Spatial and temporal trends of trace elements in tree cores along the industrial Mahoning River, Northeast Ohio

by

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ABSTRACT

Waterways throughout the industrialized world have suffered from long histories of pollution and abuse. The Mahoning River in Northeast Ohio is considered one of the five most contaminated rivers in the United States, and has received large amounts of industrial discharges for more than a century, often severely impacting the resident biota and posing risks to the human population of its surroundings. The major objective of this thesis was to measure trace element concentrations in tree cores of silver maple (*Acer saccharinum*) and American sycamore (*Platanus occidentalis*) in the Mahoning River riparian zone, by Inductively Coupled Plasma (ICP), to assess spatio-temporal patterns of metal contamination that could have value as a bio-monitor. Three sites were selected within the industrialized zone of the river between Girard OH and Lowellville OH, with a fourth reference site located below the Kirwan Reservoir (West Branch State Park) upstream from historical manufacturing activities. Cores were taken from trees at breast height (1.37 m), and carefully handled to avoid introducing foreign metals (e.g. sanded with non-metal-oxide abrasives, handled with gloves, stored in cotton-bond paper wraps). Cores were sectioned into 10-year increments and then digested and analyzed by ICP. Tree core segments served as the experimental unit for all analyses, and trace element concentrations were the dependent variables. Categorical independent variables consisted of tree species and river site, and core segment age served as a covariate. Trace element concentrations, which covaried significantly, were subjected to data reduction by Principle Components Analysis (PCA) ordination. PCA scores were analyzed by either two-factor MANCOVA (where two axes were informative) or two-factor ANCOVA for a single axis. Interestingly, considering the long industrial legacy of the Mahoning River, metal concentrations in tree cores did not significantly reflect sampling sites, and thus proximity to historical manufacturing facilities. There also was no statistical evidence of temporal patterns of trace elements within cores. Difficulties in identifying trees dating to the industrial era and of extracting long enough cores pose a challenge to such research. However, there were distinct trace element accumulation differences between the two species examined. Sycamores displayed higher concentrations of dietary essential elements (e.g. P, S, Mg), but lower concentrations of dietary-non-essential, and potentially contaminant, metals (e.g. Pb, Cd, Cu) than did silver maples. These bioaccumulation differences between the two species could reflect unexplored physiological differences that might affect trace element dynamics.

ACKNOWLEDGEMENTS

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INTRODUCTION

The Mahoning River in Northeast Ohio is considered one of the five most contaminated rivers in the United States. (Amin & Jacobs, 2013). Industries and municipalities have discharged large amounts of pollutants into the environment, often severely impacting the resident biota. Sources of contaminants in the Mahoning River are from both the steel industry, which was active from 1900–1975, and from partially treated waste discharged by the local communities. The main contaminants are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and heavy metals. The USEPA (1977) reported that during the 1970s contaminant inputs to the Mahoning River included 31,751 kilograms/day of oil and grease, 363 kilograms a day of zinc, and 227 kilograms/day of cyanide. This oil discharge was equivalent to 200 barrels per day; enough to heat 30,000 average-sized homes (Amin & Jacobs, 2013).

The global human population is ever increasing, and thus the impacts of industrial contamination may increase as well, even with the advent of cleaner production technologies. Recent studies have predicted that the world's urban population will increase from 3.9 billion in 2014 to 5.8 billion by 2050 (Carkovic et al. 2016). This urban growth is creating sustainability problems on a global scale, especially in developing countries where industrial and agricultural interests compete for land resources. Urban populations, being both dense and close to industrial sources, are often exposed to pollution, and at risk just as are the natural biota.

As of 2017, Mahoning County has an estimated population of 229,796 (United States Census Bureau, 2017). According to a study in 1994 by the Ohio EPA, legacy contamination in the sediments from the Mahoning Valley's many industrial sources, as well as loadings of organic wastes from sewer overflows and municipal WWTPs exerted an overwhelming negative effect on resident aquatic communities, and to the local environment (Ohio Environmental Protection Agency, 2018).

There are many types of contaminants that can be found in the environment, including volatile and semi-volatile organic compounds, pesticides, and metals. These contaminants can come from either point or non-point sources. A point source is a direct discharge from a facility that expels wastes as a result of its process. Non-point sources represent indirect and non-purposeful releases, including those from agriculture or from storage and disposal facilities.

Metal-rich particles are easily mobilized and may reach areas by wind and/or water erosion, and can be ingested, inhaled, or absorbed by organisms near the pollution sources (Carkovic et al. 2016). Sediment association also affects how metals can be transported in an environment. Different trace elements can display different mobilities and leaching processes (ex. Zn and Cd are similar in leaching in contaminated soils when compared to Pb). Another important transport mechanism is long ranged atmospheric transport of metals, often from coal burning and other industrial releases.

Riparian zones are areas of land that occur along streams and rivers, and include banks, floodplains, and higher terraces. They are distinct due to their unique soils and vegetation, which are influenced by the presence of water (USDA, 1996). They also may help mitigate nonpoint source pollution by capturing excess nutrients, sediments, and sometimes even contaminants. Riparian zones are considered to be an important component in efforts to monitor and/or remediate stream conditions. However, they can be very vulnerable to human degradation when they are located along rivers used for industrial purposes.

Re-naturalization can occur in an environment after abandonment of industrial facilities, much as has occurred along the Mahoning River. Such lands are referred to as "brownfields", which make up a large portion of the land area in post-industrial cities. Brownfields have been repurposed for many uses, although unfortunately residual contamination often limits their potential, and may even pose threats to human users. Also, plans of for current brownfields are driven by demands in markets and public sector prioritization, which do not always meet the requirements of local visitors or residents (Martinat et al. 2018). According to the EPA (2006), because brownfields are "real property", their expansion, reuse, or development may be complicated by the presence of industrial contaminants.

Mahoning River channel and bank sediments have accumulated many decades of industrial metal discharges. This study investigated whether there is a signature in riparian tree species increment cores that may reflect spatio-temporal patterns of metal contamination, measured by Inductively Coupled Plasma (ICP), and that could have value as a biomonitor. We may be able to answer the following questions:

1) Which dietary and non-dietary trace elements can be accumulated by riparian tree species that are rooted in contaminated floodplain soils?
2) Are the absorbed trace elements concentrated in the bark and/or yearly rings of wood?
3) Do concentrations in tree tissues reflect patterns of present-day and historical industrial land use?

4) Do any trace elements display temporal patterns as indicated by concentrations in different age increments in tree cores?

BACKGROUND

Mahoning River Geography:

The Mahoning River (Figures 1 – 7) drains 2,810 km^2 of Ohio, and it flows through seven counties. Municipalities of the watershed include Warren, Alliance, Youngstown and Lordstown. The watershed supports a wide variety of land uses, including urban developments, residential land, pastures, agricultural lands and forests. The lower portion of the Mahoning River (i.e. encompassing most of the heavy industries, and serving as the focus of this study) is 49 km long, spans two counties (Trumbull and Mahoning County), and encompasses eight communities.

At least ten low-head dams were built along the Mahoning River, mostly along the industrial reach downstream from Leavittsburg, in order to increase water availability for cooling hot machinery and steel products from the mills along its banks (Friends of the Mahoning River, 2019). The main dams of interest to this study are located in Girard, Lowellville, Struthers, and Youngstown, due to their proximities to tree core sampling sites. Figure 5 displays locations of low-head dams along the Lower Mahoning River Watershed.

The Lowellville dam was built between 1908 and 1915, and served as a concrete water supply for the Ohio Steel and Iron Co. (Village of Lowellville, 2010). The location is north of First Street at the Mahoning River Mile 13.05. It is composed of eight piers with the square ends being upstream, while, the pointed ends are downstream. The weirs are made of concrete. The dam is deteriorated. A proposed project is set in which includes dredging >7500 cubic m of contaminated sediment and removing the

Lowellville dam. The project is funded by WRRSP. (Eastgate Regional Council of Governments, 2019)

The Struthers Dam is located between the city of Struthers and the City of Campbell. It is structured in a series of five concrete piers that support a coal trestle with concrete weirs located in between the piers. The concrete abutments of the dam mark the termination points of the dam structure. The concrete of this dam is in a deteriorated condition. A proposed project is made for the dam. It includes approximately 23,000 cubic m of contaminated sedimentation to be removed from the dam, along with the damn removal. The funding for this project is from WRRSP, along with a LTV Settlement. (Eastgate Regional Council of Governments, 2019)

A dam is located in Youngstown south of downtown, and north of the Mahoning Avenue bridge. It consists of a weir composed of a series of stone and concrete fragments across the river. The proposed project for this dam includes >8000 cubic m of contaminated sediments to be removed, along with the dam removal. The project is not funded yet. (Eastgate Regional Council of Governments, 2019)

The Girard dam was built in 1832 to provide water power to grist mills, and also served as an ideal loading and unloading location s for canal boats in the reservoir above the dam. The Pennsylvania and Ohio Canal reached Girard in 1839, and the dam was rebuilt into its present two-levee form. A granite lock for the canal was built at the east end of the dam, as well. (Girard Free Library, 2019). The Girard Dam consists of a multi-component grouping element. This includes a large abutment, a dam, and a large wall on the river bank. The concrete dam and arched timber crib ranges across the river in an arc structure, with the curve facing upstream in the northern direction. The center weir is a straight drop off with a gap in the center in which appears constructed in the dam's design. A 1999 inspection report from the ODNR displayed the dam being made of timber-crib, with a concrete cap. The proposed project for this dam includes removing the dam, along with dredging contaminated soil. (Eastgate Regional Council of Governments, 2019)

The northern portion (predominately Trumbull County and draining Mosquito Creek Reservoir) has an elevation range of .274 -.304 km. As the watershed extends southward (extending into Portage, Mahoning, Stark, Columbiana, and Lawrence county) the elevation increases to an average range of .295 - .365 km. The elevations around the northern portion of Mahoning River average .274 km, while the surrounding land around the southern portion of the Mahoning river average at an .320 km elevation (Figure 4).

Mahoning River History:

On February 16, 1846, the Ohio government authorized the creation of Mahoning County. The county was named after the Mahoning River by the residents, in which "Mahoning" is the Native American word meaning "salt licks" (Ohio History Connection). The last three decades of the nineteenth century were rapid growth years for the area's population and industrialization of the Mahoning Valley. By 1900, the Mahoning Valley's population had grown to forty-five thousand, compared to only eight thousand in 1870. As the valley began to urbanize, it also began to modernize. As the century neared its end, the Youngstown economy had evolved from that of a frontier village to an industrial city (Blue et al. 1995).

The Mahoning Valley was an ideal place for steel industries because it is rich in coal and iron ore and is in close proximity to railways and water resources. In fact, during the steel industry's most active years, the river was not only used for industrial purposes, but also served as a water source for local populations (Friends of the Mahoning River, 2019).The mining of coal and its use in blast furnaces to produce iron led the industrialization of the mid-nineteenth century. Although iron production was confined to areas along the Mahoning River, it was not exclusive to Youngstown. Industries also developed in smaller towns throughout Mahoning County. Downriver from Youngstown, iron making thrived in Struthers and Lowellville. This spurred a population increase of immigrants from southern and eastern Europe who arrived in the area to compete for industrial work. This led to the Mahoning Valley having a diverse population, along with an increase in commercial establishments, public services, and cultural amenities. By the start of the great depression c. 1930 the population had risen to 170,000, mainly in Boardman, Coitsville, Lowellville, Struthers and Youngstown (Blue et al. 1995).

Republic Iron and Steel Corporation in Warren Ohio was incorporated in 1899, and converted the former Brown-Bonnell iron plant into a steelworks with Bessemer converters. U.S. Steel Company (headquartered in Pittsburgh, Pennsylvania) was founded in 1901, and was America's first billion dollar corporation. The company created a sheet mill plant at Niles, Ohio with an annual capacity of 48,000 tons of black steel sheets (Butler, 1921). Youngstown Sheet and Tube Company was developed locally by James A. Campbell and George D. Wick as a means of heading off complete outside ownership of Youngstown's plants. (Blue et al. 1995).

The steel industries declined during the great depression, but made a comeback during the 1940s as demands for war materiel expanded greatly. However, during the 1970s, the industries again struggled. On September 1977, Republic Steel, U.S. Steel, and Youngstown Steel & Tube announced the end of their Youngstown operations. Within five years of closings, unemployment reached over 20 percent and remained in the double digits for more than a decade. Deindustrialization became dominant in the area. (Linkon & Russo, 2002, p. 131)   This left the river, along with its industries, effectively abandoned.

Mahoning River Industrial Legacy:

Although industrial sites that previously polluted the river are now largely abandoned, their contaminants are still present in river channel and riverbank sediments. Pollutants such as polycyclic aromatic hydrocarbons (PAHs) are present along with trace metals (nickel, lead, arsenic, cadmium, mercury) that were discharged from the industries. Contaminants can be flushed back and forth between water, channel sediments, and river bank sediments during water level fluctuations. (Amin & Jacobs, 2013). Through this cycling, trace metals can accumulate in floodplain soils, and potentially be taken up by local biota.

Industrial contaminants are not the only pollution legacy faced by the Mahoning River, although they are often the most persistent form of environmental degradation. For example, dissolved oxygen is noticeably lower (5 parts per million 67 percent of the time, and less than 3 ppm 16 percent of the time) due to municipal waste discharges which deleted the dissolved oxygen of the lower reaches of the Mahoning River. Sulfate from wastes disposal and acid mine drainage made up the largest quantity of dissolved solid load in the Mahoning River. (Bednar et al. 1968).

Trace metal contamination comes from many different types of sources, the most common being from the expansion of mining industries, steel industries, pesticide uses and other anthropogenic sources. Once released into the environment from a specific source, trace metals such as lead, cadmium, zinc, nickel, copper, arsenic, chromium, and mercury cannot be biodegraded. Once released, the contaminants can travel through the air, or enter a water system where they are distributed in soils, and enter an ecosystem. Thus, they could enter a food chain through edible plant parts in which would cause health problems to many organisms. Although certain metals are actually beneficial to organisms (e.g. micronutrient metals such as iron, copper, and zinc), an excess of even these “dietary essential” metals can have toxic effects.

A summary of heavy metal human health-related issues includes that the intake of lead, arsenic, and cadmium can damage the nervous and endocrine systems, circulatory, skin cancer, malignancy, and benign prostatic hyperplasia (Jing et al. 2018). If consumed in excess, heavy metals can lower energy levels, damage the brain, kidney, lung, liver, and blood composition along with other important organs. Common ailments for long termed exposures can also lead to a gradual progression of physical, muscular and neurological degenerative processes that imitate diseases like Alzheimer’s, Parkinson’s, and multiple sclerosis (Jaishankar et al. 2014).

