have a C/N ratio >20, whereas algae have a C/N ratio ranging from 4 to 10 (Meyers & Teranes 2001). Deforestation increased soil mobility, causing more terrigenous material, including land plant matter, to be washed into the pond, elevating the C/N ratio. Records of herbaceous *Ambrosia* pollen and magnetic susceptibility cores

from Narragansett Bay also show evidence of widespread deforestation and soil mobilization during mid-to-late 1700s (Salacup 2014).

Previous coring of Mashapaug Pond found that a similar decrease of 40% for oak pollen and an increase of 30% for herbaceous plant pollen occurred between 1700 and 1750, suggesting that significant tracts of forest were replaced by open fields during this period (Bernabo 1977). Based on this previous work, sediment cores from Mashapaug Pond would be expected to exhibit evidence of deforestation and increased soil mobilization in the early 1700s. In particular, the C/N ratio would increase, as seen in Lake Pleasant, percentage of organic materials (C and N) would decrease, and the concentration of elements indicative of terrigenous source material, such as titanium (Ti) would increase.

4c. Plant and Soil Analysis

Plants incorporate heavy metals from atmospheric, soil, and water sources into their leaf tissue. While certain micronutrient metals, such as copper, nickel, and zinc, are vital at low concentrations, they become toxic to plants at higher concentrations. Other metals, including arsenic, chromium, mercury, and lead are absorbed by plants despite the fact that they are not biologically necessary, and are toxic even at low concentrations (Peralta-Videa et al. 2009). Plant uptake and tolerance of heavy metals is dependent on genetic traits of the plant, metal solubility, and proximity to the source of pollution among other factors (Baxter & Dilkes 2012; Cataldo & Wildung 1978; Goolsby & Mason 2015; Jung 2008). Uptake of metals by plants deemed “hyperaccumulators” can be used for bioremediation (Kocić et al. 2014), and used for analysis of environmental conditions (Fernández et al. 2007; Maisto et al. 2013).

Herbarium specimens have been used to study past environmental conditions in a variety of ways, including tracking nitrogen availability (McLauchlan et al. 2010), monitoring the spread of invasive species, and assessing changes in phenology (Lavoie 2013). Retrospective analysis of heavy metal concentrations has been conducted using lichen (Minganti et al. 2014), mosses (Herpin et al. 1997; Ochota & Stebel 2013; Saxena et al. 2008; Shotbolt et al. 2007; Weiss et al. 1999), and vascular plants (Peuelas & Filella 2002; Rodríguez Martín et al. 2014; Rudin et al. 2017).

A key limitation of previous studies has been their inability to distinguish between atmospheric and terrigenous sources of metals. Accumulation through roots and deposition on leaf surfaces are both potential sources for metals measured in herbaceous leaf material. Atmospheric deposition is indicative of a regional signal, whereas uptake from the soil indicates a more local signal, so differentiating between these two sources informs our understanding of contamination sources. In an urban watershed in Michigan, concentrations of Pb in near-surface soil were found to be 15.5 times the background preindustrial levels, presenting a significant metals source (Murray et al. 2004). Although many aspects of soil chemistry, including soil pH, cation exchange capacity, organic matter content, and soil texture, have been found to influence the bioavailability of metals, total metal concentration in the soil is the main control on the plant uptake of metals from the soil (Jung 2008). By measuring the concentrations of heavy metals in soil immediately adjacent to where plants are collected, it is possible to assess the relative influence of local soil contamination and regional atmospheric pollution on plant uptake.

This study seeks to build upon previous work that used herbarium specimens from four sites around Rhode Island to compare historical and contemporary concentrations of copper (Cu), lead (Pb), and zinc (Zn) in the leaves of herbaceous plants (Rudin et al. 2017). The present study provides a more detailed analysis of one site, Mashapaug Pond, and supplements the previous work by sampling plants, soils, and pond sediments in order to document and assess past and present as well as local and regional effects on metal concentrations in plants. We expect to find that variations in soil concentration are replicated in associated plants. Additionally, we anticipate that concentrations of metals will be higher in historical plant specimens collected during the peak of industrial activity in Providence.

Methods

Land Use Analysis

ArcGIS was used to map urban and industrial development within the Mashapaug Pond watershed, an area of 4 km². The watershed used was determined by Michael Murphy, a graduate student in sociology, in order to facilitate future collaboration. Sanborn fire insurance maps from the Brown Digital Repository were used for 1889 and 1900, and aerial images from Rhode Island Geographic Information System (RIGIS) for the years 1939, 1962, 1988, and 2014. Current road and pond spatial data files were also downloaded from RIGIS.

The images were georeferenced based on road and pond outlines, using the RI State Plane Feet projection. The images for each year were combined into a Mosaic Database and clipped to the watershed boundary extent. The composite images were used to digitize land use polygons. Land use was partitioned into the following categories: Commercial/Industrial, Highway, Park/Cemetery, Residential, School, Unknown, and Water. Areas under construction or apparently vacant were classified as unknown. The area covered by each land use type was calculated for each year.

Sediment Analysis

Sediment cores were collected from the deepest section of Mashapaug Pond, as determined by a bathymetric map (RIDEM), and the depth was measured to be 4.6 m. 3 sediment cores were collected by piston-coring, approximately 1 m apart, with lengths of 134.5 cm, 129 cm, and 100 cm. The sediment-water interface was preserved in the second and third cores, and the core tops were stabilized with floral foam. Cores were split, and 3-4 smear slides were made for each core. The working half of core 2 was sampled at 1 cm intervals, and every other sample was freeze-dried for 48 hours for further analysis.

The 3 cores were analyzed using a GeoTek Multi-Sensor Core Logger (MSCL). Before the cores were split, wet bulk density was measured by Gamma Ray Attenuation Porosity Evaluator (GRAPE) analysis, and magnetic susceptibility was measured by a loop sensor. The cores were split and described, and a photo-record of the archive half of each core was created using Linescan Imaging. The working half of each core was then

scanned with an X-Ray Fluorescence (XRF) spectrometer and magnetic susceptibility point sensor mounted to the MSCL.

We chose core 2 for further analysis because the sediment-water interface was intact, and primary XRF scanning suggested that the core was well preserved and extended well into the preindustrial period. Plugs of approximately 3 cc were collected every 5 cm in the top 50 cm of the core, and every 10 cm to a depth of 110 cm. These were sent to Flett Research Ltd (Winnipeg, MB). for Pb²¹⁰ radioisotope dating.

The core was then sampled at 1 cm intervals, and every other sample was freeze-dried. Hg concentration of the dried sediment samples was measured using the Milestone DMA-80 Mercury Analyzer, following EPA Method 7473 (EPA 2007b) for samples of 50 mg (0-70 cm) or 150 mg (70-130 cm). NIST 1575 (pine needles) and NIST 2702 (Montana soil) were run as standards. CE Instruments Model NC2100 elemental analyzer was used to measure carbon and nitrogen content in 5 mg samples throughout the core, with the same standards. Handheld XRF was used to measure metal concentrations, using two 60-second beams.

Finally, 12 dried samples underwent partial acid digestion in the Milestone Ultrawave SRC Microwave Digestion System to dissolve the organic material and make heavy metals available for measurement following EPA Method 3051A (EPA 2007a). We used 0.2 g of each sample, along with National Institute of Standards and Technology Standard Reference Material (NIST) 2702, 1646a, and SDO-1, combined with 5 ml of 70% double-distilled nitric acid in a pre-weighed glass test tube with a Teflon cap. The samples, along with reagent blanks, were loaded into the Ultrawave, pressurized to 40 bars, and heated to 175° C for 15 minutes. After cooling, approximately 2.5 ml of the digested samples were passed through a 0.45 µm Millipore Millex-HV syringe filter and diluted by a factor of 5 with 18.2 Mohm-cm deionized water. The specific dilution for each sample was determined gravimetrically.

ICP-AES was used to measure levels of As, Cr, Cu, Ni, Pb, and Zn. Samples were measured on a Thermo Scientific iCAP 7400 DUO. Inorganic Ventures EPA Quality Control Standard IV-28 (QC-28; all metals = 0.026 µg/g) and a verification standard (As = Cr = 0.106 µg/g, Cu = 0.264 µg/g, Ni = 0.423 µg/g, Pb = 0.053 µg/g, and Zn = 0.212 µg/g) interspersed between every 10 samples to assess the precision and accuracy of the machine. QC-28 measurements were consistently close to 0.027 µg/g confirming the reliability of the Ultrawave Digestion and ICP-AES. Calibration curves were generated with a maximum of 0.5 µg/g As, 1.0 µg/g Ni, 2.0 µg/g Cr, and 5.0 µg/g Cu, Pb, and Zn. Based on analyses of blanks, all of which contained < 0.002 µg/g of the measured metals, the detection limit of Cu, Pb, and Zn was estimated to be 0.001 µg/g.

Plant Analysis

Herbarium specimens were taken from the Brown University Herbarium following two sets of criteria designed to limit phylogenetic and geographic variation. First, 14 herbarium specimens from six plant families, collected between 1890 and 1895 around Mashapaug Pond were also sampled (Table 1). Between 2015 and 2016 we also collected contemporary specimens (n=11) from two small parks on the southwest side of the pond, J. T. Owens Park and Murphy Trainer Park. We collected specimens that

belonged to families represented in the historical herbarium collection, and when possible we collected congeners (species from the same genus) to control for phylogenetic variation in metal accumulation.

Family	Species	Lifespan	Historical	Contemporary
Apiaceae	<i>Cicuta bulbifera</i>	P	1895 (n=3)	
	<i>Daucus carota</i>	B		2015
Asteraceae	<i>Eurybia divaricata</i>	P		2015, 2016
	<i>Lactuca scariola</i>	B/A	1894 (n=2), 1895	
	<i>Lactuca</i> sp.	-		2015
Cyperaceae	<i>Carex blanda</i>	P		2015, 2016
	<i>Carex muhlenbergii</i>	P	1890, 1892	
Juncaceae	<i>Juncus acuminatus</i>	P	1893 (n=2)	
	<i>Juncus articulatus</i>	P	1892	
	<i>Juncus tenuis</i>	P		2015, 2016
Plantaginaceae	<i>Plantago rugelii</i>	P	1892	2015, 2016
Polygonaceae	<i>Persicaria lapathifolia</i>	A	1893	
	<i>Polygonum aviculare</i>	P/A	1893	
	<i>Polygonum</i> sp.	-		2016

Table 1: List of historical and contemporary species sampled from Mashapaug Pond. Lifespan refers to the perennial (P), biennial (B), and annual (A) growth types.

Year	Genus species	Municipality	Locality Notes
1844	<i>Plantago major</i>	Providence	--
1844	<i>Plantago virginica</i>	--	Near Providence
1869	<i>Plantago lanceolata</i>	Providence	Field
1873	<i>Plantago lanceolata</i>	Providence	--
1878	<i>Plantago lanceolata</i>	Providence	--
1879	<i>Plantago lanceolata</i>	Providence	Brown University Campus
1884	<i>Plantago major</i>	Providence	--
1887	<i>Plantago lanceolata</i>	Providence	Waterman St.
1892	<i>Plantago lanceolata</i>	Providence	Fields, East Ave.
1892	<i>Plantago lanceolata</i>	Providence	In fields near East. Ave.
1892	<i>Plantago rugelii</i>	Providence	Shore Mashapaug Pond
1900	<i>Plantago major</i>	Providence	Brown University Campus
1900	<i>Plantago lanceolata</i>	Providence	--
1905	<i>Plantago lanceolata</i>	Providence	Brown University Campus
1905	<i>Plantago lanceolata</i>	Providence	Brown University Campus
1911	<i>Plantago aristata</i>	Cranston	Sandy soil, Wentworth Ave. Edgewood
1952	<i>Plantago aristata</i>	East Providence	Near Luther's Corner, dry meadow
1975	<i>Plantago lanceolata</i>	Providence	Harmony St.
2015	<i>Plantago rugelii</i>	Providence	Southwest shore of Mashapaug Pond; Murphy Trainer Park
2016	<i>Plantago rugelii</i>	Providence	Southwest shore of Mashapaug Pond; Murphy Trainer Park

Table 2: List of specimens (n=20) of the genus *Plantago* collected within Providence County from 1844 – 2016. -- indicates that no information was provided by the specimen label.