Chronic arsenic contamination mainly displays skin manifestations. Pigmentation and keratosis are specific skin lesions that indicate chronic toxicity. Chronic lead exposure can lead to mental retardation, birth defects, autism, allergies, dyslexia, hyperactivity, brain damage, kidney damage and may even cause death. Acute symptoms can cause headache, loss of appetite, vertigo, abdominal pain, renal dysfunction, fatigue, sleeplessness, arthritis, hallucinations and hypertension.

Mercury exposure to humans was found to lead to nervous system ailments. Cadmium exposure is linked to morphological changes in kidneys, along with premature birth and reduced birth weights in human pregnancies. Chromium exposure in humans can lead to inhibition of erythrocyte glutathione reductase, which lowers methemoglobin to hemoglobin. Excess aluminum can change the evolution of secondary hyperparathyroidism in which leads to bone disease, and aluminum-induced osteomalacia. Human exposed to iron in excess are at risk of asbestosis, which is the second most important causes of lung cancer. (Jaishankar et al. 2014).

The contamination released from industrial sources also has a profound effect on the aquatic life in the Mahoning River (OEPA, 1996). Fish community performance was consistently poor in the Warren area, and evidence of this included very low biological index scores, high numbers of fish with external anomalies, absence of pollution sensitive species, and an abundance of pollution tolerant species. Thus, many of the remaining problems are the result of past and current discharges of toxic substances in relation to steel making. High loadings of organic waste continue to be discharged primarily from municipal wastewater treatment plants, and sewer overflows, but adverse effects on aquatic life were overshadowed by those in relation to the contaminated sediments. (OEPA, 1996).

Many types of trees grow in the Mahoning River's banks, including silver maple, eastern cottonwood, American sycamore, American elm, and box elder. The silver maple is known for its abundance along the Mahoning River (ODNR Division of Forestry, 2017). Thus, different species of trees may be affected differently by the toxic metal pollutants, probably absorbed at different rates. However, it is unknown if this response is different among tree species, along with how high the metals travel up the tree after the roots absorb them.

Dendroanalysis:

Dendroanalysis was first developed in the 1960s, and is a biomonitoring approach that examines elemental concentrations in tree rings and other tissues. (Hristovski & Melovski, 2010). The concentrations of elements in tree rings may reveal accumulation pathways, including from soil composition and by atmospheric contamination. A common assumption is that the concentration of metals in tree rings should correspond to the availability of metals in the ecosystem during the period when tree rings were formed. (Cocozza et al. 2016). Thus, temporal patterns might also be revealed, because tree rings provide a record of wood accumulation over a tree's life. Analyses can be carried out on waterlogged, preserved, or dry wood samples. Dried core samples were used for this thesis. Cores should be taken at a spot on the trunk where the tree shows regular growth and solid wood, without distortion.

Dendroanalysis studies have often demonstrated accumulation of trace elements in trees exposed to spills or from discharges from local industrial facilities (e.g. Watmouth et al. 1999, Watmouth and Hutchinson 2002, Medeiros 2008, Bilo et al. 2017, Jung and Ahn 2017). The method has been applied globally, with such studies conducted in Europe (Hristovski & Melovski, 2010, Cocozza et al. 2016, Lageard et al. 2008), Asia (Jung & Ahn, 2017), South America, (Locosselli et al. 2018) and North America

(McHugh, et al. 2016). Dendroanaylsis has been used to biomonitor a variety of industrial contaminants in trees, but lead in particular has served as a marker for temporal changes in pollution deposition, with specific reference to the decrease in vehicle emissions after removal of lead from motor fuels starting in the 1970s (Lageard et al. 2008).

One source of contaminants to trees would be the soil in which they growing, and from which trees could accumulate contaminants through the roots as dissolved constituents. (Hristovski & Melovski, 2010). Thus, soil sampling near the trees is one way to potentially assess the pool of available pollutants. Another source of trace element accumulation in trees is from atmospheric deposition to the leaves. Tree leaves are very efficient in absorbing atmospheric precipitates, which may include metals and other pollutants (Labidi et al. 2017).

Trace elements absorbed from the surroundings can be accumulated in growth rings laid down at the time, and serve as a temporal marker. However, they can also move throughout the tree after absorption (Hristovski & Melovski, 2010). The movement of fluids throughout the wood is known as radial translocation, which occurs along the lateral ray and typically results in metal transport across the rings and into the heartwood. This could confound patterns of trace element distribution that are more closely tied to xylem transport in sapwood. For example, Hristovski & Melovski (2010), examining trace element concentrations in wood from felled European beech (*Fagus sylvatica*) at a relatively unpolluted site in Macedonia, found that internal translocation accounted for much of the distribution pattern between regions of the tree.

There is a small group of plants known as hyperaccumulators, which can accumulate certain metalloids and metals to levels far above those in the surrounding environment (Fernando et al. 2007). Such plants, many of them herbaceous, have been proposed for phytoremediation, i.e. being used to actively remove contaminants from the environment for recovery or confined disposal elsewhere (as cited in Fernando et al. 2007).

Figure 1. Upper Mahoning river watershed (blue), and the lower watershed portion (purple).

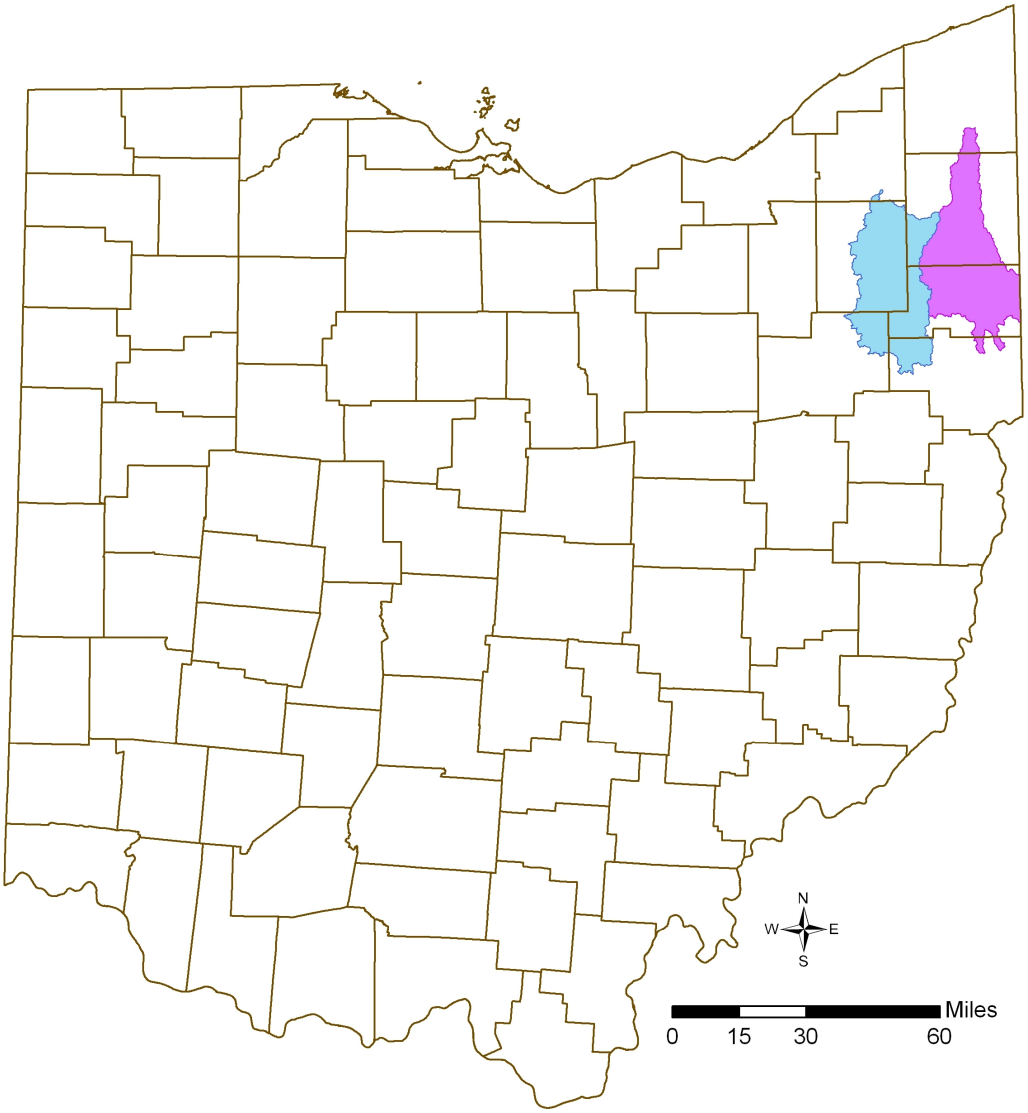

N
W
E
S
Miles
0
15
30
60

Figure 2. Mahoning River Watershed, with major political subdivisions and larger reservoirs shown. Industrial legacy region and upstream reference indicated by red boxes. https://web.archive.org/web/20100705005402/http://www.ysu.edu/mahoning_river/watershed_mahoning.jpg

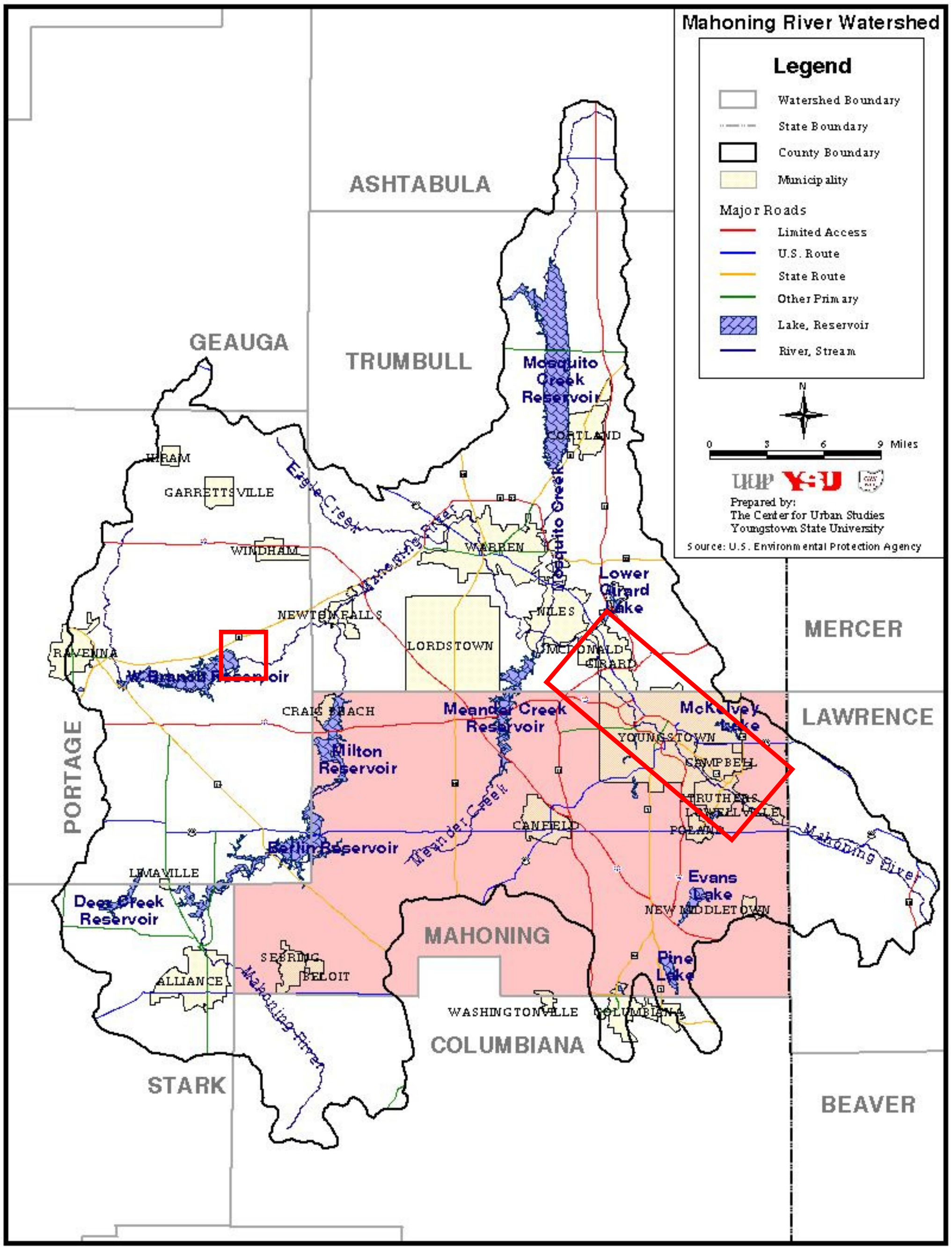

Mahoning River Watershed
Legend
Watershed Boundary
State Boundary
County Boundary
Municipality
Major Roads
Limited Access
U.S. Route
State Route
Other Primary
Lake, Reservoir
River, Stream
N
0
3
6
9 Miles
Prepared by:
The Center for Urban Studies
Youngstown State University
Source: U.S. Environmental Protection Agency
ASHTABULA
GEAUGA
TRUMBULL
MERCER
LAWRENCE
PORTAGE
MAHONING
COLUMBIANA
STARK
BEAVER
Mosquito Creek Reservoir
Mosquito Creek
CORTLAND
HIRAM
GARRETTSVILLE
Eagle Creek
WINDHAM
Mahoning River
WARREN
Lower Girard Lake
NEWTON FALLS
NILES
LORDSTOWN
MCDONALD
GIRARD
RAVENNA
W. Branch Reservoir
CRAIG BEACH
Meander Creek Reservoir
McKelvey Lake
YOUNGSTOWN
CAMPBELL
Milton Reservoir
STRUTHERS
LOWELLVILLE
CANFIELD
POLAND
Meander Creek
Berlin Reservoir
Mahoning River
LIMAVILLE
Evans Lake
Deer Creek Reservoir
NEW MIDDLETOWN
SEBRING
BELOIT
ALLIANCE
Pine Lake
Mahoning River
WASHINGTONVILLE
COLUMBIANA

Figure 3. Study sites, along with past and present industry locations, in the industrial zone of the Mahoning River watershed.