Second, 20 specimens of the genus *Plantago* collected between 1844 and 2016 throughout Providence County were sampled (Table 2). The species sampled included *P. aristata* (n=2), *P. lanceolata* (n=11), *P. major* (n=3), *P. rugellii* (n=3), and *P. virginica* (n=1).

Approximately 0.5-1.0 g of leaf material was removed from each specimen. For both historical and recently collected specimens we pooled leaf material from 2-5 specimens of the same genus from each location to ensure adequate material for analysis without removing excess tissue from any individual specimen. Leaf material was freeze-dried for 48 hours and ground into a fine powder for analysis.

Freeze-dried leaf material was acid-digested using the same method as used on sediment samples. This method was designed for digesting the organic components of soils and sediments, and was adapted for use on plant material. Using the Ultrawave Microwave Digestion System instead of a standard microwave allowed us to use a smaller quantity of leaf material, reducing the amount of material removed from each specimen. We used 0.2 g of each sample, along with National Institute of Standards and Technology Standard Reference Material (NIST) 1575 (pine needles), 1515 (apple leaves), and reagent blanks. ICP-AES was used to measure levels of As, Cr, Cu, Ni, Pb, and Zn in the samples. Calibration curves were generated for the metals of with a maximum of 0.1 µg/g for all metals. Plant specimens were analyzed in the same run as sediment samples, as described above. Measurements of As and Ni were near or below the detection level, and were excluded from further analysis.

In addition, we considered studying Hg in the plant specimens. The Milestone DMA-80 Mercury Analyzer was used to measure the Hg concentration of dried leaf material following EPA Method 7473 (EPA 2007b). A subset of the historical samples was run twice and in each case we encountered difficulties. This was attributed to high levels of Hg in samples due to treatment of mercuric chloride insecticide that saturated the column and detector. Mercuric chloride was a common treatment in the past for herbarium collections to reduce insect damage to the specimens (Purewal et al. 2007; Oyarzun et al. 2007).

Soil Analysis

Adjacent to each of the plant specimens collected in 2016 (n=5), two 20 cm long soil cores (A and B) were collected within a 1 m radius of the plant. The cores were split into 0-5 cm, 5-10 cm, and 10-20 cm parcels, which were freeze-dried for 48 hours in preparation for analysis, as is typical for soil samples collected in the Northeastern United States (Hoskins & Ross 2009; Pikul & Walker n.d.). Handheld XRF was used to measure metal concentrations of freeze-dried soil samples, using two 60-second beams.

Results

Land Use Analysis

Sanborn fire insurance maps (1889, 1900) and aerial images (1939, 1962, 1988, 2014) were used to map urban and industrial development of the Mashapaug Pond watershed (Fig. 2). As of the late 1800s, the watershed was mostly undeveloped, although a few industrial sites and residential neighborhoods are present in the 1889 and 1900 maps.

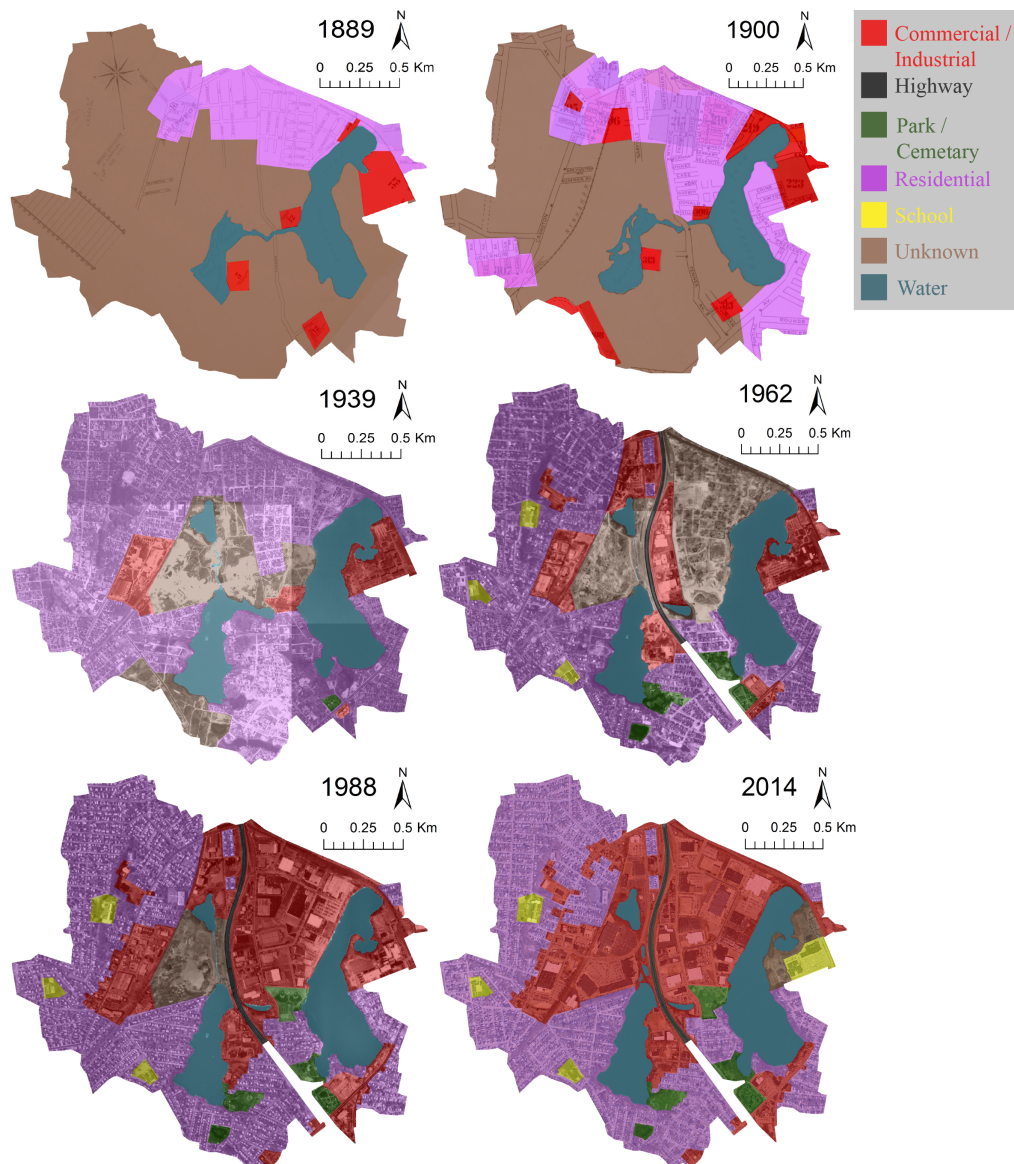


Figure 2: Land use maps of the Mashapaug Pond watershed for 1889, 1900, 1939, 1962, 1988, and 2014. Land use is categorized as Commercial/Industrial (red), Highway (black), Park/Cemetery (green), Residential (purple), School (yellow), Unknown (brown), and Water (teal).

In 1889 the watershed was on the outskirts of the city, and is barely represented on the map. The scattered industrial sites included the American Enamel Company, Earl Carpenter and Sons Ice Dealers, Molter’s What Cheer Brewery, Metropolitan Facing Works, and the Gorham Manufacturing Company factory, which was under construction at the time (Anon 1889). At this point, only 20% of the watershed was developed. Based on historical records, the unknown area is presumed to be agricultural although it may also have been partially forested. By 1900, the residential area had increased, and additional commercial and industrial sites included Narragansett Brewing Company, Tin Clad Paint Shop, a print shop, a sausage factory, and a coal dump. Notes from the Sanborn maps indicate that the majority of these industries relied on coal and coal oil for fuel and gas for lighting, and many had adjacent blacksmith’s shops and storage sheds that contained paints and oils. The Union Railroad also runs through the watershed, and both the Elmwood Station and Cranston Station are located within the watershed.

By 1939, residential development had expanded, such that nearly the entire watershed was developed. Little industrial expansion is visible on the aerial image, although the quality of this image is low. The center of the watershed in the 1939, 1962, and 1988 images resembles a sand and gravel pit, however no mention of a gravel pit has been found in oral histories, city documents, or historical reports, so this area has been labeled “Unknown.” The construction of Route 10 through the watershed in 1960 caused major changes that are evident in the 1962 map. The formerly residential area west of Mashapaug Pond was demolished and in this image was under construction. By 1988 this area has been redeveloped into the Huntington Expressway Industrial Park, which increased the amount of Commercial/Industrial land use and straightened the shoreline of Mashapaug Pond. The northwestern bank of the pond was filled in and straightened as part of this development. By 2014, Dr. Jorge Alvarez High School had been built on the former Gorham site on the eastern side of Mashapaug Pond.

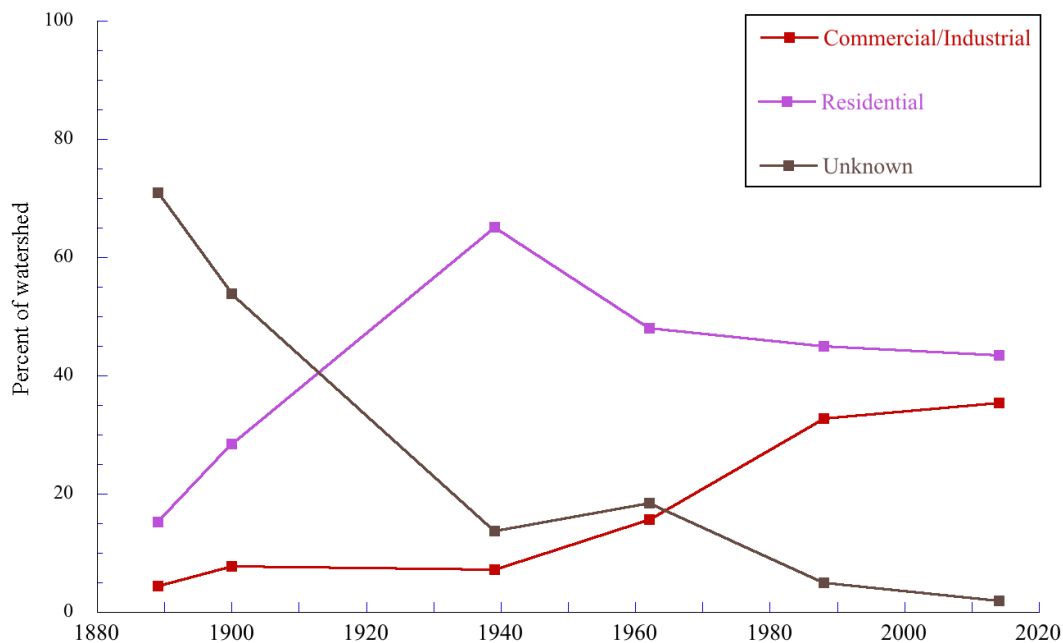


Figure 3: Percentage of Mashapaug Pond watershed (4 km2) with Residential and Commercial/Industrial land use, and the percentage of land use that is unknown.

Overall the residential development increased first within the watershed, followed by a more gradual but steady increase in commercial and industrial development (Fig. 3). While there has been fragmented commercial and industrial development since the earliest map studied, the percentage of Commercial/Industrial development increased in every period of the watershed's history. The period of greatest increase, between 1962 and 1988, reflects the construction of the Huntington Expressway Industrial Park. This construction is evident in the decline of residential land use between 1939 and 1962.