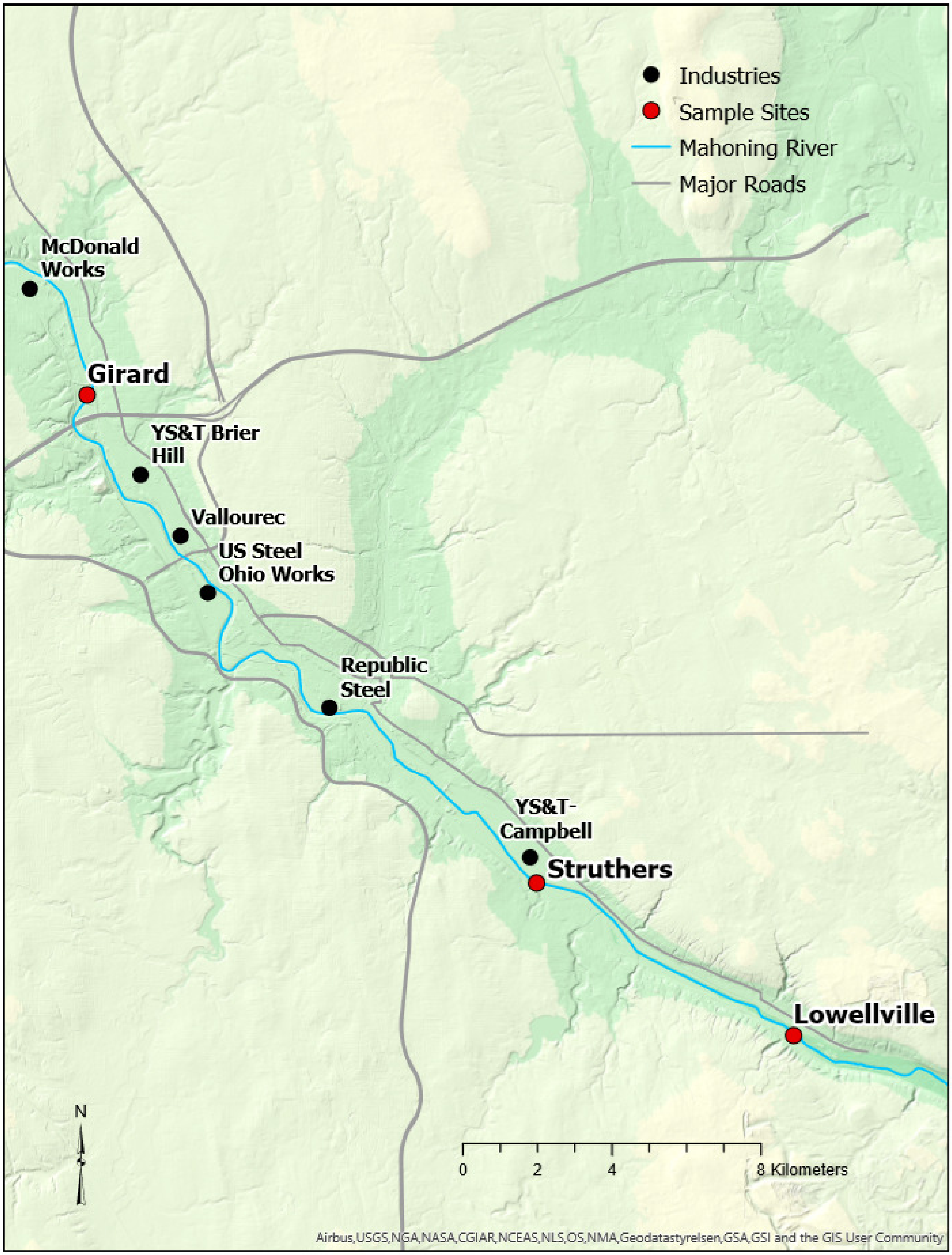
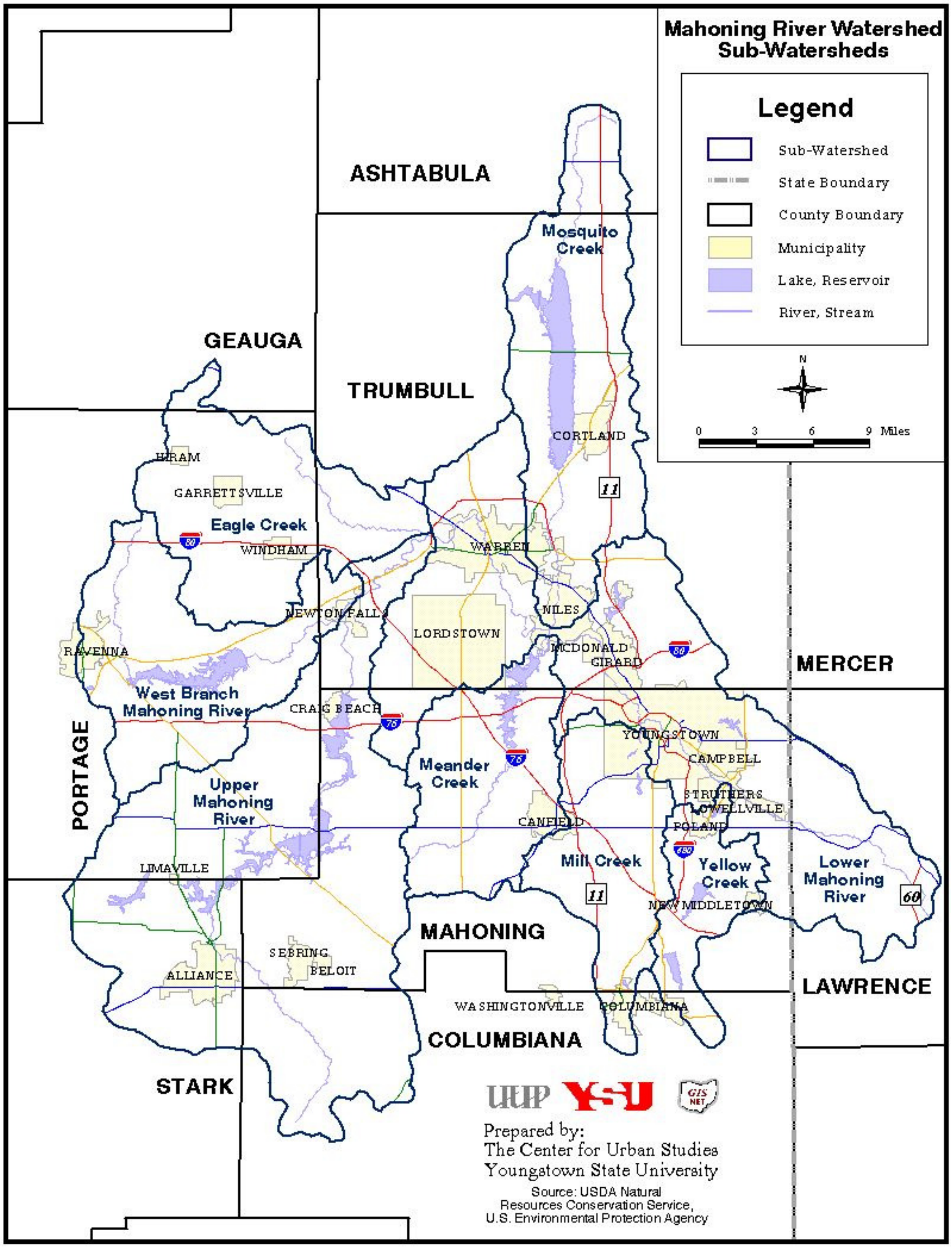

Industries
Sample Sites
Mahoning River
Major Roads
McDonald Works
Girard
YS&T Brier Hill
Vallourec
US Steel Ohio Works
Republic Steel
YS&T-Campbell
Struthers
Lowellville
N
0
2
4
8 Kilometers
Airbus,USGS,NGA,NASA,CGIAR,NCEAS,NLS,OS,NMA,Geodatastyrelsen,GSA,GSI and the GIS User Community

Figure 4. Sub-watersheds of the Mahoning River watershed.

(https://web.archive.org/web/20100705004802/http://www.ysu.edu/mahoning_river/watershed_sub_watersheds.jpg



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Youngstown State University
Source: USDA Natural Resources Conservation Service, U.S. Environmental Protection Agency

Figure 5. Land uses within the Mahoning River Watershed.

https://web.archive.org/web/20100705003315/http://www.ysu.edu/mahoning_river/watershed_landuse.jpg

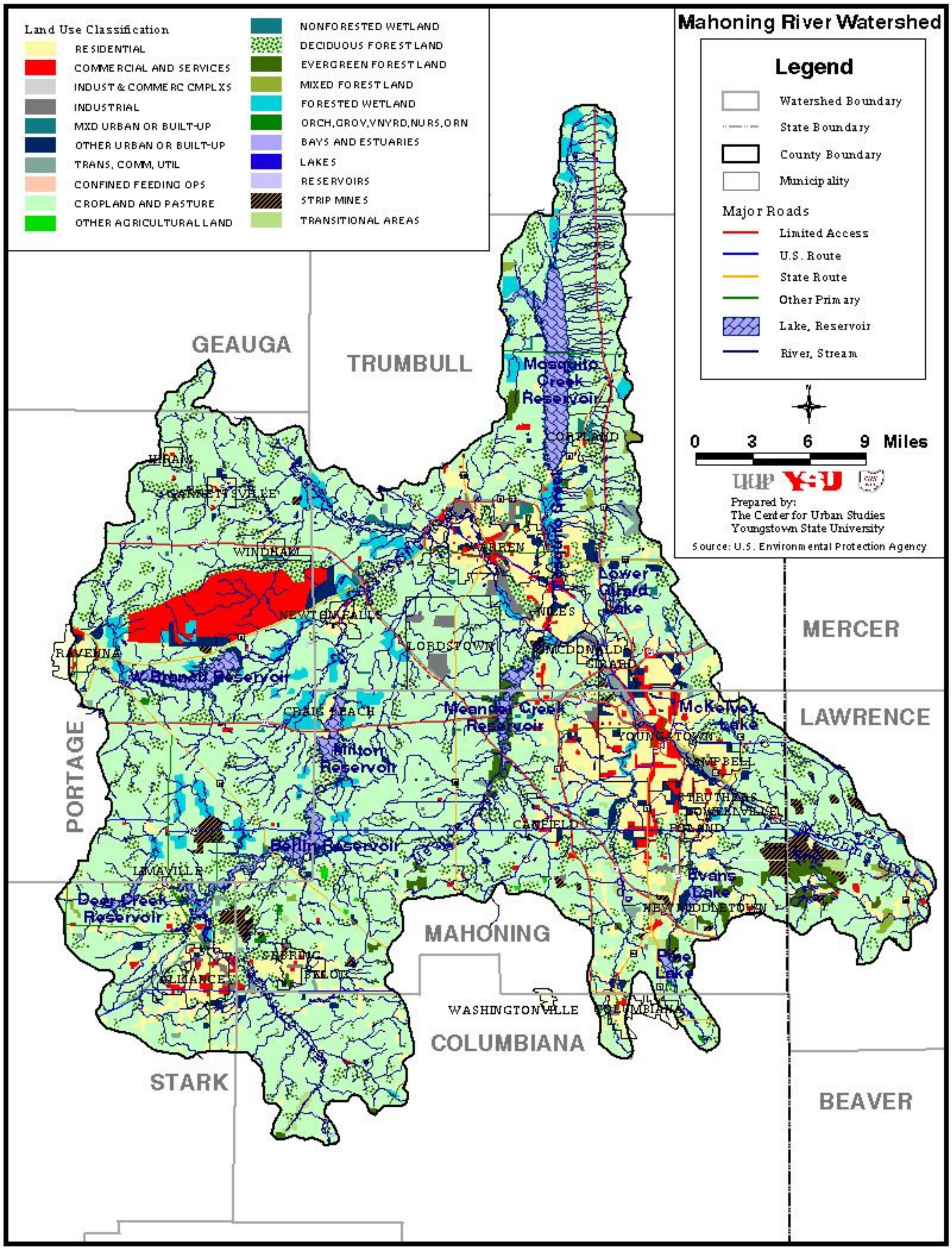
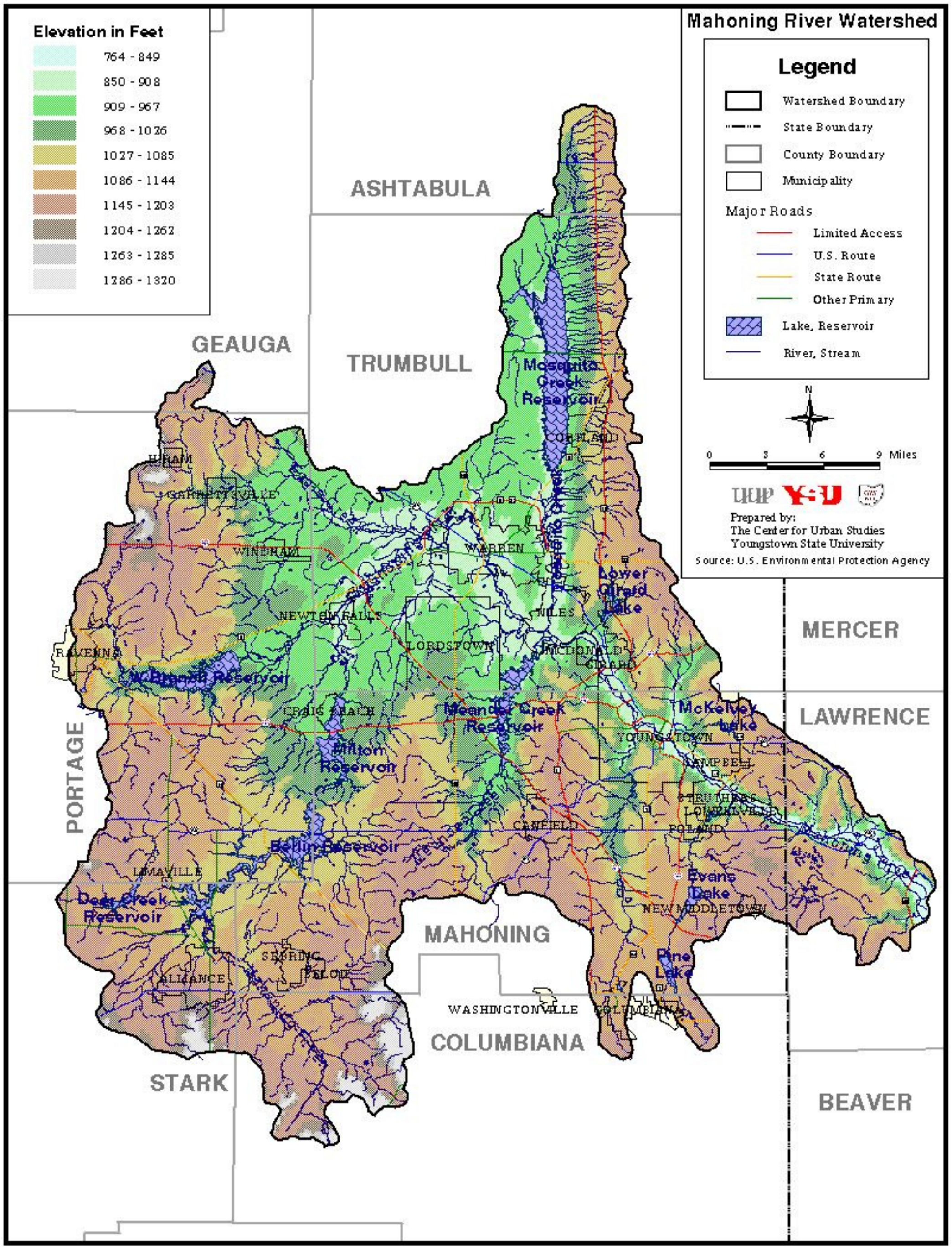

Land Use Classification
RESIDENTIAL
COMMERCIAL AND SERVICES
INDUST & COMMERC CMPLXS
INDUSTRIAL
MXD URBAN OR BUILT-UP
OTHER URBAN OR BUILT-UP
TRANS, COMM, UTIL
CONFINED FEEDING OPS
CROPLAND AND PASTURE
OTHER AGRICULTURAL LAND
NONFORESTED WETLAND
DECIDUOUS FOREST LAND
EVERGREEN FOREST LAND
MIXED FOREST LAND
FORESTED WETLAND
ORCH,GROV,VNYRD,NURS,ORN
BAYS AND ESTUARIES
LAKES
RESERVOIRS
STRIP MINES
TRANSITIONAL AREAS
Mahoning River Watershed
Legend
Watershed Boundary
State Boundary
County Boundary
Municipality
Major Roads
Limited Access
U.S. Route
State Route
Other Primary
Lake, Reservoir
River, Stream
N
0 3 6 9 Miles
Prepared by:
The Center for Urban Studies
Youngstown State University
Source: U.S. Environmental Protection Agency
GEAUGA
TRUMBULL
PORTAGE
MERCER
LAWRENCE
MAHONING
COLUMBIANA
STARK
BEAVER
Mosquito Creek Reservoir
CORTLAND
HIRAM
GARRETTSVILLE
WINDHAM
WARREN
NEWTON FALLS
NILES
Lower Girard Lake
LORDSTOWN
RAVENNA
W. Branch Reservoir
MCDONALD
GIRARD
CRAIG BEACH
Meander Creek Reservoir
McKelvey Lake
YOUNGSTOWN
Milton Reservoir
CAMPBELL
STRUTHERS
LOWELLVILLE
POLAND
CANFIELD
Berlin Reservoir
LIMAVILLE
Deer Creek Reservoir
Evans Lake
NEW MIDDLETOWN
SEBRING
ALLIANCE
BELOIT
Pine Lake
WASHINGTONVILLE
COLUMBIANA

Figure 6. Land elevation (in feet) within the Mahoning River Watershed.https://web.archive.org/web/20100705002337/http://www.ysu.edu/mahoning_river/watershed_elevation_ft.jpg)



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Source: U.S. Environmental Protection Agency

Figure 7. Locations of dams within the Lower Mahoning River Watershed (i.e. industrial legacy segment downstream from Leavittsburg. https://web.archive.org/web/20030816035630/http://www.ysu.edu/mahoning_river/bralich_map/Environmental%20Maps/lm_dams.jpg)

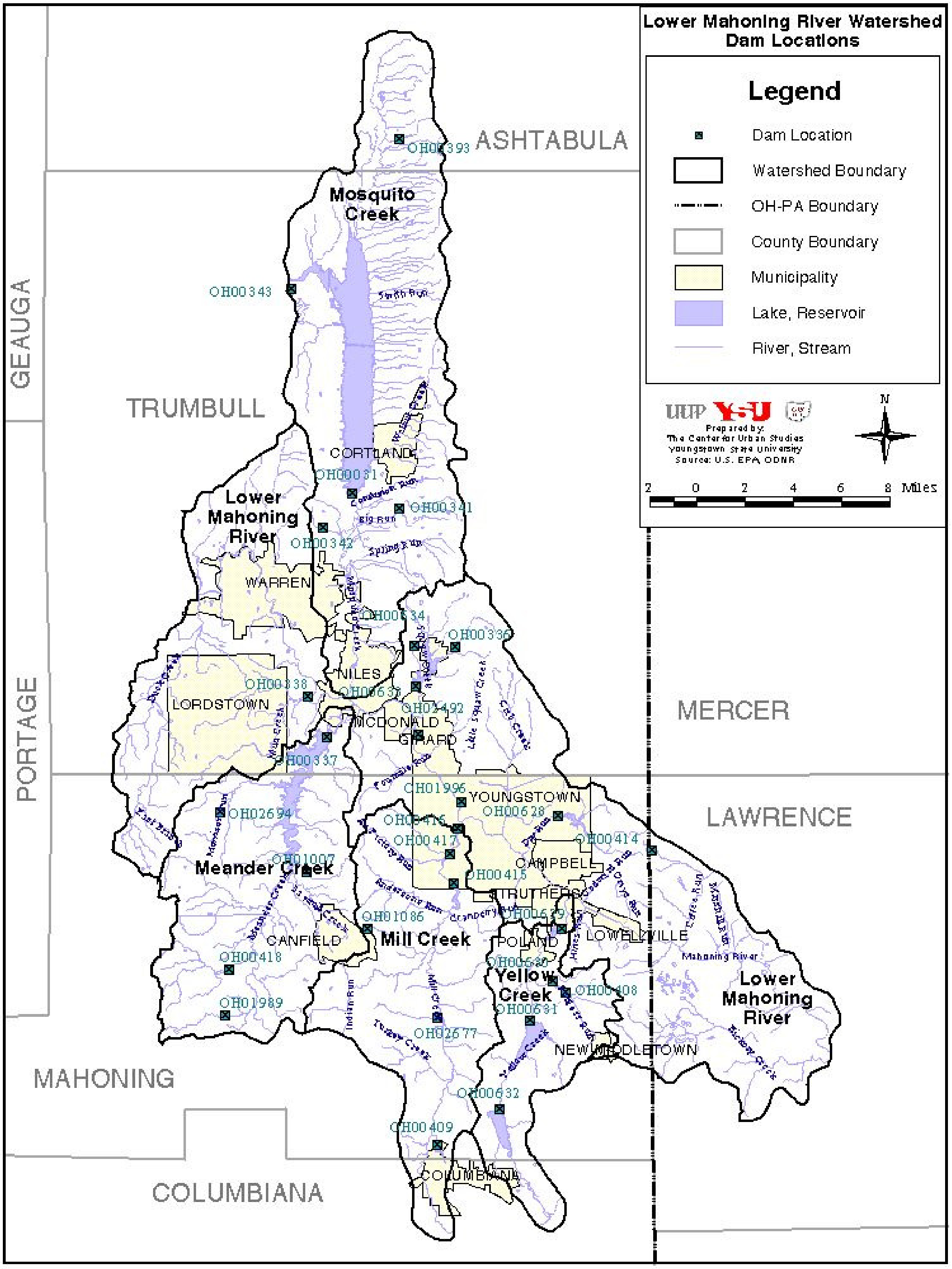
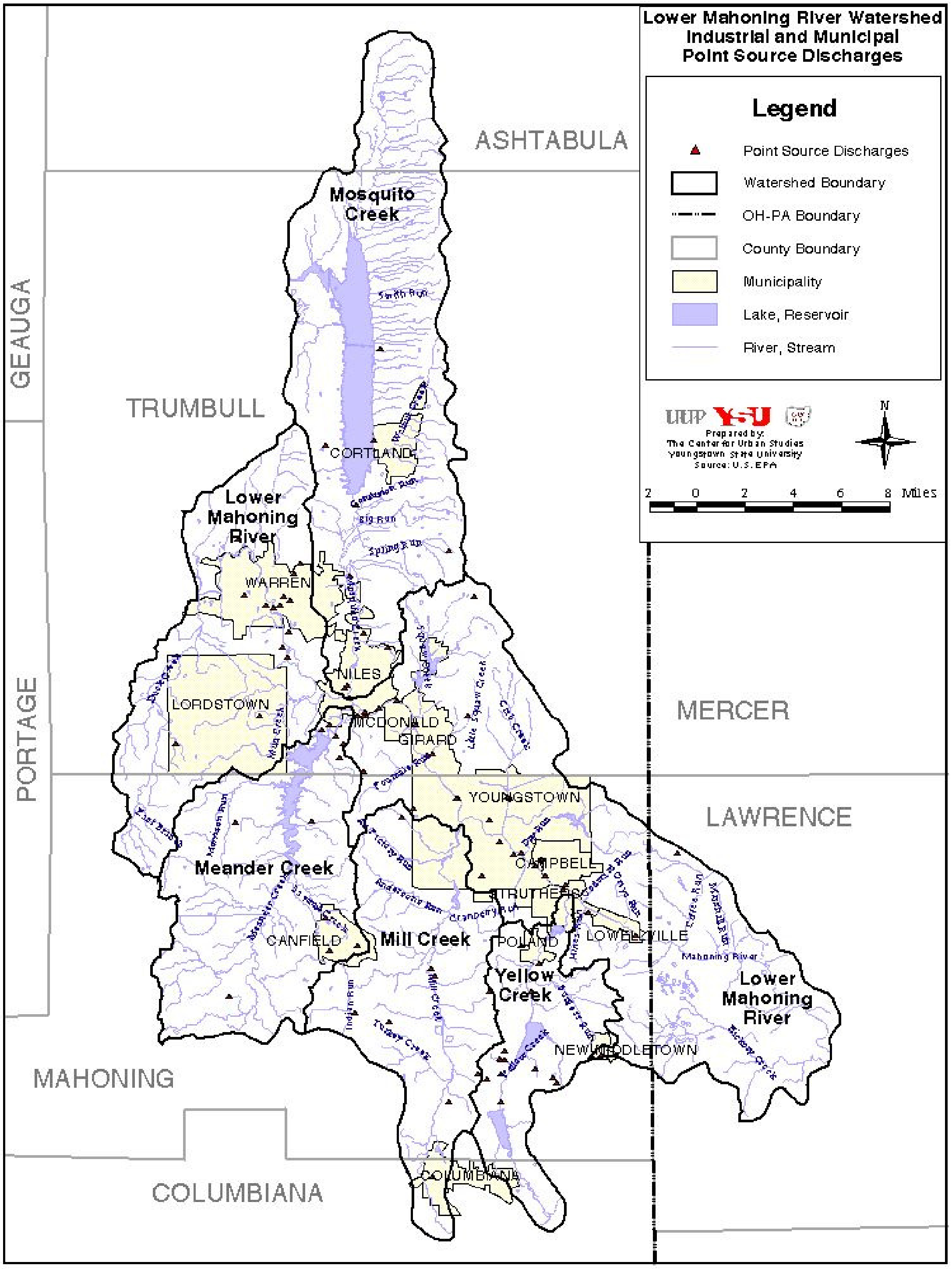

Lower Mahoning River Watershed
Dam Locations
Legend
Dam Location
Watershed Boundary
OH-PA Boundary
County Boundary
Municipality
Lake, Reservoir
River, Stream
Prepared by:
The Center for Urban Studies
Youngstown State University
Source: U.S. EPA, ODNR
N
2 0 2 4 6 8 Miles
ASHTABULA
GEAUGA
TRUMBULL
PORTAGE
MAHONING
COLUMBIANA
MERCER
LAWRENCE
Mosquito Creek
Lower Mahoning River
Meander Creek
Mill Creek
Yellow Creek
Lower Mahoning River
CORTLAND
WARREN
NILES
LORDSTOWN
MCDONALD
GIRARD
YOUNGSTOWN
CAMPBELL
STRUTHERS
CANFIELD
POLAND
LOWELLVILLE
NEW MIDDLETOWN
COLUMBIANA
OH00393
OH00343
OH00031
OH00341
OH00342
OH00334
OH00336
OH00338
OH00635
OH02492
OH00337
OH01996
OH00628
OH02694
OH00416
OH00417
OH00414
OH01007
OH00415
OH01086
OH00629
OH00418
OH00630
OH00408
OH01989
OH00631
OH02677
OH00632
OH00409
Smith Run
Big Run
Spring Run
Little Squaw Creek
Crab Creek
Mill Creek
Indian Run
Yellow Creek
Mahoning River
Hickory Creek

Figure 8. Point source discharges in lower Mahoning River.

2003https://web.archive.org/web/20050122222742/http://www.ysu.edu/mahoning_river/bralich_map/Environmental%20Maps/lm_point_source.jpg)


Lower Mahoning River Watershed
Industrial and Municipal
Point Source Discharges
Legend
▲ Point Source Discharges
Watershed Boundary
OH-PA Boundary
County Boundary
Municipality
Lake, Reservoir
River, Stream
YSU
Prepared by:
The Center for Urban Studies
Youngstown State University
Source: U.S. EPA
N
2 0 2 4 6 8 Miles
ASHTABULA
GEAUGA
TRUMBULL
PORTAGE
MERCER
LAWRENCE
MAHONING
COLUMBIANA
Mosquito Creek
Lower Mahoning River
Meander Creek
Mill Creek
Yellow Creek
CORTLAND
WARREN
NILES
LORDSTOWN
MCDONALD
GIRARD
YOUNGSTOWN
CAMPBELL
STRUTHERS
CANFIELD
POLAND
LOWELLVILLE
NEW MIDDLETOWN
COLUMBIANA
Smith Run
Big Run
Spring Run
Little Squaw Creek
Cat Creek
Mill Creek
Indian Run
Mahoning River
Hickory Creek

MATERIALS AND METHODS

Site Selection:

The segment of the Mahoning River that was investigated was the ~50 km stretch that extends from Girard, Ohio to the Pennsylvania border below Lowellville, Ohio (Figure 1), and has been determined to have contaminated riverbank sediments (OHEPA, 1996; Amin & Jacobs, 2013). A minimum of four sites were selected in this river reach. I also included a reference site upstream at the outflow of the Kirwan Reservoir, on the West Branch in Portage County.

At river mile (RM) 41.5, chromium and lead were found in sediment downstream of Copperweld Steel, and lead at RM 38.9 downstream from Dickey Run storm sewer (Thomas Steel) (Figure 8). From this point to the mouth in Pennsylvania, arsenic, copper and cadmium were found at highly elevated levels. The Dickey Run stormsewer received water from Thomas Steel and the discharge zone is located in the bank of the river, so this is one location that will be considered for investigation. Another area that was noted in a 1994 survey was the bank along the WCI Steel area (RM 37.15 to 35.86) where slag was leaching into the river and banks. The wetland adjacent to the river (around RM 35.4) was also filled with slag waste potentially leaching into the river banks and river. Other areas that were identified in 1994 as having elevated heavy metals include the City of Niles wastewater treatment effluent (RM 28.86), Campbell wastewater treatment effluent (RM 15.89), and Struthers wastewater treatment effluent (RM 14.32) (OHEPA 1996). These areas were considered for sampling.