The amount of land designated as unknown decreased over the time period studied, in large part due to improved photographic clarity in later years. The Sanborn maps, while limiting in that some areas are unmapped, provide useful descriptive labels. These maps and images show the spread of urban and industrial development, however they do not show the process of land clearing for agriculture or development. To understand this aspect of the land use history, we must turn to the sediment core.

Sediment Analysis

Historically meaningful interpretation of sediment cores depends upon establishing an accurate age model. Radioisotope analysis performed by Flett Research Ltd. on Pb^{210} , Po^{209} , Po^{210} and Ra^{226} showed that Pb^{210} declined irregularly but approximately exponentially with depth. Unsupported Po^{210} was calculated by subtracting the nearest Ra^{226} measurement (taken at 4-6, 40-41, and 110-111 cm), from total Po^{210} activity. From 0-31 cm depth in the core, Ra^{226} activity was higher than the Po^{210} activity below 31 cm, so the remainder of the core is considered to be at background level.

Sediment accumulation rates ($\text{g}/\text{cm}^2/\text{year}$) and sedimentation rates (cm/yr) were calculated for the upper 31 cm of the core (Table 3), based on both a linear regression model and a Constant Rate of Supply (CRS) model. From 7-31 cm, the sedimentation rate was relatively constant at 0.38 so this rate was extrapolated for the entire core length. The age at the base of the Pb^{210} section at 31 cm was calculated to be 1938, and the age of the bottom of the core at 129 cm was calculated to be 1679. The sedimentation rate was applied as an age model cumulatively, such that for a given depth d_2 the age is calculated to be the age at depth d_1 plus difference in depth between d_1 and d_2 divided by the sedimentation rate over that section. The year of deposition was calculated as 2016-age, and resulting duration of the core is calculated to be 337 years.

Due to the limitations of the radioisotope analysis, this is an approximation, and it is likely that the sedimentation rate varied along the length of the core. In particular, when examining sediment sources, we observe significant fluctuation in terrigenous material, which would alter the sedimentation rate. However, using this age model, the heavy metal profiles closely resemble cores collected in Narragansett Bay (Bricker 1993; Corbin 1989; Goldberg et al. 1977; King et al. 2008), which also date the increase in Cu, Pb, and Zn concentration as beginning in 1850. This corroborates the age model constructed for the Mashapaug Pond core.

Sample ID (from Mashapaug Pond – Core 2)	Extrapolated Lower Section Depth (cm)	Po-210 Total Activity (DPM/g)	Po-210 Unsupported Activity (DPM/g)	Age at Bottom of Extrapolated Section in Years (CRS Model)	Accumulation Rate (g/cm ² /yr)	Sedimentation Rate (cm/yr)	Age: Years Before Present (BP)	Year
0-1 cm	3.00	22.41	18.10	3.7	0.1394	0.2702	3.7	2012
5-6 cm	7.75	25.81	21.50	12.1	0.0975	0.5965	12.1	2004
9.5-10.5 cm	12.75	25.90	21.59	22.8	0.0609 - 0.0813	0.3805	23.9	1992
15-16 cm	18.00	21.64	17.33	37.5	0.0609 - 0.0813	0.3805	38.4	1978
20-21 cm	23.00	13.08	8.77	47.8	0.0609 - 0.0813	0.3805	51.5	1964
25-26 cm	28.00	12.08	7.77	63.1	0.0609 - 0.0813	0.3805	64.7	1951
30-31 cm	33.00	8.81	4.50	77.1	0.0609 - 0.0813	0.3805	77.8	1938
35-36 cm	40.50	6.18				0.3805*	90.9	1925
45-46 cm	53.00	5.80				0.3805*	117.2	1899
60-61 cm	65.50	3.53				0.3805*	156.6	1859
70-71 cm	90.50	2.59				0.3805*	182.9	1833
110-111 cm	111.00	2.60				0.3805*	288.1	1728

Table 3: Age model results, including total Po²¹⁰, unsupported Po²¹⁰, and sedimentation rate (as measured by Flett Research Ltd.). DMP = disintegrations per minute; CRS model = constant rate of supply. Age was calculated to be $[age_{d2}] = [age_{d1}] + [d2 - d1] / [SedRate_{d2}]$. * Sedimentation rate was extrapolated from higher in the core.

Metals of interest were measured by handheld XRF in both sediment and soil (As, Cr, Cu, Ni, Pb, Si, Ti, Zn). Additionally, following partial acid digestion, 11 sediment samples were measured using ICP-AES (As, Cr, Cu, Ni, Pb, Zn). ICP analysis yielded measurements 1.3 – 1.8 times higher than XRF measurements (Fig. 4). The correlation between XRF and ICP measurements had $R^2 < 0.85$ for all metals, and as low as $R^2 = 0.425$ for As (Table 4). Correlations were weaker when the intercept was fixed at 0. A correlation was also developed for certified soil and sediment standards (n=14), comparing measurement using the handheld XRF with the certified values for metals. With the intercept fixed at 0, the $R^2 > 0.95$ for all relationships except Ti, for which $R^2 = 0.915$ (Table 4). The standard-adjusted XRF measurements were used in all further analysis of sediment and soil samples because of their high degree of correlation and their basis in certified values. Additionally, ICP measurements were examined for As and Ni as these two metals had the lowest correlation between ICP and XRF measurements, and the potential of spectral interference between As and Pb in XRF measurements (Nagata et al. 2006).

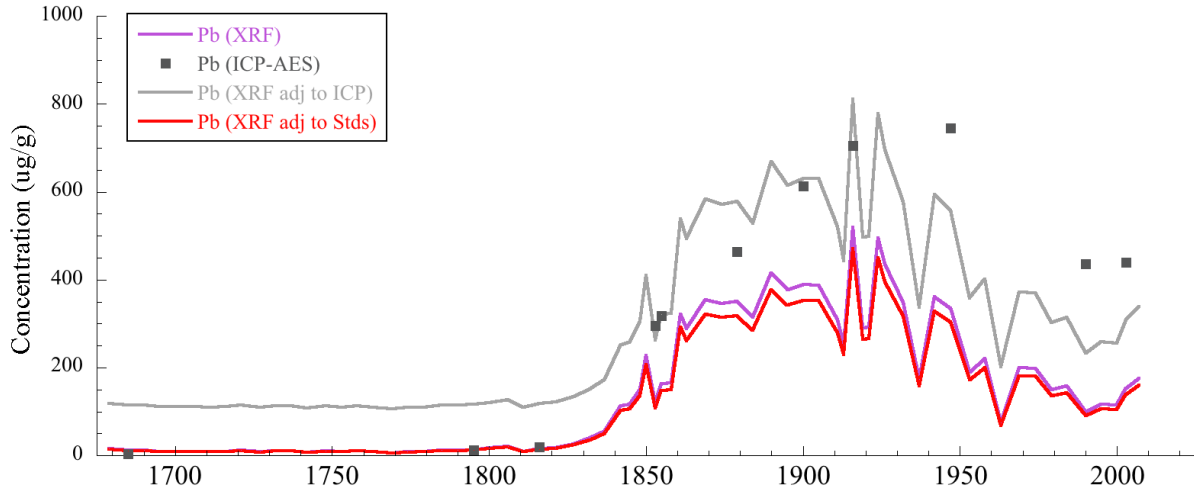


Figure 4: Concentration of Pb ($\mu\text{g/g}$) in a sediment core from Mashapaug Pond measured by ICP-AES, dry handheld XRF, and dry handheld XRF adjusted based on correlation developed for sediment standard certified values XRF measurements.

Metal	ICP Correction ICP = [x]*XRF	R ²	Standard Correction Certified = [x] * XRF	R ²
As	1.350 * XRF + 4.668	0.425	1.070	0.988**
Cr	1.474 * XRF + 24.411	0.828	1.579	0.956**
Cu	1.728 * XRF + 83.434	0.818	0.883	0.990***
Ni	1.361 * XRF + 1.956	0.671	0.996	0.955**
Pb	1.373 * XRF + 97.673	0.789	0.908	0.999***
Si	--	--	0.649	0.974**
Ti	--	--	0.845	0.915*
Zn	1.536 * XRF + 79.996	0.815	0.961	0.999***

Table 4: Correction factors for handheld XRF measurements on dry sediment and soil based on A) handheld XRF measurements of certified standards (n=13), and B) handheld XRF and ICP-AES measurements of dried sediment samples from Mashapaug Pond (n=11). Si and Ti were not measured with ICP-AES. * R² > 0.9; ** R² > 0.95; *** R² > 0.99

Using the age model and adjusted measurements of all metals, we can turn to analysis of the sediment core. Measurements of C, N, Ti, and Si indicate fluctuations in major sediment sources (Fig. 5). C and N, indicators of biological production, are highest deep in the core, with a pre-1760 baseline of approximately 20% C and 2% N. From 19.83% C and 2.07% N in 1758, biogenic material declined steeply, reaching a minimum of 6.15 %C and 0.61 %N in 1806. Simultaneously, terrigenous sediment indicators Si and Ti, which were lowest in the bottom of the core, increased from 6891.98 $\mu\text{g/g}$ Si and 321.67 $\mu\text{g/g}$ Ti in 1758 to 13573.80 $\mu\text{g/g}$ Si and 1528.22 $\mu\text{g/g}$ Ti in 1806.

After this fifty-year period of rapid change, C and N increased gradually to around 14.0% C and 1.4% N in the top of the core. Si and Ti gradually and erratically began to decline, and by the present returned to approximately 12000 $\mu\text{g/g}$ Si and 600 $\mu\text{g/g}$ Ti (Fig. 5). Neither C and N nor Si and Ti have entirely returned to their respective baseline conditions. Prior to 1760, the ratio of C/N fell between 11.0 and 12.2, (Fig.6), remained below 13.0 until around 1860. At this time, the ratio increased sharply to over

15, reaching a maximum of 17.63 in 1879. The C/N ratio has gradually decreased to around 12. This almost certainly means that sedimentation prior to 1750 was much slower than the extrapolated rate, because dilution by terrigenous sedimentation increased after that time.