Site A: Lowellville

Lowellville contained many places that employed mine and industry facilities along the Mahoning River. Places such as Youngstown Sheet & Tube, J&L Steel/Cold Metal Products and Sharon Steel's Lowellville works drew water from this area and discharged waste into the river. This made the Lowellville sampling site an ideal candidate for this research. (Grilli, 2017)

Site B: Struthers

Located in Struthers, massive steel industries were very active in the early 1900s. An example of this was Campbell Works (was named East Youngstown and later renamed in Campbell's honor). The mill was several miles long, and went into Youngstown and Struthers. It had four blast furnaces, 12 hearth furnaces, Bessemer converters, , butt-weld tube mill, hot strip mills, 9- and 12-inch bar mills and seamless tube mills (KJP, 2012).

Site C: Girard

Girard was known for the A. M. Byers Steel Company (formerly the Girard Iron Company). In 1939, the company closed leaving behind an 80-acre plot located east of the Mahoning River and west of State Street making it an ideal site to study for industrial legacies (Harris & Dale, 2019)

Site D: Kirwan Reservoir outflow, West Branch State Park

Kirwan was chosen as a reference site. The reservoir is upstream from the industrial sources, and is hydrological and upwind above the pollution. This site will be used to compare the metal results to the contaminated sites.

Tree Selection

This thesis focused on two of the most important riparian tree species in the Northeast, both of which are also abundant along the Mahoning River. *Acer saccharinum* (silver maple) were studied due to its abundance along the Mahoning River and elsewhere in northeast Ohio (ODNR Division of Forestry, 2017). It is very fast growing (24 inches per year average in height), and tolerates a wide range of soil conditions, ranging from acidic to alkaline soil, dry soil and moist. It grows to 50' to 80' with spread of a height 2/3 wider than the tree is tall. Silver maple prefers deep, moist acidic soil, and can withstand both flooding and partial droughts. It has a widespread root system, and has many beneficial wildlife values. It provides nesting sites for migratory birds, feeds squirrels in early spring, and is used as habitat for beaver communities. (Arbor Day Foundation, 2019).

American sycamore (*Platanus occidentalis*), another important riparian species along the Mahoning River, was likewise included. The sycamore has broad leaves but is most recognizable by its bark that is peeling into patches of white and grey. This tree is also very high in wildlife value, in which it attracts a large range of bird species to inhabit it. It seasonally loses leaves, matures at a height of 22 – 30 m, and at a width of 16 – 20 m. It is intolerant of drought conditions, but is tolerant of flooding/ draining conditions. It is also known for its accelerated growth rates (The Morton Arboretum, 2019).

In order to examine tree rings dating back to the time of major steel industry operations, trees that appear to exceed 40 years of age are to be selected. Healthy, undamaged trunks were selected, in order to avoid coring rotted wood.

Tree coring

Tree core samples were taken using a 16-inch Hagloff increment borer at breast height (1.37m), which is the standard height employed in forestry and forest research, intended to exclude the root flare of larger trunks. The tree core rings give an accurate reading of the tree's age, and in this study, of what contaminants may have been present at different stages of the tree's life.

Each core extracted was separated into temporal intervals of 10 years, which consistently provided sufficient wood for metals analysis. When handling the cores, plastic food service gloves were used to prevent any possible foreign contamination of the samples. To reveal the age rings, a range of non-metal-oxide containing sandpaper grits from 60 thru 220 was used. Cores were never glued down in any way, as is the procedure when they are intended to be archived. First, in order remove any debris that might have been transferred across age rings as the core was drilled and extracted, the entire outer surface was sanded with the coarser grits. Next, to allow better resolution of age rings, one side of each core was sanded flat, finally being smoothed with the finer grits. In between sanding procedures, Kimtech wipes were used on the samples to remove excess sawdust. New sandpapers and wipes were used on each core to avoid cross contamination. Each core was cut into 10-year age intervals with a stainless steel 10-blade scalpel. Core samples were then placed into acid- and metal-free cotton bond paper packets, which were labeled by site, species/individual, and age interval.

Inductively Coupled Plasma (ICP) Analysis of Tree Cores

Inductively Coupled Plasma is a type of emission spectroscopy that uses the inductively coupled plasma to make atoms and ions excited that produce electromagnetic radiation at different wavelengths that are characteristic of a particular element. The emission's intensity gives indications of the concentration of the element within the sample. The sensitivity of this technique varies by element, from 1ppm to 10ppb.

Each core sample was placed into a crucible (Fisherbrand FB-965-K), weighed, and then placed into an incinerator for 5 hours at 500 ºC. The incineration procedure was used to ash the cores samples, in order to prepare them for digestion. Before digestion samples were left in the furnace to cool for 40 minutes, and then placed in a desiccator to cool to room temperature to preserve as much as the ashed core sample as possible. The samples were then weighed again to get a post weight to observe what was lost in the incineration process. Next, the samples were then diluted with a 300ml of HCL, 100 HNO3, and 1L of pure water mixture. 10mls of this mixture were placed into each crucible by using a 10ml serological pipette. The crucibles were then placed on a Corning PC-420D heat rack set at 100ºC to aid in digesting the cores. After, the cores were then transferred into 15 ml falcon tubes using Fisherbrand disposable pipettes.

Liquid samples were diluted and spiked with standards and solid samples are made into a liquid (in this case digested). After the solutions are properly diluted, the peristaltic pump transports the solution into the plasma torch of the ICP machine. Solid samples should be between 250 and 500mg. Water samples should be acidified, and any liquid samples containing low mercury concentrations should be stored in glass containers in which is mixed with 10% nitric acid. ICP analysis can be used to identify residual catalyst in polymers, flame retardants, amounts of inorganic fillers, microbial agents, and metals (SGS Polymer Solutions, 2019). Thus we will use the ICP to observe if trace metals will be present in the tree core samples, as well as in the soil samples near the trees.

To assure quality of result from ICP analysis, quality control (QC) checks were completed every 15-20 samples and standard reference material (SRM, pine tree needles 1575A) was processed and analyzed consistent with sample analysis. QC checks were made using standard solutions (1.5 ml of inorganic ventures YW-STD-3 was used and 7.7 µL of multiple heavy metals was used to create this standard for the ICP process (solutions: manganese 1000µg/ml HN03Claristas, MO assurance, peak performance p/n 400-Intri400 sb1000, and peak performance –p/o 54400-single element ti standard). to verify the calibration was still valid during analysis. If the QC checks failed, the calibration was reestablished. Results from the SRM analysis were compared to the certified and reference metal concentrations with most falling in the range of 70-110% recovery (Appendix 3). The detection limit was determined for each analytical line and any numbers below the detection limit are noted and considered an estimated value (SPEX CertiPrep Inc. 2006).

Pre ordered standards were used to make calibration points for ICP-AES Standards for calibration were used from Peak Performance CPI, along with Assurance SPEX Certiprep. A QC (quality control) standard was also used every fifteen samples. A standard reference material of pine needles (SRM) will be used to check the methodology.

Data analysis

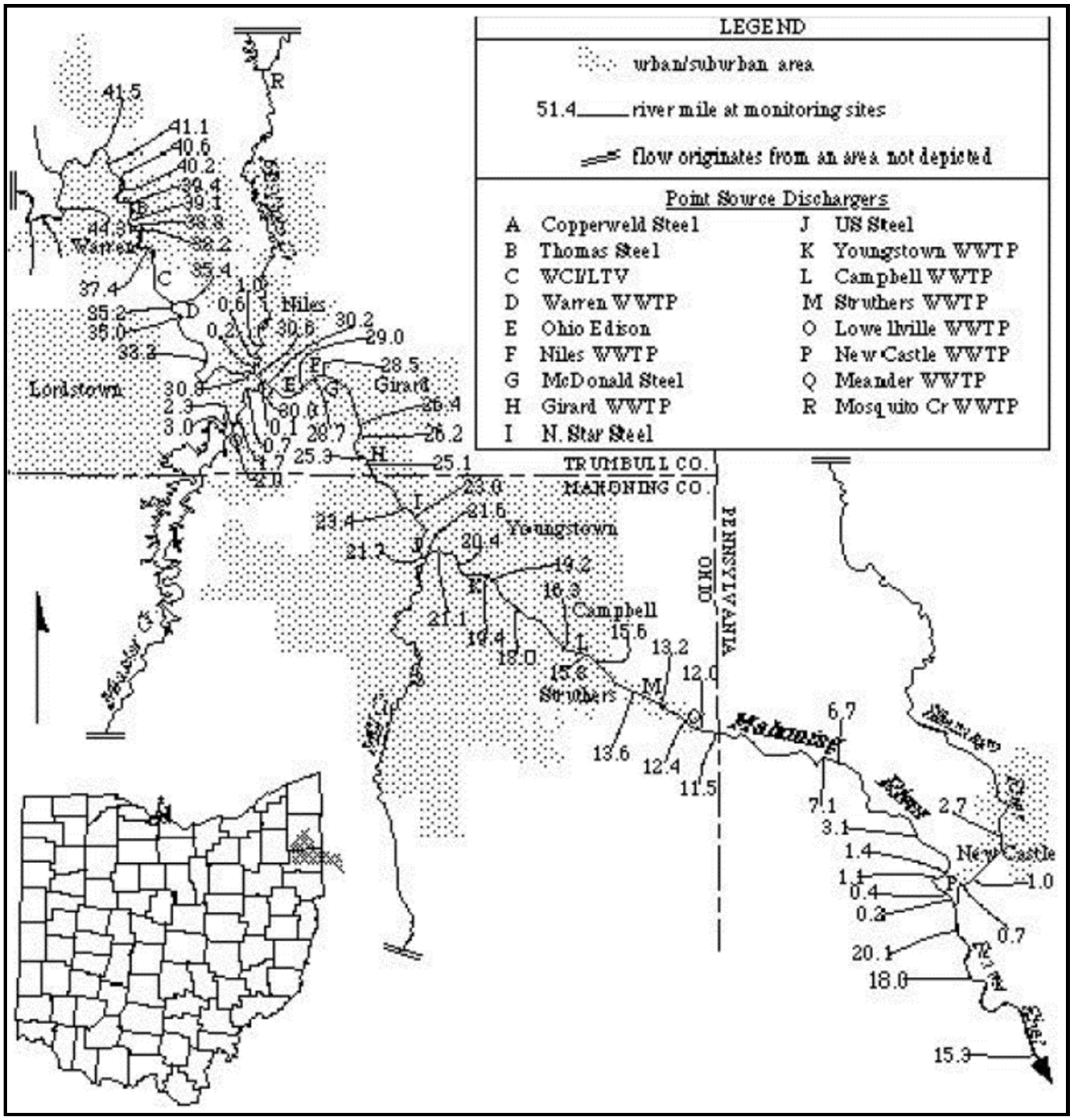
Tree core segments served as the experimental unit for all analyses. Trace element concentrations were the dependent variables, and were segregated into dietary essentials vs. non-essentials where informative. The latter, including lead, cadmium, and excessive concentrations of otherwise necessary elements such as copper, can act as environmental contaminants. All analyses were run on the entire suite of reliable trace element data, and then subsequently after removal of abundant and environmentally conservative nutrient elements phosphorus, sulfur, calcium, and magnesium. The latter analysis was intended to more specifically assess patterns among elements that might act as contaminants.

The independent variables consisted of tree species, river site, and core segment age. Species and river site are categorical, and served as factors in MANCOVA and ANCOVA analyses. Core segment age served as a covariate.

Trace element concentrations were subjected to exploratory Pearson correlation analysis to initially gauge the degree of covariance, which was highly significant. Thus, trace element concentrations were subjected to data reduction by Principle Components Analysis (PCA) ordination.

Principle Components Analysis scores were analyzed by either two-factor MANCOVA (where two PCA axes were informative) or two-factor ANCOVA for a single PCA axis. Tukey's post-hoc comparisons were employed for significant factors. Principle Components scores were also regressed on core segment age, in order to independently gauge any influence of this covariate, largely to confirm that this relationship was not significant. All statistical analyses were conducted using Statistics Package for the Social Sciences (SPSS), version 20.0.

Figure 9. River map of the Lower Mahoning River noting river miles, cities and sewer discharges (OHEPA 1996).

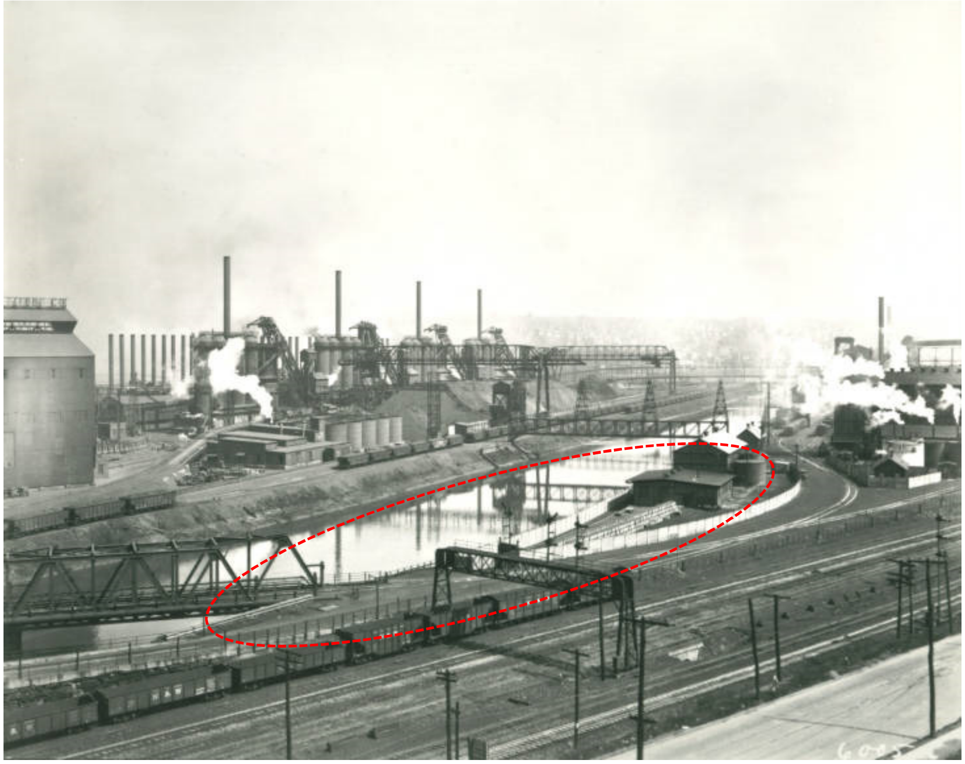

LEGEND
urban/suburban area
51.4 river mile at monitoring sites
flow originates from an area not depicted
Point Source Dischargers
A Copperweld Steel
B Thomas Steel
C WCI/LTV
D Warren WWTP
E Ohio Edison
F Niles WWTP
G McDonald Steel
H Girard WWTP
I N. Star Steel
J US Steel
K Youngstown WWTP
L Campbell WWTP
M Struthers WWTP
O Lowellville WWTP
P New Castle WWTP
Q Meander WWTP
R Mosquito Cr WWTP
Warren
Niles
Girard
Lordstown
Youngstown
Campbell
Struthers
New Castle
TRUMBULL CO.
MAHONING CO.
OHIO
PENNSYLVANIA
Mahoning
Meander Cr.
Mosquito Cr.
41.5
41.1
40.6
40.2
39.4
39.1
38.8
38.2
44.3
35.4
37.4
35.2
35.0
33.3
30.8
30.6
30.2
29.0
28.5
26.4
26.2
28.7
25.3
25.1
23.0
23.4
21.6
21.7
20.4
19.2
16.3
21.1
17.4
18.0
15.6
15.8
13.2
12.0
13.6
12.4
11.5
6.7
7.1
3.1
1.4
1.1
0.4
0.2
2.7
1.0
0.7
20.1
18.0
15.3

.

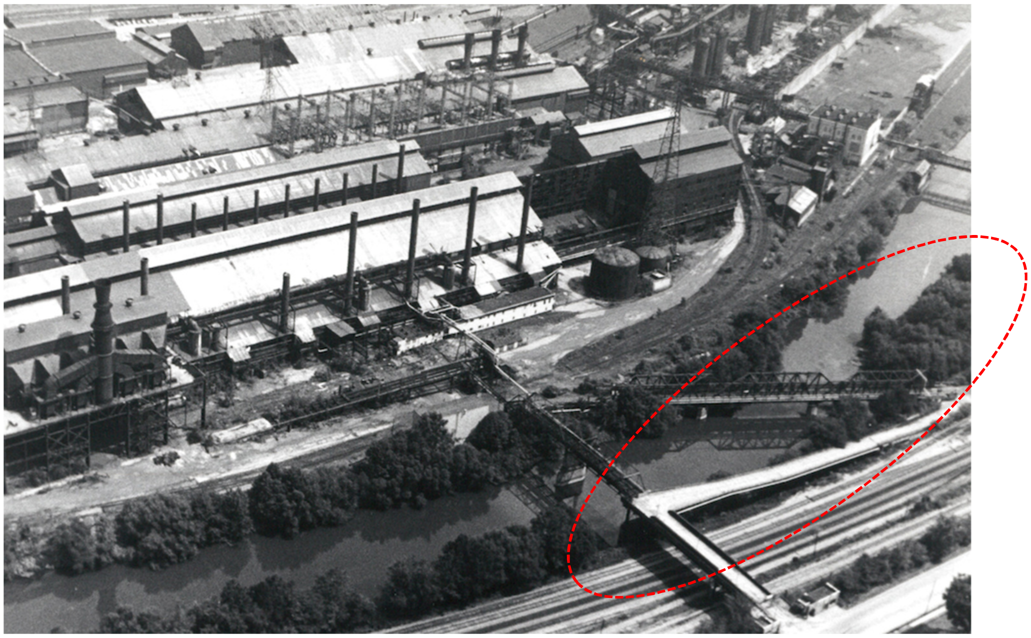
Figure 10. Aerial image of Site A, Lowellville.

Figure 11. Aerial image of Site B, Struthers.

Figure 12. Historical and present-day photographs of sampling site C, Struthers, former home of the Youngstown Sheet and Tube Campbell Works.



Early 20th Century



Mid 20th Century

Present day

Figure 13. Aerial image of Site C, Girard.

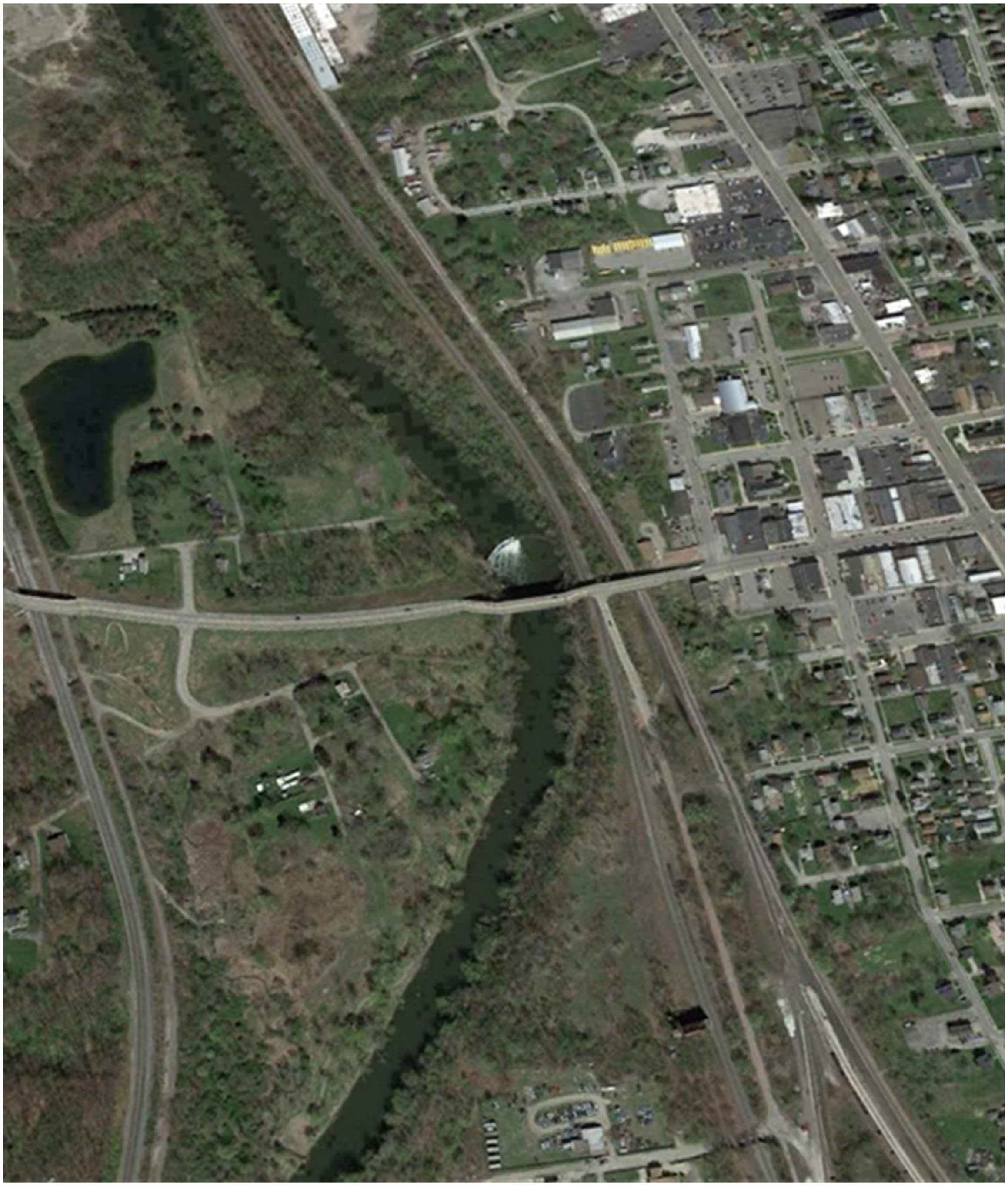


Figure 14. Aerial image of Site D Kirwan Reservoir (the upper portion represents the region, while the lower portion displays the sampling area).

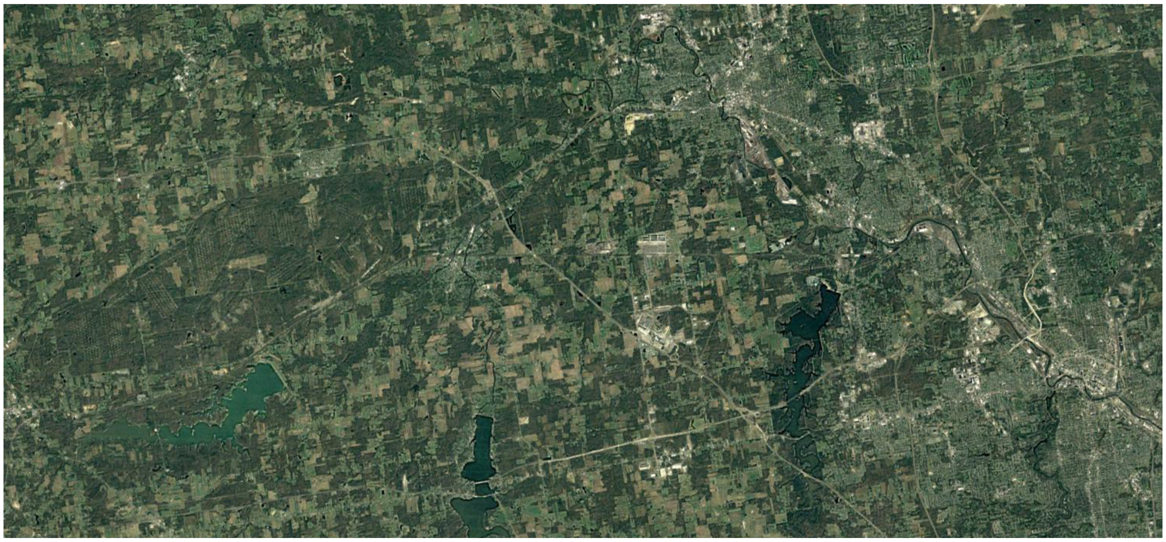


Figure 15. Inductively Coupled Plasma apparatus used for determination of metal concentrations in tree core segments.


Thermo
SCIENTIFIC
iCAP 6000 SERIES

RESULTS

Forty tree cores were collected from the four sites, 17 of which were American sycamore and 23 silver maple. Nine cores could not be used for ICP analysis of metals, as they were too fragile and broken to be able to be prepared. Of the remaining 31 cores that were analyzed, two were eliminated from consideration because ICP inexplicably returned all zero values for some metals. The remaining 29 cores were judged suitable for inclusion (see Appendix 1).

Table 1 indicated that all of the pairings of trace elements are either positively correlated with one another, or uncorrelated (i.e. coefficient near zero), there were no negative correlations. Correlation coefficients were highest when pairing elements that act as biologically essential nutrients (e.g. phosphorus, calcium, sulfur, magnesium), and when paring trace metals that are considered industrial contaminants in high concentrations (e.g. cadmium, lead, copper). The trace elements most strongly correlated were calcium and magnesium (both alkali earth metals), magnesium and phosphorus, and magnesium and sulfur (Table 1).

Results of Principle Components Analysis on the highly covarying data set of 11 trace elements are presented in Tables 2 and 3. The first two components were used for ordination due to their explaining a higher portion of the total data variance (54.67% cumulative). Loadings of the original trace element variables are presented in Table 3. All trace elements load positively on PCA axis 1 (i.e. the x axis in ordination graphs). In contrast, nutrient trace elements calcium, phosphorus, sulfur, and magnesium loaded negatively on PCA axis 2 (the y axis), while all other trace metals loaded positively.

Ordination of trace element PCA scores are shown in Figures 17 (all core segments) and 18 (site x species data centroids). It was evident that American sycamore tended to be distributed below the x axis, and silver maple above. This trend is even more clear in Figure 18 that plots the centroids. Sycamores, especially at the Kirwan Reservoir reference site, had greater concentrations of micronutrient elements. Silver maples tended to have greater concentrations of potential industrial contaminant metals in Lowellville.

Results of Multivariate Analysis of Covariance (MANCOVA), using PCA1 and PCA2 as dependent variables, site and species as factors, and core segment age as a covariate, are presented in Tables 4 and 5. Both factors and the covariate were significant in the multivariate sense (Table 4), so the PCA scores were examined separately through univariate ANCOVAs (Table 5).

Site, species, and site x species interaction were all highly significant for both PCA axes (Table 5). The age covariate was significant for PCA1 scores ($p = 0.036$), but not for PCA2 ($p = 0.082$). However, regression of PCA1 scores on core segment age yielded a very low R^2 (0.018), and was in fact a non-significant relationship as a stand-alone regression rather than as part of an Analysis of Covariance (Figure 19). PCA2 scores were again not significantly related to tree core segment age (Figure 20).

Re-examining the results of the factorial aspects of the statistical design (i.e. site and species) in light of the significant interaction, results of post-hoc Tukey's paired comparisons among the eight site x species combinations are presented in Tables 6 (PCA1) and 7 (PCA2).

Table 6 indicated that overall trace element concentrations (i.e. represented by the x-axis in Figures 17 and 18) in Lowellville silver maples were significantly higher than those in Struthers and Girard silver maples. Additionally, overall trace element concentrations were significantly higher in Kirwan Reservoir sycamores than in silver maples at Struthers, Girard, and Kirwan. Overall trace element concentrations were higher in both Struthers and Kirwan sycamores than in the silver maples at the same sites (Table 6). Interestingly, Struthers and Girard silver maples had the lowest overall concentrations of trace elements (see Figure 18), which were statistically lower than a broad range of site x species combinations all along the Mahoning River, including cores from the Kirwan reference site (Table 6).

Table 7 presents differences among site x species combinations in concentrations of micronutrient trace elements (i.e. loading negatively on the PCA2 y-axis in Figures 17 and 18) vs potentially contaminant trace metals (i.e. loading positively on the axis). Although silver maples from all sites plotted above the x-axis in Figures 17 and 18, they did not differ from one another in PCA2 scores (Table 7). Likewise, Struthers sycamores did not differ statistically from any of the silver maples. Lowellville sycamores did not differ from Struthers, Girard, and Kirwan silver maples, but had significantly lower PCA2 scores than silver maples at the same site. Girard sycamores had significantly lower PCA2 scores than Lowellville silver maples, but differences with silver maples at the other three sites were narrowly non-significant (p values from 0.054 – 0.117). PCA2 scores for Kirwan reservoir reference site sycamores were significantly lower than for all other site x species combinations (Table 7).

Tables 8 and 9 present the results of a second Principle Components Analysis focused only on the seven trace metals that loaded positively on the PCA2 y axis as shown in Table 3 and Figures 17 and 18 (i.e. after removing the environmentally conservative nutrient trace elements). Only one principle component was statistically informative (Eigenvalue >1.0), and explained 46.58% of total data variance. Loadings of the original trace element variables are presented in Table 9. As with all trace elements originally analyzed (Tables 2 and 3, Figures 17 and 18), all of these seven metals load positively on this PCA axis.

Results of univariate Analysis of Covariance (ANCOVA), using these new PCA scores as a dependent variable, site and species as factors, and core segment age as a covariate, are presented in Table 10. Site was a significant factor, but, unlike when the entire data set was analyzed, species was not. However, a site x species interaction was again highly significant. Core segment age was not a significant covariate. Again, in light of the significant interaction, results of post-hoc Tukey's paired comparisons among the eight site x species combinations are presented in Table 11.