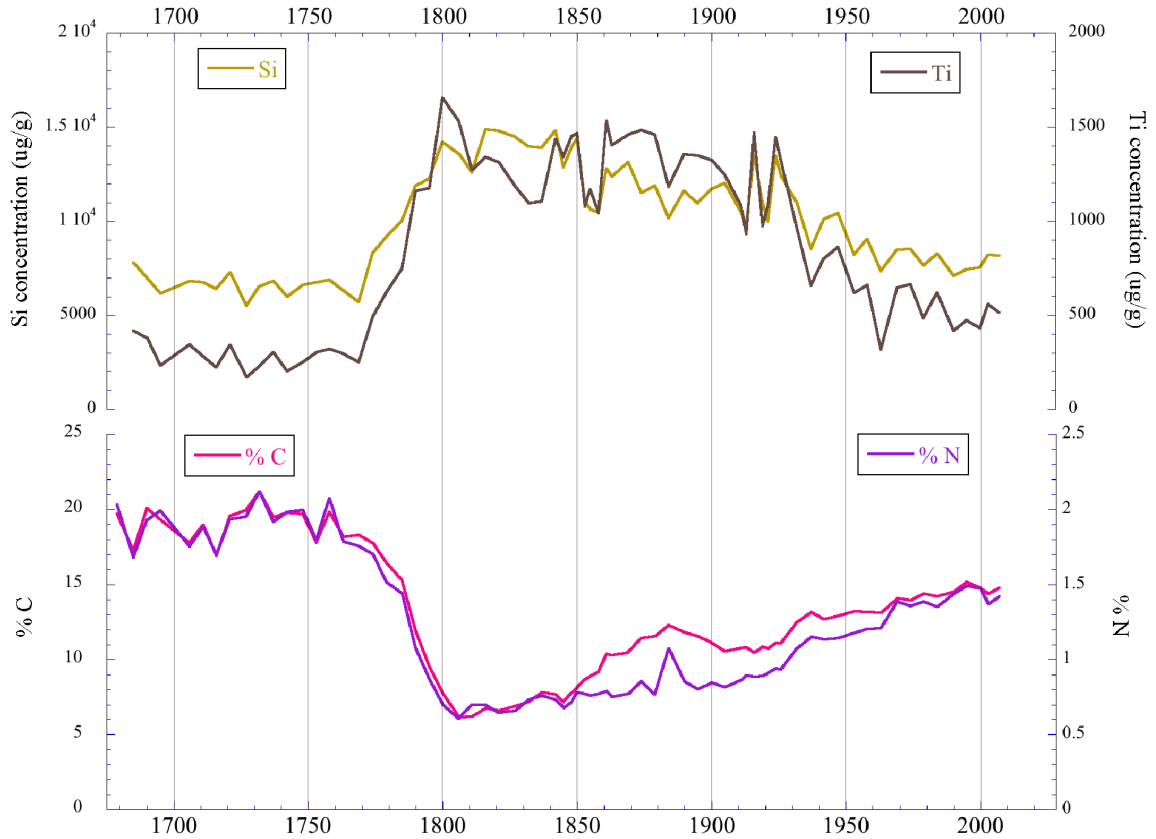


Figure 5: Profile of concentration ($\mu\text{g/g}$) of Ti and Si (upper) and percentage of C and N (lower) measured in sediment core from Mashapaug Pond.

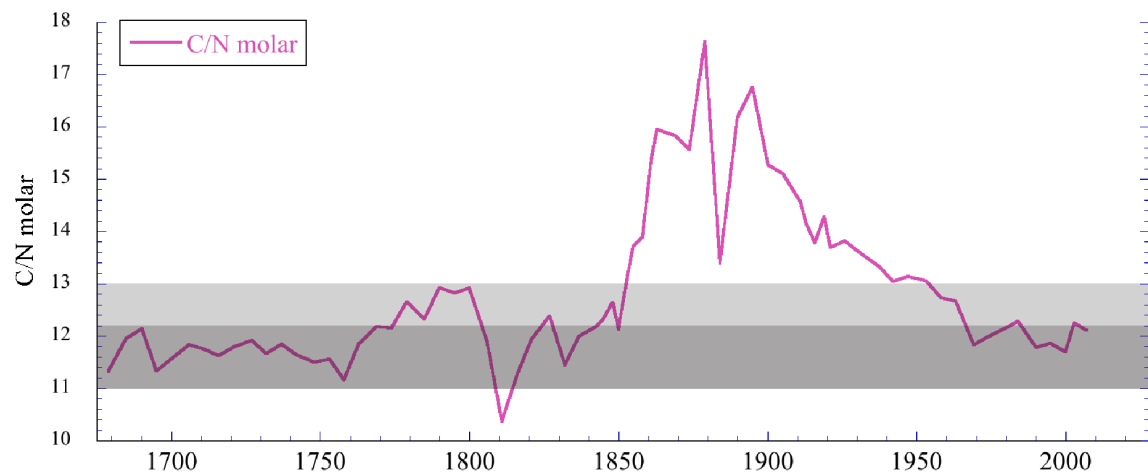


Figure 6: Profiles of the molar ratio of C and N measured in a sediment core from Mashapaug Pond. The dark grey band indicates the pre-1750 range (11.0 - 12.2), while the light grey band indicates the pre-1850 range (11.0-13.0).

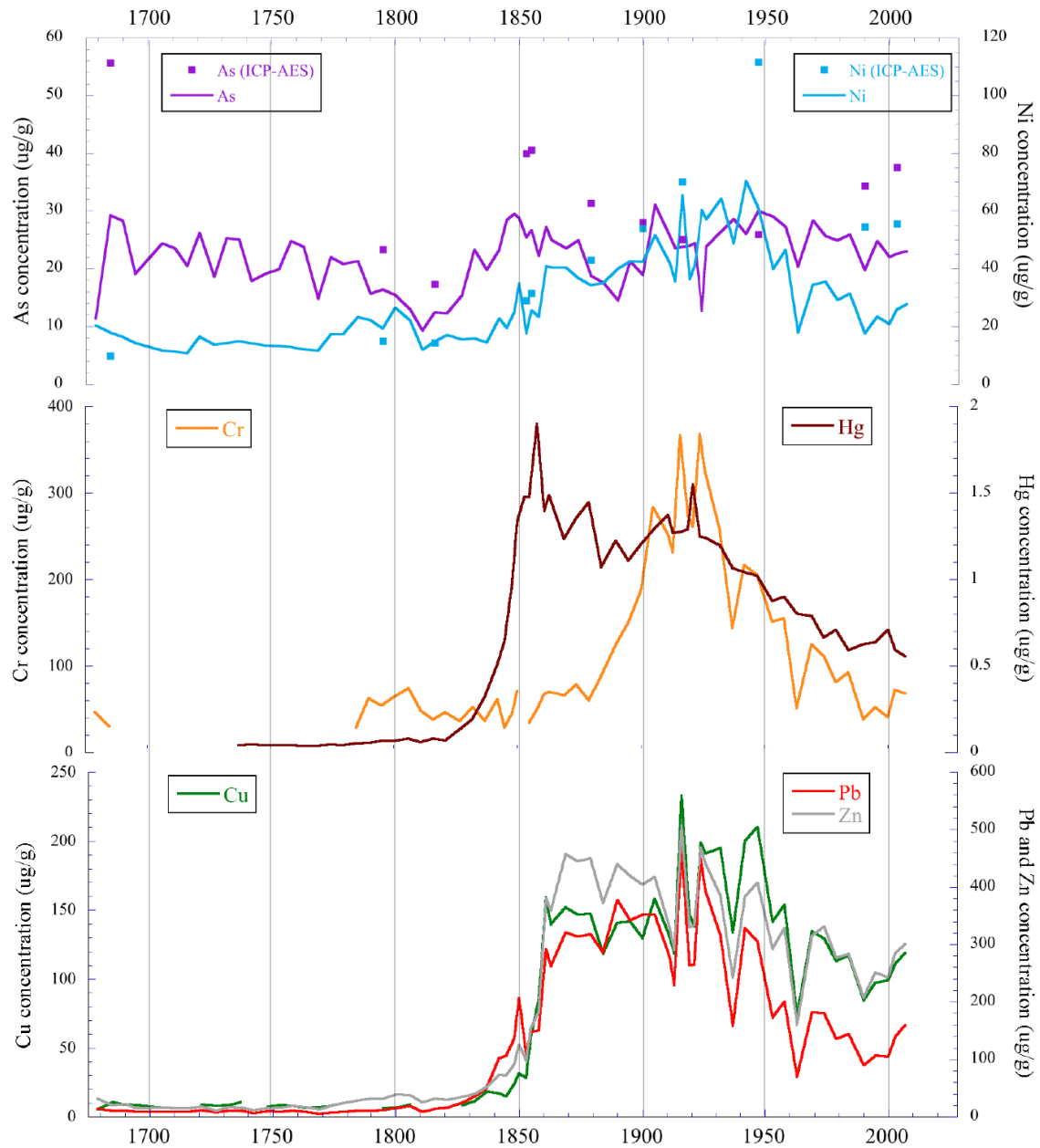


Figure 7: Profiles of XRF-measured concentration ($\mu\text{g/g}$) of As and Ni (upper), Cr and Hg (middle), and Cu, Pb, and Zn (lower) in a sediment core from Mashapaug Pond. Gaps indicate where concentrations were below detection. ICP-AES measurements of As and Ni are also included.

Examining the concentrations of the heavy metals studied in the sediment core, several distinctive patterns emerge (Fig. 7). Concentration of Cu, Hg, Pb, and Zn increased dramatically from a base level of <12 , <0.06 , <12 , and $<30 \mu\text{g/g}$, based on the 15 samples dated pre-1760. This date falls well before the beginning of the America Industrial Revolution, commonly cited as the construction of the Slater Mill on the Seekonk River, RI in 1790 (Marlow 2016; Nixon 1991). In the 30 year period between 1832 and 1861, concentrations rose from 11.22 to 159.45 $\mu\text{g/g}$ Cu, 0.20 to 1.40 $\mu\text{g/g}$ Hg,

35.85 to 291.97 $\mu\text{g/g}$ Pb, and from 39.53 to 380.34 $\mu\text{g/g}$ Zn. Hg peaked earliest, in 1858, and Cu, Pb, and Zn all peaked in 1916. Since their peak levels, all four metals have declined, although inconsistently. At the top of the core, the concentrations of Cu, Hg, Pb, and Zn all remain an order of magnitude about base level.

Cr also shows a striking increase above pre-1760 concentrations. Pre-1760, Cr is largely below the detection limit of the handheld XRF, but those values measured give a base level of <90 $\mu\text{g/g}$, and Cr concentration remains below this level until 1884. Cr concentration increase abruptly from 88.26 $\mu\text{g/g}$ in 1884 to 366.88 in 1916. Beginning around 1930, Cr concentration begins to decrease, dropping to <90 by 1979.

Ni also increased, but does not follow the same profile as Cu, Pb, and Zn. Ni varied between 10 and 30 $\mu\text{g/g}$ until 1858, and then slowly and inconsistently increased to a peak of 70.34 $\mu\text{g/g}$ in 1942, as measured by handheld XRF, or 111.54 in 1947 as measured by ICP-AES (Fig. 7). Following this peak, Ni decreased to base levels of <30 $\mu\text{g/g}$ by 1979 according to XRF measurements, but ICP-AES measurements suggest Ni levels are >50 $\mu\text{g/g}$ in the upper part of the core.

As is the only metal that does not show a clear increase during the industrial period, according to both XRF and ICP-AES measurements. Both methods indicate that As varied between 10 and 30 $\mu\text{g/g}$ for the length of the core (with one anomalously high measurement of 55.70 $\mu\text{g/g}$ at the bottom of the core), with no discernable trends.

Overall, from 1850 onwards, heavy metal concentrations are significantly higher than pre-1790. Additionally, variation in concentration is more extreme and more jagged in the later half of the core. Generally, the concentration of metals varies in unison, such that peaks and valleys in the profiles align. The profiles of Cu, Pb, and Zn are especially similar, whereas Cr, Hg, and Ni all peak at different times, indicating that the input sources these metals to Mashapaug Pond vary somewhat independently.

Additionally, all metals except for As decline in concentration over the course of the 20th century, as does the concentration of terrigenous elements, Ti and Si. Organic components, %C and %N, however, increase over this period. In order to compare the decrease in metals to the decrease in terrigenous material, the ratio of Cr, Pb and Hg to Ti was calculated along the length of the cores (Fig. 8). All three heavy metals increased similarly to the profiles shown in Figure 7, however they did not decrease in the same way. Relative to Ti, Pb and Hg never decreased below the peak industrial period level of approximately 0.25 and 0.0015 respectively. Beginning around 1950, Cr declined but has not returned to pre-industrial levels.