With the dietary essential nutrients now factored out, Lowellville silver maples again had higher trace metal concentrations than Struthers and Girard silver maples, and also now Girard sycamores (Table 11). A major change, however, is that Kirwan reservoir sycamores no longer differ statistically from any other samples of cores (Table 11).

Table 1. Bivariate Pearson correlation matrix of 11 trace elements in tree core segments.

Correlations

		Ca	Cd	Cu	Fe	Mg	Mn
Ca	Pearson Correlation	1	.263**	.221**	.204**	.777**	.259**
	Sig. (2-tailed)		.000	.004	.007	.000	.001
	N	172	172	171	172	172	172
Cd	Pearson Correlation	.263**	1	.512**	.405**	.198**	.382**
	Sig. (2-tailed)	.000		.000	.000	.009	.000
	N	172	173	172	173	172	173
Cu	Pearson Correlation	.221**	.512**	1	.578**	.316**	.414**
	Sig. (2-tailed)	.004	.000		.000	.000	.000
	N	171	172	172	172	171	172
Fe	Pearson Correlation	.204**	.405**	.578**	1	.296**	.160*
	Sig. (2-tailed)	.007	.000	.000		.000	.036
	N	172	173	172	173	172	173
Mg	Pearson Correlation	.777**	.198**	.316**	.296**	1	.175*
	Sig. (2-tailed)	.000	.009	.000	.000		.022
	N	172	172	171	172	172	172
Mn	Pearson Correlation	.259**	.382**	.414**	.160*	.175*	1
	Sig. (2-tailed)	.001	.000	.000	.036	.022	
	N	172	173	172	173	172	173
P	Pearson Correlation	.286**	.239**	.239**	.194*	.553**	.059
	Sig. (2-tailed)	.000	.002	.002	.011	.000	.444
	N	172	173	172	173	172	173
Pb	Pearson Correlation	.236**	.467**	.401**	.385**	.253**	.168*
	Sig. (2-tailed)	.002	.000	.000	.000	.001	.028
	N	170	171	171	171	170	171
S	Pearson Correlation	.510**	.251**	.487**	.227**	.568**	.299**
	Sig. (2-tailed)	.000	.001	.000	.003	.000	.000
	N	172	173	172	173	172	173
Sn	Pearson Correlation	.405**	.580**	.484**	.317**	.305**	.254**
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.001
	N	172	173	172	173	172	173
Zn	Pearson Correlation	.209**	.352**	.357**	.326**	.216**	.094
	Sig. (2-tailed)	.006	.000	.000	.000	.005	.219
	N	171	172	171	172	171	172

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Correlations

		P	Pb	S	Sn	Zn
Ca	Pearson Correlation	.286**	.236**	.510**	.405**	.209**
	Sig. (2-tailed)	.000	.002	.000	.000	.006
	N	172	170	172	172	171
Cd	Pearson Correlation	.239**	.467**	.251**	.580**	.352**
	Sig. (2-tailed)	.002	.000	.001	.000	.000
	N	173	171	173	173	172
Cu	Pearson Correlation	.239**	.401**	.487**	.484**	.357**
	Sig. (2-tailed)	.002	.000	.000	.000	.000
	N	172	171	172	172	171
Fe	Pearson Correlation	.194*	.385**	.227**	.317**	.326**
	Sig. (2-tailed)	.011	.000	.003	.000	.000
	N	173	171	173	173	172
Mg	Pearson Correlation	.553**	.253**	.568**	.305**	.216**
	Sig. (2-tailed)	.000	.001	.000	.000	.005
	N	172	170	172	172	171
Mn	Pearson Correlation	.059	.168*	.299**	.254**	.094
	Sig. (2-tailed)	.444	.028	.000	.001	.219
	N	173	171	173	173	172
P	Pearson Correlation	1	.140	.334**	.299**	.187*
	Sig. (2-tailed)		.068	.000	.000	.014
	N	173	171	173	173	172
Pb	Pearson Correlation	.140	1	.193*	.378**	.202**
	Sig. (2-tailed)	.068		.011	.000	.008
	N	171	171	171	171	170
S	Pearson Correlation	.334**	.193*	1	.432**	.425**
	Sig. (2-tailed)	.000	.011		.000	.000
	N	173	171	173	173	172
Sn	Pearson Correlation	.299**	.378**	.432**	1	.525**
	Sig. (2-tailed)	.000	.000	.000		.000
	N	173	171	173	173	172
Zn	Pearson Correlation	.187*	.202**	.425**	.525**	1
	Sig. (2-tailed)	.014	.008	.000	.000	
	N	172	170	172	172	172

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

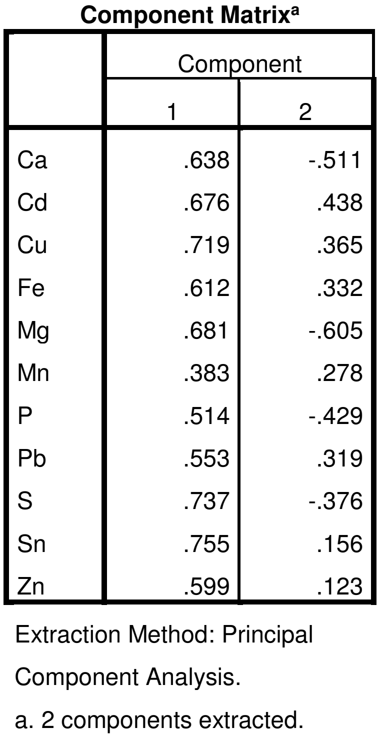
Table 2. Principle Components Analysis of 11 trace elements from Mahoning River silver maple and sycamore tree core segments (total of 173 core segments). The first two PC axes, graphed in Figures 17 and 18, represent 54.67% of data variance.

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.407	40.064	40.064	4.407	40.064	40.064
2	1.607	14.606	54.670	1.607	14.606	54.670
3	1.058	9.615	64.285			
4	.918	8.347	72.632			
5	.743	6.753	79.384			
6	.720	6.542	85.926			
7	.454	4.129	90.055			
8	.367	3.341	93.396			
9	.316	2.875	96.271			
10	.282	2.560	98.831			
11	.129	1.169	100.000			

Extraction Method: Principal Component Analysis.

Table 3. “Loadings” of trace elements on PCA axes 1 and 2 (components). These are equivalent to correlation coefficients, and range from -1.0 to 1.0.



Component Matrix[a]

	Component	
	1	2
Ca	.638	-.511
Cd	.676	.438
Cu	.719	.365
Fe	.612	.332
Mg	.681	-.605
Mn	.383	.278
P	.514	-.429
Pb	.553	.319
S	.737	-.376
Sn	.755	.156
Zn	.599	.123

Extraction Method: Principal Component Analysis.

a. 2 components extracted.

Figure 16. Principle Components Analysis ordination of trace elements in 169 tree core segments. Closed symbols are silver maple; open symbols sycamore. Sampling sites indicated by color as follows: blue = Lowellville, green = Struthers, red = Girard, yellow = Kirwan Reservoir.

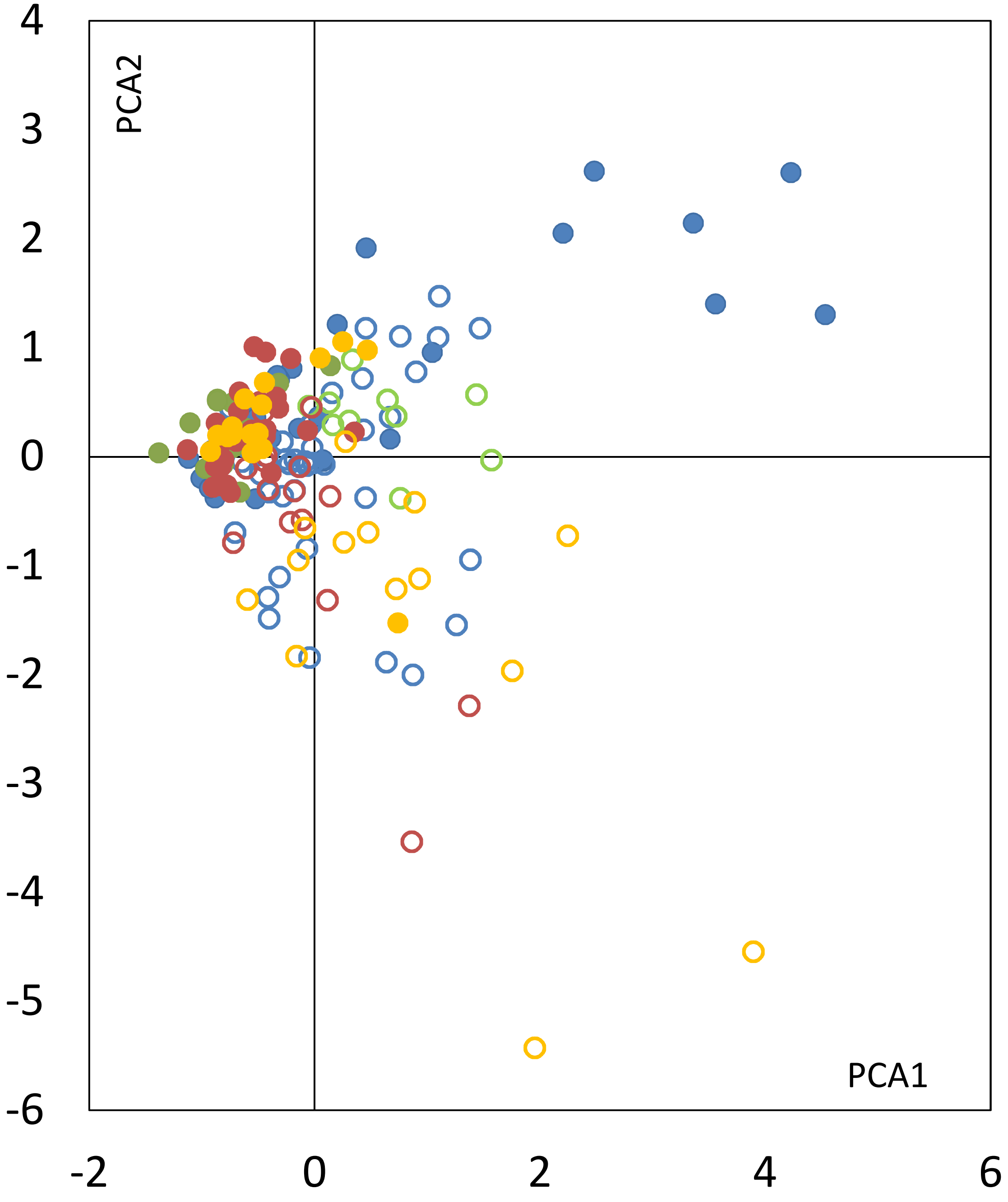

4
3
2
1
0
-1
-2
-3
-4
-5
-6
PCA2
PCA1
-2
0
2
4
6

Figure 17. PCA ordination of data centroids (i.e. average PCA scores for silver maple and sycamore at the four sampling sites).

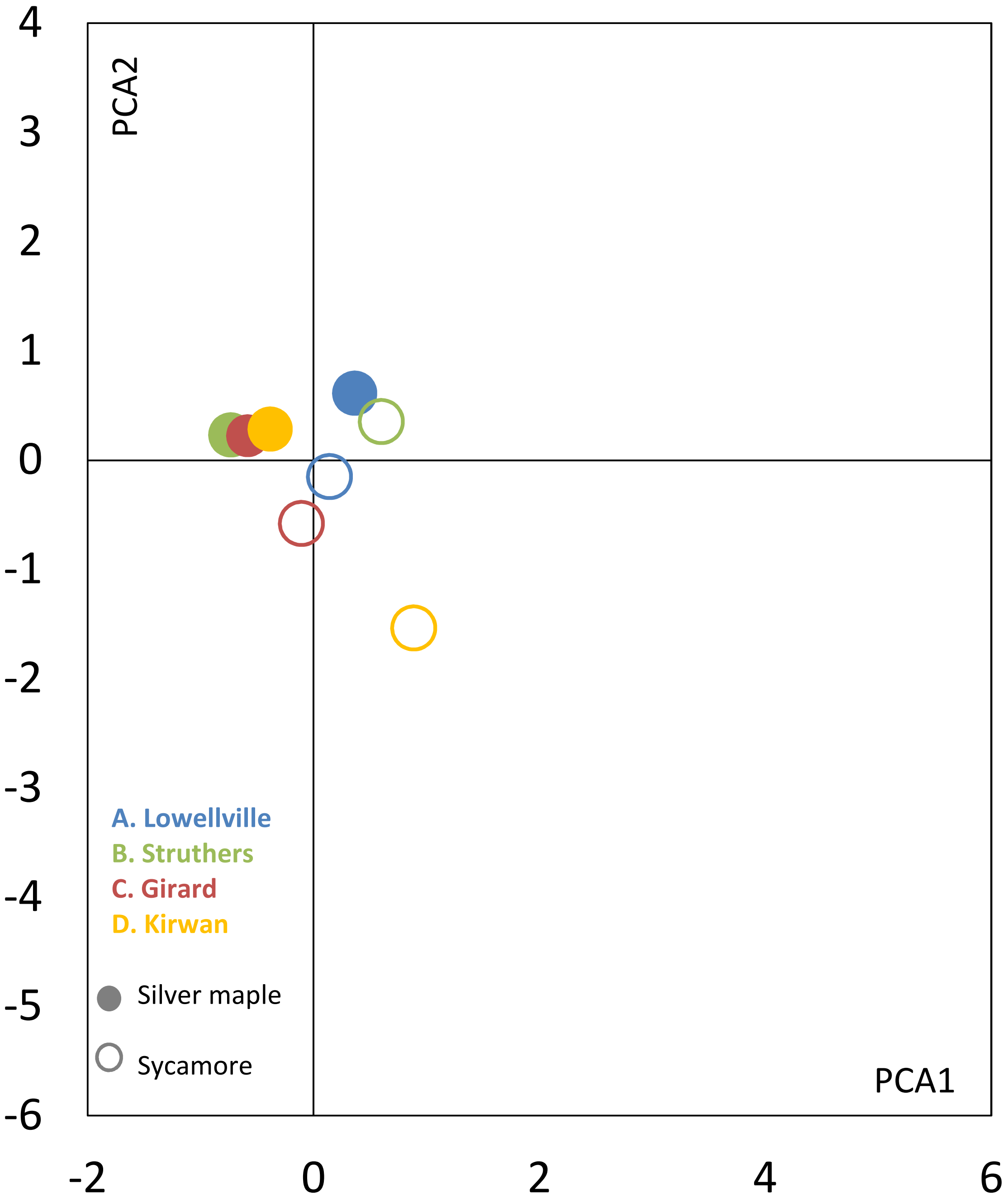

4
3
2
1
0
-1
-2
-3
-4
-5
-6
PCA2
A. Lowellville
B. Struthers
C. Girard
D. Kirwan
Silver maple
Sycamore
PCA1
-2
0
2
4
6

Table 4. Multivariate results from two-factor MANCOVA of trace element Principle Components Analysis scores. The PCA is presented in Tables 1 and 2, and graphed in Figures 17 and 18.