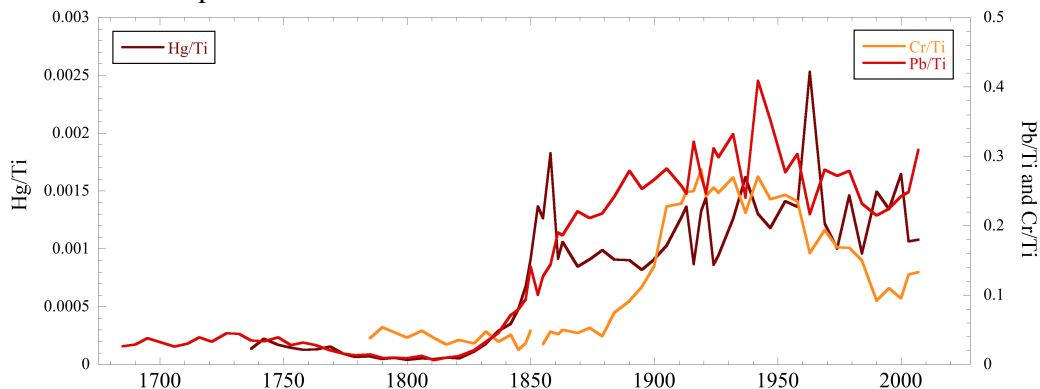


Figure 8: Ratios of Hg, Cr, and Pb ($\mu\text{g/g}$) to Ti ($\mu\text{g/g}$), over time.

Plant Analysis

The first method of comparing past and present pollution limited the geographic scope to Mashapaug Pond, comparing closely related specimens from 1890-1895 and 2015-2016. Overall, measurements of Cr, Cu, Pb, and Zn showed no consistent trend between the two periods (Fig. 9).

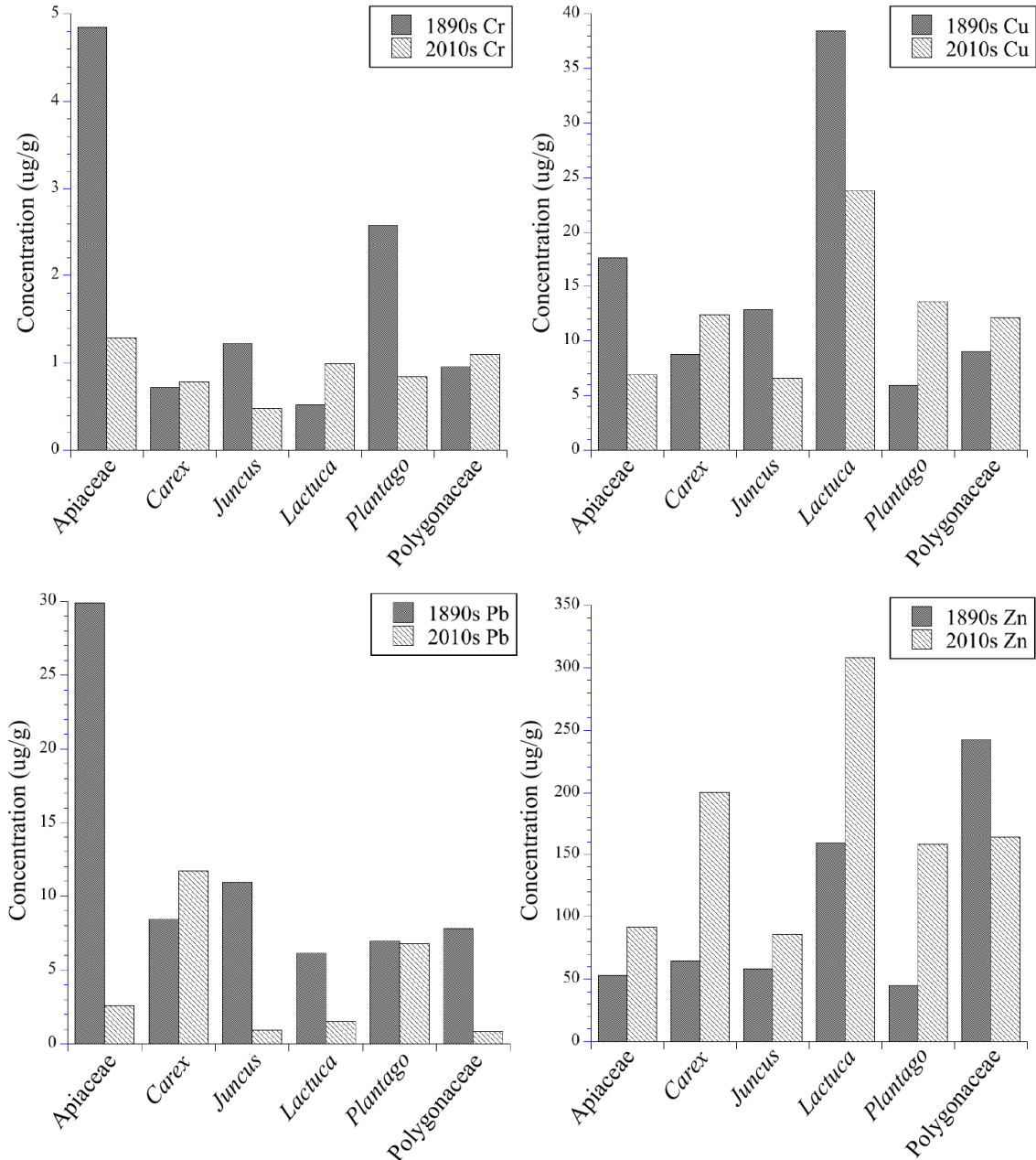


Figure 9: Metal concentrations ($\mu\text{g/g}$) in congener (*Carex*, *Juncus*, *Lactuca*, *Plantago*) and confamilial (Apiaceae, Polygonaceae) specimens collected near Mashapaug Pond during two periods: 1890-1985 and 2015-2016. Counterclockwise from top left: Cr, Cu, Zn, Pb.

Concentration of Pb decreased over time for all except *Carex*, with differences in concentration ranging from -0.155 to -27.305 $\mu\text{g/g}$. Zn increased for all except Polygonaceae, and changes were similarly variable in magnitude. Concentrations of Cr and Cu in *Carex*, *Lactuca*, and Polygonaceae increased from past to present, while they decreased in Apiaceae, *Juncus*, and *Plantago*. Apiaceae specimens had higher concentrations of Cr, Cu, and Pb historically, whereas *Carex* specimens had lower concentrations of these metals historically, and other taxa showed no clear pattern. The decreases were generally of greater, although inconsistent, magnitude.

The second method of focused on specimens in the genus *Plantago* collected between 1844 and 2016 in Providence County. The limited geographic and phylogenetic scope provides an opportunity to make meaningful temporal comparisons. The time frame covered by this sampling is indicative of the Brown University Herbarium collection as a whole, with few specimens collected before 1850, an abundance of specimens between 1880 and 1910, sparse collections between 1920 and 2010, and renewed collecting activity in recent years. Thus, the bulk of the specimens were collected during the height of industrial activity in Providence, RI, and specimens were not collected early enough to establish a pre-industrial baseline.

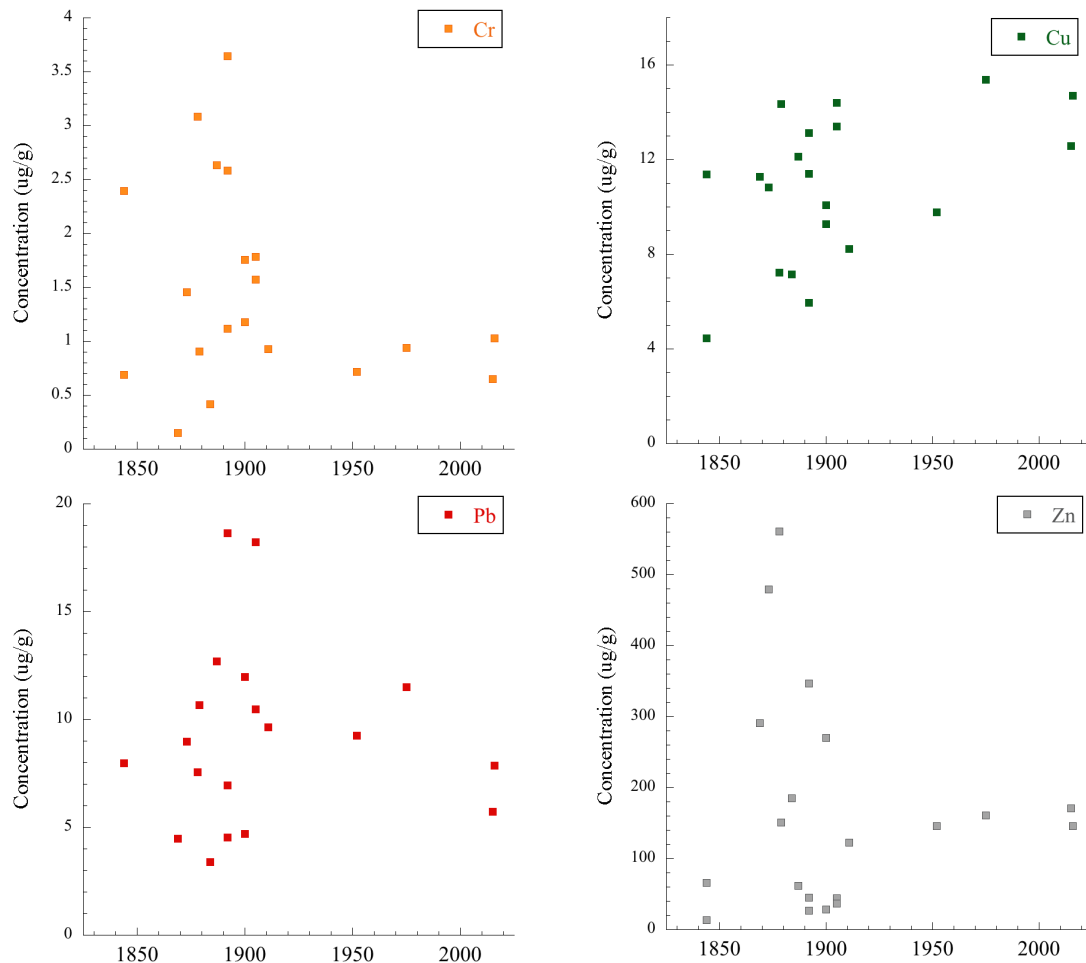


Figure 10: Concentration ($\mu\text{g/g}$) of metals in *Plantago* specimens ($n=20$) collected in Providence County between 1844 and 2016. Clockwise from upper left: Cr, Cu, Zn, Pb.

Measurements by ICP-AES of Cr, Cu, Pb, and Zn concentrations ($\mu\text{g/g}$) in the *Plantago* time series are shown in Figure 10. For all four metals, the time period with the greatest range of concentrations was between 1880 and 1910, the period when the most specimens were collected. For instance, the range in Pb concentration for the three specimens collected in 1892 (4.541 – 18.649 $\mu\text{g/g}$) covers almost the entire range in Pb concentration across all specimens. For Cr, Pb, and Zn, measurements since 1952 were between the minimum and maximum overall values, and generally low. Recent measurements of Cu were among the highest concentrations, and the peak measurement of 15.380 $\mu\text{g/g}$ was observed in the 1975 specimen.

Soil Analysis

In order to assess the relative influence of local and regional contamination on plant uptake of metals, soil cores were collected alongside plant specimens in 2016. We used the top 10 cm of soil at each site for comparison, as this is the section of the soil most likely to be in contact with the roots of herbaceous plants. Collections were made within a 6250 m² area at Murphy Trainer Park, on the southwest edge of Mashapaug Pond, which is bounded by Route 10, a residential neighborhood, and a parking lot and shopping plaza containing Save-a-Lot Grocery Store, RadioShack, Beauty Works Providence, Family Dollar, and Advance Auto Parts, among other businesses (Fig. 11).

Figure 11 shows the comparison between sites for Pb concentration in soils and plants. For both categories, Pb concentration is dramatically higher at site 4 than any of the other sites. Concentrations of Cr, Cu, and Zn in the soil at site 4 are also far greater than at other sites, although this difference is less extreme for Cr (Table 5). The *Carex* collected at site 4 has the highest concentration of Zn, but the concentration of Cr and Cu fall within the range measured from other sites. Additionally, the *Plantago* plant specimen has a higher concentration of Pb relative to the soil at site 5, compared to other plants. Phylogenetic variation in plant uptake and exclusion may be significant in understanding these different responses.

Site	Type	Cr ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)
1	Soil (0-10 cm)	66.379	22.057	66.238	97.443
	Plant (<i>Persicaria longisetata</i>)	1.099	12.112	0.849	164.043
2	Soil (0-10 cm)	122.262	30.342	48.582	165.717
	Plant (<i>Juncus tenuis</i>)	0.340	1.752	0.283	61.850
3	Soil (0-10 cm)	59.611	13.126	28.869	70.621
	Plant (<i>Eurybia divaricata</i>)	0.753	6.762	0.900	299.908
4	Soil (0-10 cm)	133.513	286.324	1213.978	1456.795
	Plant (<i>Carex sp.</i>)	0.876	8.406	19.775	320.261
5	Soil (0-10 cm)	86.974	24.349	85.495	94.643
	Plant (<i>Plantago rugellii</i>)	1.026	14.702	7.871	145.766

Table 5: Cr, Cu, Pb, Zn concentrations ($\mu\text{g/g}$) in top 10 cm of soil (mean of 0-5 and 5-10 cm sections) and plants collected at 5 locations in Murphy Trainer Park, on the southwest corner of Mashapaug Pond.

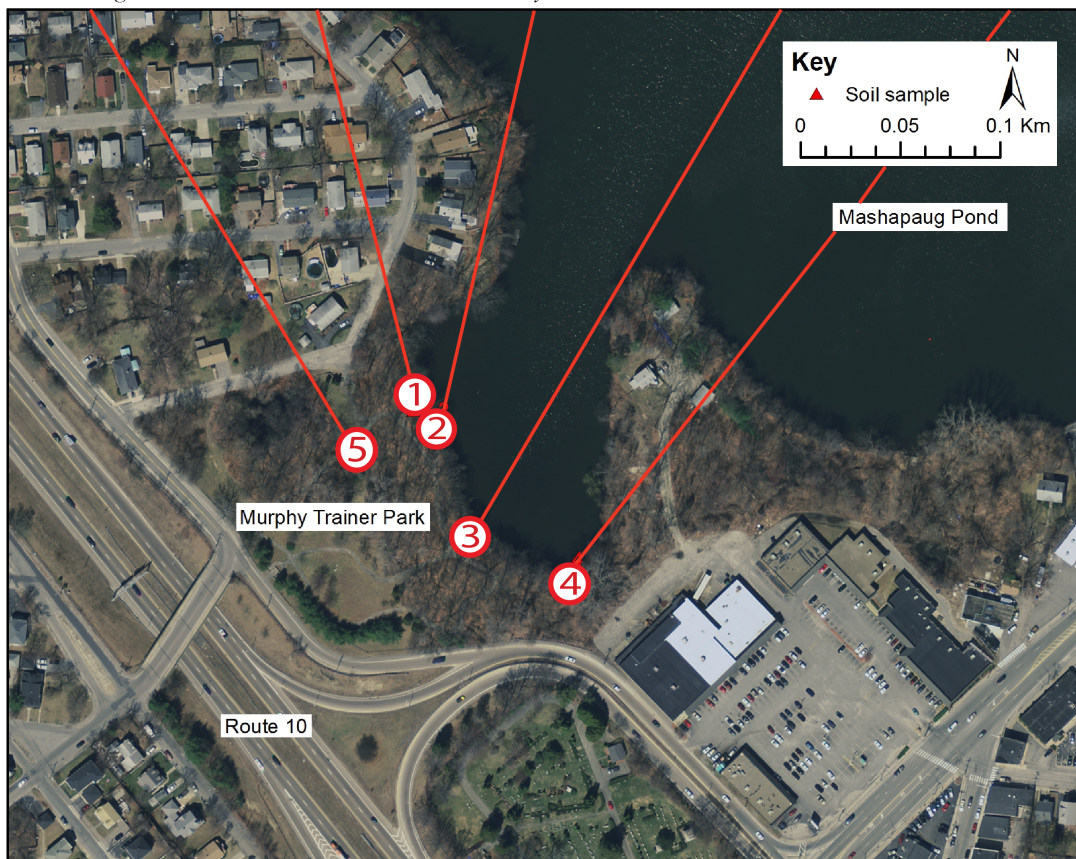
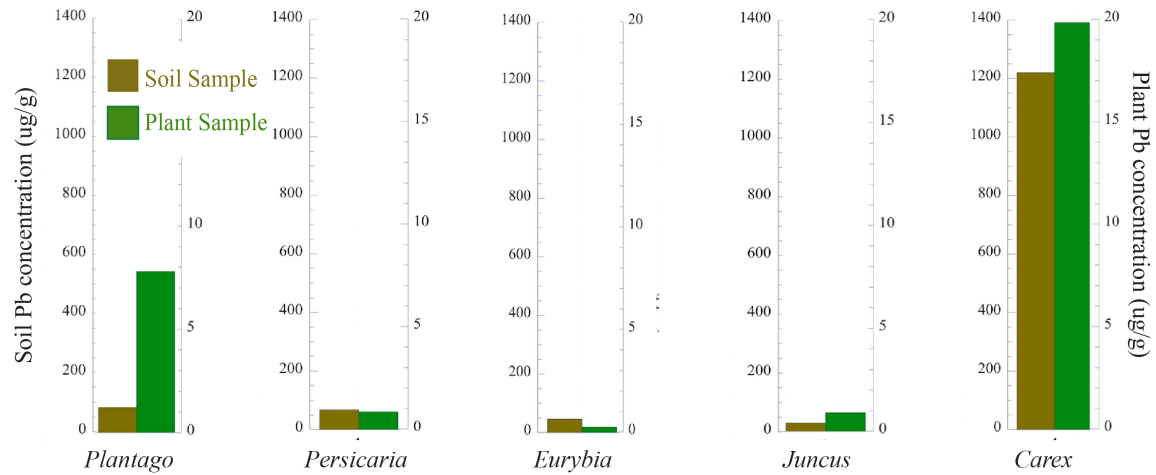


Figure 11: Comparison in concentration ($\mu\text{g/g}$) of Pb measured in plant and soil samples collected from 5 sites in Murphy Trainer Park on the southwestern side of Mashapaug Pond. Soil measurements are the average of two soil cores, from 0-10 cm.

Examining the soil alone, site 4 has a far greater concentration of heavy metals than the other sites studied (Fig. 12). In particular Cu, Pb, and Zn are extremely elevated at site 4. The elevated concentrations at site 4 are further exaggerated at greater depth. For all metals except As, the 10-20 cm concentration at site 4 was the highest measured (Table 6). Looking at Cu for example, the overall average for all depths at sites 1, 2, 3,

and 5 was 20.702 $\mu\text{g/g}$, while at site 4 the concentrations measured at 0-5, 5-10, and 10-20 cm respectively were 232.73, 339.92, and 3314.72 $\mu\text{g/g}$. While consistently high at site 4, the 10-20 cm range did not necessarily have higher metal concentrations than the 0-10 cm range at other sites.

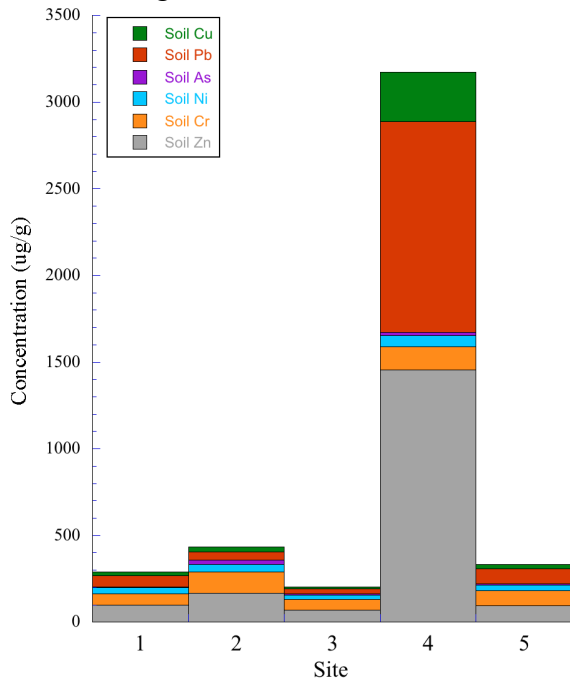


Figure 12: Cumulative concentration ($\mu\text{g/g}$) of all metals at all sites in top 10 cm of soil (mean of 0-5 and 5-10 cm sections from two cores, collected within 1 m of each other).

Site #	Depth (cm)	As ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)
1	0-5	4.61	67.89	21.49	39.89	58.61	97.66
	5-10	5.19	63.36	22.62	28.54	73.87	97.23
	10-20	6.80	61.83	13.52	21.73	71.14	67.30
2	0-5	31.52	183.39	37.01	49.90	43.37	156.30
	5-10	15.42	61.13	23.67	39.97	53.80	175.14
	10-20	15.14	50.09	26.79	48.39	134.85	101.58
3	0-5	3.40	65.66	15.70	29.86	30.81	75.91
	5-10	4.56	53.57	10.55	24.88	26.93	65.33
	10-20	2.86	79.51	ND	18.22	14.00	42.27
4	0-5	17.50	119.50	232.73	64.96	1117.34	1240.16
	5-10	23.66	147.53	339.92	61.66	1310.61	1673.43
	10-20	ND	632.77	3314.72	233.21	7142.62	12366.98
5	0-5	8.47	100.14	23.31	30.98	85.29	116.42
	5-10	6.99	73.80	25.39	32.89	85.70	72.86
	10-20	4.60	53.35	7.66	53.38	25.38	47.85

Table 6: Concentration ($\mu\text{g/g}$) of As, Cr, Cu, Ni, Pb, Zn at all Murphy Trainer Park sites, for depth ranges of 0-5, 5-10, and 10-20 cm. At each site, 2 soil cores were collected, and average for each depth range was taken. ND indicates where measurements were outside the detection limits of the handheld XRF

Discussion

Land Use Analysis

Mapping land use changes with historical maps and aerial images provides a baseline understanding of the timing of development in the watershed. Using oral histories and historical documents as reference material, GIS can be used to quantitatively track changes in land use types. The expectations, that industrial areas would increase throughout the time period studied and that residential development would peak prior to the construction of Route 10, were based on historical records. Land use mapping confirmed both hypotheses, and for the most part, visual assessment of land use types aligned with historical documentation of development (Kulik & Bonham 1978; Anon 1916). Land use mapping also showed that the construction of Route 10 and the Huntington Industrial Park, between 1960 and 1970, was a period of major change in the watershed: rezoning reduced the residential area, increased the commercial/industrial area, and the northwest shore of the pond was straightened with infill during the construction.

Maps and images from six years were analyzed, at intervals of 10-40 years. Similar studies of urban expansion used between two and six years for analysis, with intervals of 10-20 years between each analysis (Garnier et al. 2013; LeBlanc & Fortin 2015; Liu & Yang 2015; Malik et al. 2013; Schneider et al. 2015). The number of years mapped is consistent with the scope of similar studies, and because development occurs on the scale of decades, analyzing aerial images at shorter time intervals may or may not have been useful. Prior to 1939, aerial images were unavailable and analysis relied on Sanborn fire insurance maps, which are only available for the years 1889 and 1900. No detailed maps of the watershed could be acquired earlier than 1889, so it was not possible to map land use prior to the first industrial development on Mashapaug Pond, and in 1889 Mashapaug Pond was the edge of the city, so parts of the watershed, and of both Mashapaug and Spectacle Pond, are cut off by the map. A Sanborn map from 1921 is also available in the Brown University archives, but the pages that contain the Mashapaug Pond watershed are missing, creating a gap between 1900 and 1939. This gap is unfortunately timed, as it contains the period of most rapid residential expansion.

Both Sanborn maps and aerial images have limitations in terms of detail and accuracy. Sanborn maps are fire insurance maps, and thus only include buildings. Blank areas on the maps could be forested, agricultural, vacant or put to other uses. One historically documented site that is not included on the maps is the Hebrew Cemetery, which has been located in the southeastern portion of the watershed since 1849 (Anon 1916). Even Tongue Pond, which is documented because the Narragansett Brewery was built on its shore (Kulik & Bonham 1978), does not appear on either Sanborn map. Despite these limitations, the Sanborn maps do include useful labels that provide information about the specific industries present, as well as their water sources and the type of fuel burned. In aerial images, particularly early ones that tend to be grainy and blurred, it is difficult to confidently differentiate between residential and commercial areas, and even more difficult to identify the type of industrial or commercial development present.

The accuracy of aerial image mapping could be improved by identifying commercial and industrial locations using archival phonebooks to verify and augment visual identification. This approach is currently being undertaken in the Mashapaug Pond watershed by Michael Murphy and the Superfund Research Project at Brown University, using phonebooks for the cities of Providence and Cranston from 1950 to present. The two advantages of this technique are the ability to gather information about the type of industry and the ability to identify small, visually inconspicuous sites.

An area of interest for further investigation is mapping the expansion of paved areas, such as roads and parking lots, in the watershed. In this analysis, it would be important to differentiate between paved and unpaved roads, as only 31.5% of streets in the West Elmwood neighborhood on the western shore of Mashapaug Pond were paved as of 1960 (Malley 1960). Phosphorus and nitrogen-rich runoff into the pond from streets and storm drains has been a source of concern due to the increased potential for the toxic algae blooms (Kuchar 2011; RIDEM 2007; Salit 2011). Mapping the area covered by streets and parking lots, in the same way that the highway was mapped, could help assess runoff-related risks to Mashapaug Pond, and to the Roger Williams Park ponds downstream. Furthermore, the land use history contextualizes, and corroborates the sedimentary timeline.

Sediment Analysis

Sediment cores collected from Mashapaug Pond provide a continuous record of environmental conditions in the watershed, as indicated by the influx of various materials. Concentrations of metals and organic matter present in the sediment allow us to look deeper into land use changes to the watershed documented by GIS analysis: deforestation; regional industrialization; local industrialization; and deindustrialization (Fig. 13).

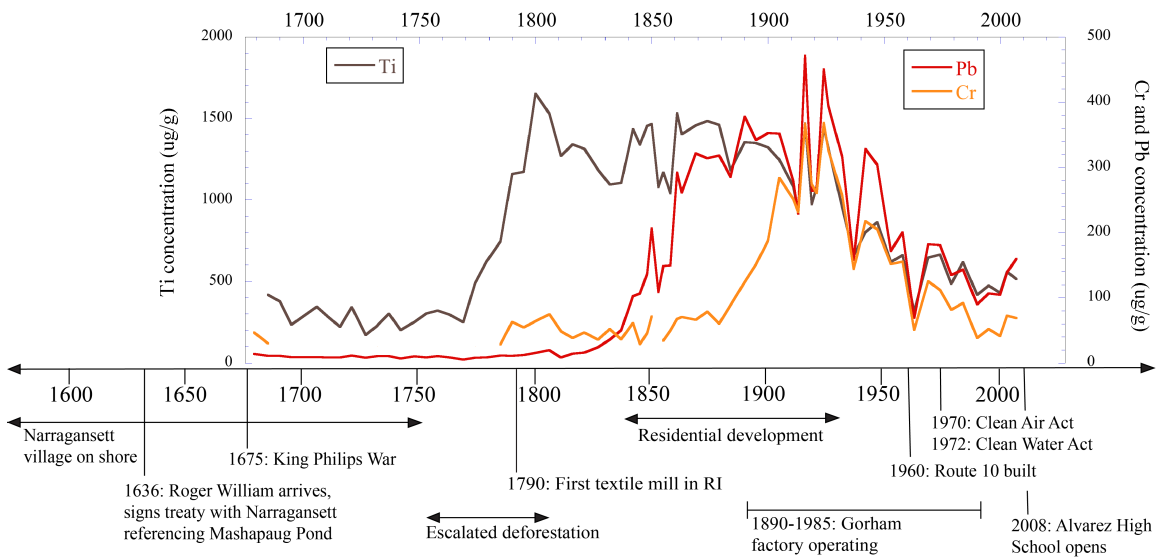


Figure 13: Profile of concentration ($\mu\text{g/g}$) of Cr, Pb, and Ti in a sediment core from Mashapaug Pond, along with a timeline of major local events.

For the most part, the sedimentary record parallels historical records, aligns with previous research, and deepens our understanding of land use change in and around the Mashapaug Pond watershed. Furthermore, sediment core analysis helps determine the historical environmental presence of heavy metals for analysis of plant specimens.

The earliest evidence of land use change present in the sediment core is of deforestation and increased soil mobilization. Beginning around 1760, the percentage of Ti and Si, elements found in terrigenous soil, increased rapidly, diluting organic materials C and N (Fig. 5). The increase in terrigenous input can be attributed to the twin processes of deforestation and soil tilling for agriculture, both of which decrease soil stability and allow greater quantities of soil to be washed into the pond. The timing of deforestation in the second half of the 18th century aligns with other studies conducted nearby, including cores collected from Narragansett Bay (Kaushal & Binford 1999; Salacup 2014).

However, evidence of deforestation was expected to be found as early as 1700, as pollen records in cores collected from Mashapaug Pond show that the percentage of herbaceous pollen began to increase and the percentage of oak pollen began to decrease at that time (Bernabo 1977). The incongruity between these estimates of the timing of deforestation may be due to differences in the age models applied to the cores collected by Bernabo and myself. Bernabo's age model was based on the assumption that deforestation began around 1700, making his age calculations circular. Pollen counts in our core could be used to assess the age-model agreement between the core studied, and Bernabo's cores.

One expected type of evidence for deforestation was an increase in the C/N ratio, as found in Lake Pleasant, MA and attributed to an increase in terrigenous organic material ($C/N > 20$) as opposed to algae ($4 < C/N < 10$), as terrigenous material was increasingly washed into the pond (Kaushal & Binford 1999). Around 1770, the C/N ratio increased above the previous maximum of 12.2 (Fig. 6), and this small increase may have been due to alterations in the ratio of terrigenous and algal organic material due to deforestation. However, the C/N ratio increased far more dramatically around 1860. This unanticipated C/N increase cannot be attributed to deforestation or soil mobilization, and will be discussed further in following paragraphs.

The second major story that the core tells is that of regional industrialization. The concentration of Cu, Ni, Pb, and Zn began to increase around 1850 (Fig. 7). The profiles of Cu, Pb, and Zn are extremely similar, and all three are used in a wide variety of industrial processes. The increase in heavy metal concentrations predates industrial development in the Mashapaug Pond watershed, and thus is indicative of atmospheric deposition from regional industrialization. The earliest documented industrial activity located within the watershed was the Earl Carpenter Icehouse, which harvested ice from the ponds from 1849-1920 (Anon 1916), and fabric, metal working, and brewing industries were not established around Mashapaug Pond until the 1880s and 90s (Kulik & Bonham 1978). Cu, Ni, Pb, and Zn are used in a wide variety of industrial processes, and their increase coincides with the growth of Providence into a hub of industrial manufacturing, and metal-working in particular.

The increase in Hg slightly predates the other metals. While Hg is used in some industrial manufacturing processes such as paper production (Naja & Volesky 2009), the primary source of Hg is likely to be coal combustion (Nriagu & Pacyna 1988). Coal-powered steam engines replaced the first water-powered mills in Rhode Island, and coal

was the main power source in many of the early industries surrounding Mashapaug Pond (Anon 1889). Another heavy metal emitted through both coal combustion and industrial processes is As, and it is surprising that As does not increase with Hg and the other industrial metals, a result corroborated by ICP analysis, indicating that the discrepancy is not merely the result of spectral interference with Pb in XRF analysis (Fig. 7).

The increase in C/N ratio to above 13.0 occurred around 1860, and peaked in the late 1800s (Fig. 6). The timing of this change in C/N ratio during the same period that industrial heavy metals were rapidly increasing suggests that, rather than being related to deforestation as found by Kaushal and Binford (1999), the change may be related to industrialization. A causal relationship between organic material sources and industrial activity cannot be conclusively identified by the work conducted, although the co-occurrence Analysis of the specific organic components present would be necessary to further examine the changes in C/N observed.

The Cr profile has a distinctly different shape from that of the other heavy metals. Cr increases from $<90 \mu\text{g/g}$ in 1884 to $>250 \mu\text{g/g}$ between 1900 and 1930 (Fig. 7). The period of elevated Cr closely parallels the peak production period of Gorham Manufacturing Company and other industries located on the shores of Mashapaug Pond. Gorham opened their silver and bronze foundry on the northeastern shore of the pond in 1890 (Soules n.d.). Other metalworking and electroplating industries were established in the Mashapaug Pond watershed around the same time, such as the American Enamel Company and Metropolitan Facing Works, and these industries are likely to have used Cr in production (Naja & Volesky 2009; Kulik & Bonham 1978; Anon 1889). The fact that the increase in Cr lags behind other metals by several decades suggests that other metals provide a record of regional industrialization, while Cr records the activity of metal industries located specifically within the Mashapaug Pond watershed.

Following peak levels of Cr, Pb and other heavy metals in the early 1900s, concentrations have decreased. By the top of the sediment core, Cr had decreased to pre-industrial concentrations, and Pb had decreased to approximately half of the peak industrial concentrations. It is possible that these declines are due, at least in part, to deindustrialization and increased regulation, as has been concluded by other authors (Mahler et al. 2006). However this explanation has several flaws. The area of land devoted to industrial and commercial activity increased throughout the 20th century, particularly with the construction of the Huntington Industrial Park on the western shore of Mashapaug Pond. Regulation may have altered industrial practices, such that heavy metal pollution decreased despite increasing industrial land use. However, the Clean Air and Clean Water Acts were not passed until 1970 and 1972 respectively. Heavy metal concentration begins to decrease well before the passage of these major environmental regulations, which suggests the need for an alternative explanation: that the decrease in heavy metal concentration is due in part to dilution by organic matter.

Increased biological productivity, spurred by increasing use and runoff of phosphorus-rich fertilizers, as well as increased atmospheric deposition of N (Hastings et al. 2013), could have diluted the concentration of metals in the sediment, and partially explain the decline in the concentration of both heavy metals and terrigenous elements. The high concentrations of dissolved phosphorus washed into the pond from storm drains, Spectacle Pond, and overland runoff is currently a source of concern regarding the health of the pond, as it leads to algae blooms and hypoxia (RIDEM 2007).

Important evidence for this explanation is the co-occurring decrease in both terrigenous and heavy metal concentrations. Between 1930 and present, Ti concentration also decreased, following an almost identical path to that of Pb and Cr (Fig. 13), whereas the percent organic C and N in the sediment increased over this period (Fig. 5). Indeed, relative to Ti, Pb and Hg do not decrease (Fig. 8), suggesting that these toxic heavy metals and terrigenous influx are being diluted by increased biological productivity. Cr does decrease relative to Ti suggesting that, in addition to dilution by organic material, input of Cr to the pond has decreased. The decrease in Cr relative to Ti is consistent with the interpretation of Cr as a marker of local electroplating industries, which declined in activity during the second half of the twentieth century.

This leaves us with a concerning conclusion: the influx of highly toxic metals to Mashapaug Pond may not have decreased since the peak industrial period. The explanation of terrigenous elements and heavy metal dilution by increased biological productivity challenges the assumption that deindustrialization and environmental regulation have reduced heavy metal pollution. Instead, these results indicate that heavy metal contamination of Mashapaug Pond is an ongoing problem, and that with existing regulations are insufficient and ineffective for protecting this urban ecosystem. Identifying modern sources of dangerous metals such as Pb and Hg should be a priority for future investigation, so that the influx of these metals can be reduced.

A primary limitation of this analysis is the potential unreliability of the age model. Pb²¹⁰ analysis performed by Flett Research Ltd. found the radioisotope activity below 31 cm in the core to be at background levels. Thus, a sedimentation rate and age model could only be constructed for the topmost 31 centimeters, or 77 years of sedimentation. Furthermore, the accuracy of ages calculated greater than 60-100 years based on Pb²¹⁰ dating is questionable (Flett n.d.). Due to the incomplete nature of the age model, the sedimentation rate calculated for the upper part of the core was extrapolated for the entire core length. Based on heavy metal profiles of sediment cores collected from Narragansett Bay and the nearby Seekonk River which also date the increase in the concentration of Pb to around 1850, this assumption appears to be justified (Bricker 1993; Nixon 1991; Salacup 2014). However, it would be overly simplistic to assume that sedimentation rate did not vary over the length of the core, particularly during the late 1700s when deforestation increased the terrigenous influx to the pond. The inability to reliably date the length of the core further limits the possibility of analyzing short-term fluctuations of metal content. Constructing a more accurate age model for the entire length of the core would be a priority for any further analysis.

Plant and Soil Analysis

Herbarium specimens can be used to track historical bioaccumulation of metals because plants incorporate heavy metals into their tissues through uptake from the soil and atmospheric deposition on their leaves (Oliva & Espinosa 2007). Previous research using herbarium specimens from Rhode Island found concentrations of Pb were higher in historical specimens than those collected in 2015. This was true both within Providence, and on Block Island, an island with no history of industrialization, suggesting that the effect of industrial pollution was regionally distributed (Rudin et al. 2017). Building on this previous work, and focusing on Mashapaug Pond, we expected to find a uniform

decrease in heavy metal concentrations. However, comparison of soil and plant samples indicate that plant uptake of heavy metals was more localized than anticipated.

By comparing topsoil and plant samples collected from the same site, the importance of local soil contamination as opposed to regional atmospheric pollution on plant uptake can be assessed (Berthelsen et al. 1995). Sampling both plants and soil from five sites confirmed the hypothesis that contamination measured within leaves is influenced by contamination of the soil. This is key, as leaf material is typically the only part of the plant available for sampling from herbarium specimens; roots, which act as a selective barrier in many plants and would be expected to have a higher concentration of metals (Cataldo & Wildung 1978), are typically not plentiful enough to sample from herbarium specimens.

All five sites sampled were located within 0.1 km of a highway in a forested park (Fig. 11). Site 4 was exposed to additional contamination as it lies in the drainage path of a parking lot, where an auto shop and several other retail spaces were located, and an area near to Site 4 was used as a dumping space and contained several paint cans of unknown age. Parking lot runoff has been found to contain elevated concentrations of Cu and Zn (Davis et al. 2001), and dumped items may have leached metals into the surrounding soil. Compared to the other sites, soil from Site 4 contained higher than expected levels of every heavy metal measured, and Cu, Pb, and Zn were all an order of magnitude higher at Site 4 than at the other sites (Fig. 12). As the concentrations were even higher below 10 cm, it is possible that leaching is ongoing, and that metals are migrating downwards in the soil.

The elevated contamination of Pb, and to a lesser extent Zn, was reflected in leaves collected from each site (Table 4). This suggests that Pb concentration in plant leaves is more dependent on uptake from the surrounding soil than from atmospheric deposition on the leaf surface, indicating that plant contamination is highly localized, to the extent that plants located only 50 m apart were found to contain significantly different concentrations of metals.

Local Cu and Cr soil contamination, however, was not paralleled in leaves, and this may be due to differences in bioavailability of metals. Uptake of metals by plants depends on several variables, including metal species solubility, soil pH, soil moisture, organic matter content, and bioaccumulation potential of the plant species (Cataldo & Wildung 1978; Peralta-Videa et al. 2009). Phylogenetic differences were evident in our sampling in the case of *Plantago*, a known metallophyte (Nadgórska-Socha et al. 2013), which was found to have an elevated concentration of Pb relative to the nearby soil. This demonstrates that different species with the same exposure accumulate metals at different rates.

The soil sampling conducted is merely a first look at relating plant contamination to soil conditions. Further analysis could involve sampling roots, stems, and leaves to better understand uptake, and rinsing leaves prior to analysis to remove metals deposited on the surface. Soil moisture, organic matter, pH, and other variables could also be studied in greater detail. We initially considered Murphy Trainer Park a single site, yet soil composition and contamination within this small area was more variable than expected, which made it difficult to differentiate between phylogenetic, temporal, and soil-based differences in plant uptake. Future work to examine these factors should rely on sampling several genera from multiple locations. These additional investigations,

while outside the scope of this study, would be useful for future work as it would improve understanding of how heavy metal concentrations measured in herbarium specimens relate to past soil conditions

The two sampling schemes each attempted to constrain the variables of location and phylogeny affecting plant uptake of heavy metals. Both methods were limited by the number of herbarium specimens from which to sample, and the lack of detailed locations notes for historical specimens.

The first sampling scheme, comparing congeners from Mashapaug Pond in the 1890s and the 2010s, focused on limiting geographic area. Concentrations of congener specimens collected in 2015 and 2016 were expected to have lower concentrations of metals than their historic counterparts, but the results were mixed. Pb was higher historically for most comparisons, while Zn was generally lower historically and Cu and Cr showed no consistent trend. While the historical specimens were collected during the height of industrialization in Providence and shortly after the construction of the Gorham silver and bronze foundry on Mashapaug Pond, land use mapping showed that the watershed itself was largely undeveloped at the time of collection (Anon 1889). Furthermore, historical specimens predate the construction of Route 10 and many roads through the watershed, and road runoff is a major source Cu and Zn (Davis et al. 2001). As in the present, contamination of soil and plants surrounding Mashapaug Pond is likely to have been highly variable, and botanists were likely to have visited remaining natural areas around the pond as opposed to industrialized sites, introducing an element of selection bias that would tend to favor less polluted sites. The lack of an overall trend can be attributed to the combined effects of limited industrialization around the pond and weak phylogenetic control in the species available for analysis.

The comparison of a congener specimens collected in 1890 and 2015 is of limited significance, as a single sample is not representative of heavy metal pollution at the time of its collection. A more informative approach is to sample intensively from a broader geographic area, such as the city of Providence. While geographic specificity is lost, the larger sample size enables the analysis to capture a greater portion the range of exposure to heavy metals present during a historical period.

The second sampling scheme, comparing *Plantago* specimens collected in Providence, focused on limiting phylogenetic diversity in order to construct a timeline. Historical *Plantago* specimens were available in Providence from 1844 to 1975, and new specimens were collected in 2015 and 2016, a longer and more complete timeline than would be possible to construct with most genera. Specimens collected prior to 1850 are rare, making the establishment of a pre-industrial baseline difficult. The concentrations of metals in these plant specimens were expected to follow a similar trend as measured in the sediment core, with the highest values expected between 1870 and 1930, and low concentrations expected in prior to 1850 and from 1950 to present. This hypothesis was confirmed for Cr, Pb, and Zn, although Cu concentration was highest in recently collected specimens (Fig. 10). During the peak industrial period, plants in some areas of the city were exposed to higher concentrations of metal pollution than measured in modern specimens from Mashapaug Pond. The localized nature of contamination observed in the soil samples suggests that wide variation concentrations measured in historical specimens should be expected.

The Brown University Herbarium has a total of 54 *Plantago* specimens from Providence County, all collected from the city of Providence and the neighboring towns of Pawtucket, East Providence, and Cranston, of which 20 were sampled. The analysis could be strengthened by sampling more specimens from the herbarium collection and collecting more modern specimens. However, the Ultrawave digestion and ICP-AES analysis conducted is time and cost intensive, and is a destructive sampling method that requires removing several leaves (>0.2 g) from the herbarium specimens. Refining non-destructive measurement techniques, such as handheld XRF for use on herbarium specimens could dramatically increase the number of specimens possible to include in analysis, improving the reliability of results. Unfortunately, the number of specimens collected around Mashapaug Pond itself is insufficient to create a profile of this kind over time. However, given the record of heavy metal accumulation in the sediment of the pond, it is likely that nearby plants were also exposed to elevated concentrations of heavy metals.

Herbarium specimens pose many challenges for historical environmental research. Information about the date and location of collection is often vague or absent, geographic and temporal representation of species is scattered and inconsistent, and any destructive analysis must be carefully planned and justified. That said, herbarium specimens provide a unique and underutilized record of past ecological conditions. Small herbaria often contain collections specific to their locale, and online coalitions of herbaria, such as the Consortium of Northeastern Herbaria, are facilitating collaboration between institutions. New tools of digitization are enabling more thorough and integrative use of herbarium collections.

Conclusion: A multi-disciplinary environmental history

The environmental history of Mashapaug Pond is closely tied to the social, political, and economic history of the surrounding area. Over the past four centuries, Mashapaug Pond has been a site of indigenous settlement and displacement, deforestation and agriculture, urban and industrial development, and remediation and activism. In many ways, the history of the pond reflects the history of Providence and urban industrial centers throughout the United States. The pond is of continued importance today, particularly in light of the construction of Alvarez High School on the former Gorham Manufacturing Company site. Sedimentary and botanical tools record the environmental history of the Mashapaug Pond watershed in previously unexplored forms, which help place the current health risks associated with the pond in context.

The sedimentary record establishes baseline concentrations of heavy metals, terrigenous matter, and organic matter, prior to 1760, from which several notable changes occur. First, deforestation and agriculture increase soil mobility within the watershed, leading to a tripling of terrigenous material (Ti and Si) between 1770 and 1800. Second, regional industrialization and coal burning led to a ten-fold increase in the concentrations of Cu, Hg, Pb, and Zn. Third, metalworking and electroplating industries on the shores of Mashapaug Pond, beginning around 1880, contributed additional sources of metal pollution, and specifically caused the concentration of Cr to increase steeply (Fig. 13). The concentrations of toxic metals such as Cr, Hg, and Pb, in the uppermost sediment remain above the pre-industrial baseline, a reminder that once heavy metals are present in

an ecosystem they are difficult to remove. Furthermore, the concentration of Pb and Hg relative to Ti have not decreased, indicating influx of these highly toxic metals to the pond is an ongoing problem that has not been adequately addressed by existing environmental regulations.

Plant samples from throughout Providence also indicate that current conditions of heavy metal pollution are below the levels recorded during the peak industrial period of the late 1800s and early 1900s. However, analysis of modern soil and plant samples demonstrates that localized pockets of high heavy metal concentration persist. This serves as an important reminder that remediation cannot be limited to major industrial sites, such as the former Gorham site, and that attention must also be paid to small-scale sources of heavy metals, such as parking lot runoff and dumping sites.

The changes documented in the Mashapaug Pond watershed are representative of the ecological consequences of unregulated industrial activity. Contact with contaminated soil, dust, water, plants, and fish pose a risk to residents, and changes the ways they are able to enjoy and interact with this urban body of water. Intertwining sedimentary, botanical, and sociological data, reveals the need for continued remediation and stewardship of this natural resource. In the words of M., an anonymous young resident of the Mashapaug Pond watershed:

I heard a rumor from off the street and in my school that the pond was infected... I want to grow up and see one day in the news for the headline I want it to say 'Mashapaug Pond Saved: No More Pollution' and then people can actually go swimming in it and do all of the water activities. (Perkins 2013)

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