Multivariate Tests[a]

Effect		Value	F	Hypothesis df	Error df	Sig.
Intercept	Pillai's Trace	.057	4.776[b]	2.000	159.000	.010
	Wilks' Lambda	.943	4.776[b]	2.000	159.000	.010
	Hotelling's Trace	.060	4.776[b]	2.000	159.000	.010
	Roy's Largest Root	.060	4.776[b]	2.000	159.000	.010
Age	Pillai's Trace	.054	4.530[b]	2.000	159.000	.012
	Wilks' Lambda	.946	4.530[b]	2.000	159.000	.012
	Hotelling's Trace	.057	4.530[b]	2.000	159.000	.012
	Roy's Largest Root	.057	4.530[b]	2.000	159.000	.012
Site	Pillai's Trace	.240	7.270	6.000	320.000	.000
	Wilks' Lambda	.772	7.307[b]	6.000	318.000	.000
	Hotelling's Trace	.279	7.343	6.000	316.000	.000
	Roy's Largest Root	.199	10.605[c]	3.000	160.000	.000
Species	Pillai's Trace	.315	36.586[b]	2.000	159.000	.000
	Wilks' Lambda	.685	36.586[b]	2.000	159.000	.000
	Hotelling's Trace	.460	36.586[b]	2.000	159.000	.000
	Roy's Largest Root	.460	36.586[b]	2.000	159.000	.000
Site * Species	Pillai's Trace	.235	7.102	6.000	320.000	.000
	Wilks' Lambda	.778	7.091[b]	6.000	318.000	.000
	Hotelling's Trace	.269	7.079	6.000	316.000	.000
	Roy's Largest Root	.172	9.186[c]	3.000	160.000	.000

a. Design: Intercept + Age + Site + Species + Site * Species

b. Exact statistic

c. The statistic is an upper bound on F that yields a lower bound on the significance level.

Table 5. Univariate results from two-factor MANCOVA presented in Table 3, which was significant for all independent variables.

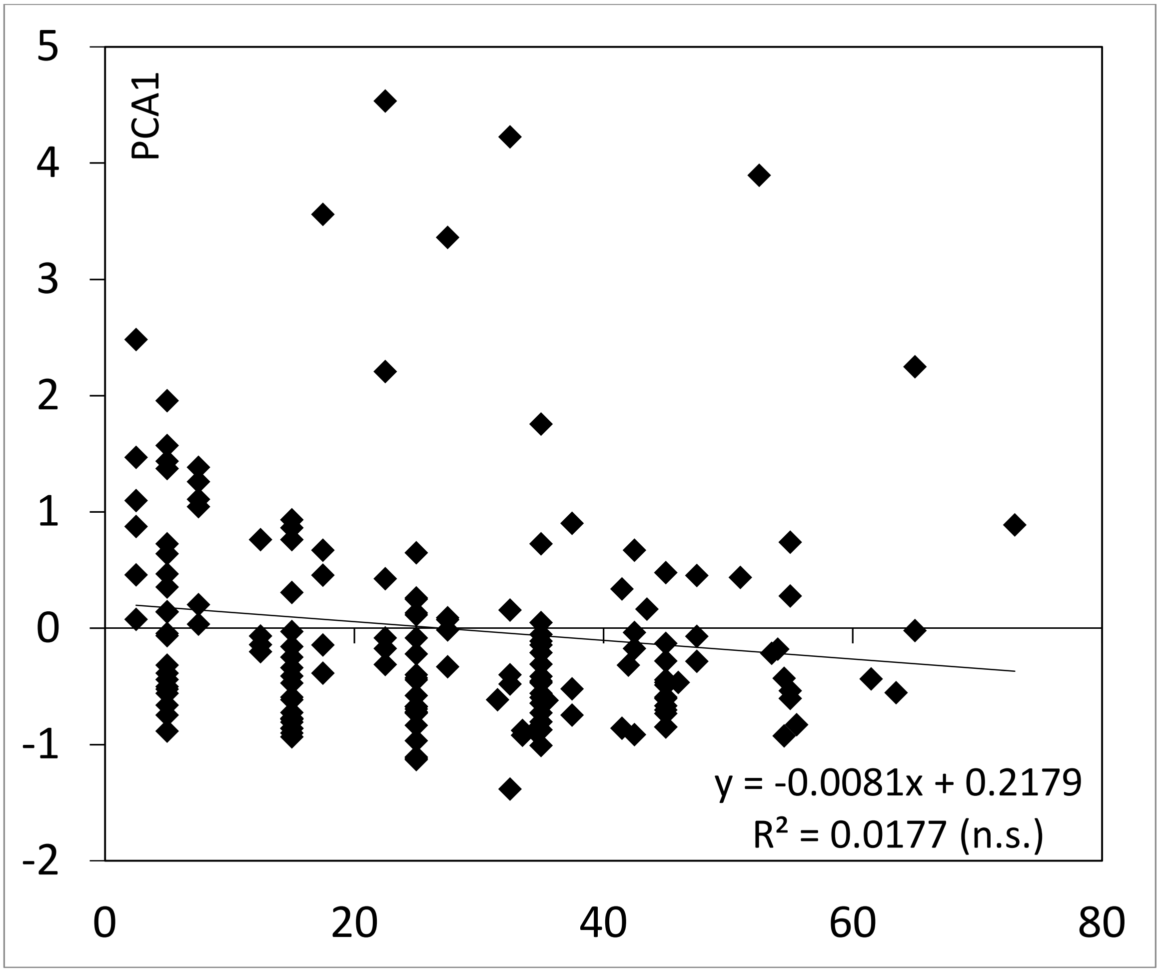
Tests of Between-Subjects Effects

Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	PCA1	43.360^a	8	5.420	6.958	.000
	PCA2	57.811^b	8	7.226	10.493	.000
Intercept	PCA1	2.987	1	2.987	3.835	.052
	PCA2	2.815	1	2.815	4.088	.045
Age	PCA1	3.485	1	3.485	4.474	.036
	PCA2	2.108	1	2.108	3.060	.082
Site	PCA1	10.288	3	3.429	4.402	.005
	PCA2	20.587	3	6.862	9.965	.000
Species	PCA1	19.466	1	19.466	24.988	.000
	PCA2	24.686	1	24.686	35.845	.000
Site * Species	PCA1	17.015	3	5.672	7.281	.000
	PCA2	13.153	3	4.384	6.366	.000
Error	PCA1	124.640	160	.779		
	PCA2	110.189	160	.689		
Total	PCA1	168.000	169			
	PCA2	168.000	169			
Corrected Total	PCA1	168.000	168			
	PCA2	168.000	168			

a. R Squared = .258 (Adjusted R Squared = .221)

b. R Squared = .344 (Adjusted R Squared = .311)

Figure 18. PCA axis 1 scores regressed on tree core age (midpoint of segment). Trendline not significant as a stand-alone regression, although core age was a significant covariate in the MANCOVA.



Age (tree core segment mid-point)

Figure 19. PCA axis 2 scores regressed on tree core age (midpoint of segment). Regression is non-significant.

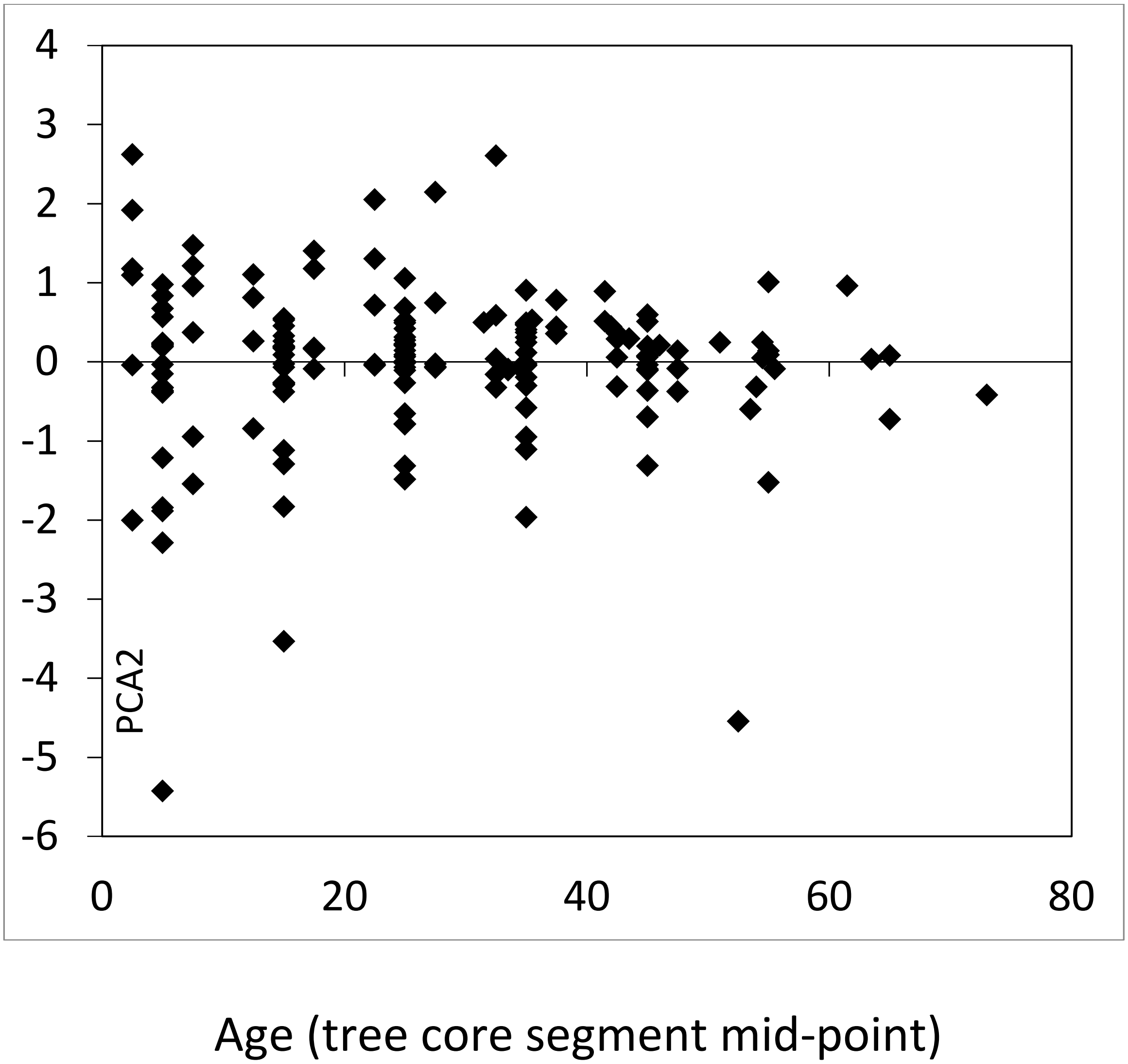

4
3
2
1
0
-1
-2
-3
-4
-5
-6
PCA2
0
20
40
60
80
Age (tree core segment mid-point)

Table 6. Post-hoc results (Tukey) for PCA1 for Site x Species interaction term from MANCOVA. OneWayFactor designations as follows: 1 = Lowellville silver maple, 2 = Lowellville sycamore, 3 = Struthers silver maple, 4 = Struthers sycamore, 5 = Girard silver maple, 6 = Girard sycamore, 7 = Kirwan silver maple, 8 = Kirwan sycamore.

Multiple Comparisons

Dependent Variable: PCA1

Tukey HSD

(I) OneWayFactor		Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.2204	.21465	.970	-.4388	.8797
	3	1.0969*	.27461	.002	.2535	1.9403
	4	-.2389	.32443	.996	-1.2353	.7575
	5	.9467*	.23483	.002	.2255	1.6679
	6	.4695	.27461	.681	-.3739	1.3128
	7	.7477	.27461	.123	-.0957	1.5910
	8	-.5238	.28725	.605	-1.4060	.3584
2	1	-.2204	.21465	.970	-.8797	.4388
	3	.8765*	.26485	.025	.0631	1.6899
	4	-.4594	.31621	.831	-1.4305	.5118
	5	.7262*	.22334	.030	.0403	1.4121
	6	.2490	.26485	.982	-.5644	1.0624
	7	.5272	.26485	.491	-.2862	1.3406
	8	-.7442	.27794	.137	-1.5978	.1094
3	1	-1.0969*	.27461	.002	-1.9403	-.2535
	2	-.8765*	.26485	.025	-1.6899	-.0631
	4	-1.3358*	.35961	.007	-2.4403	-.2314
	5	-.1502	.28145	.999	-1.0146	.7141
	6	-.6274	.31540	.492	-1.5961	.3412
	7	-.3493	.31540	.954	-1.3179	.6194
	8	-1.6207*	.32647	.000	-2.6234	-.6181
4	1	.2389	.32443	.996	-.7575	1.2353
	2	.4594	.31621	.831	-.5118	1.4305
	3	1.3358*	.35961	.007	.2314	2.4403
	5	1.1856*	.33024	.010	.1714	2.1998
	6	.7084	.35961	.505	-.3961	1.8128
	7	.9866	.35961	.117	-.1179	2.0910
	8	-.2849	.36936	.994	-1.4193	.8495

5	1	-.9467*	.23483	.002	-1.6679	-.2255
	2	-.7262*	.22334	.030	-1.4121	-.0403
	3	.1502	.28145	.999	-.7141	1.0146
	4	-1.1856*	.33024	.010	-2.1998	-.1714
	6	-.4772	.28145	.690	-1.3416	.3872
	7	-.1990	.28145	.997	-1.0634	.6654
	8	-1.4705*	.29380	.000	-2.3728	-.5681
6	1	-.4695	.27461	.681	-1.3128	.3739
	2	-.2490	.26485	.982	-1.0624	.5644
	3	.6274	.31540	.492	-.3412	1.5961
	4	-.7084	.35961	.505	-1.8128	.3961
	5	.4772	.28145	.690	-.3872	1.3416
	7	.2782	.31540	.987	-.6905	1.2468
	8	-.9933	.32647	.054	-1.9959	.0094
7	1	-.7477	.27461	.123	-1.5910	.0957
	2	-.5272	.26485	.491	-1.3406	.2862
	3	.3493	.31540	.954	-.6194	1.3179
	4	-.9866	.35961	.117	-2.0910	.1179
	5	.1990	.28145	.997	-.6654	1.0634
	6	-.2782	.31540	.987	-1.2468	.6905
	8	-1.2714*	.32647	.004	-2.2741	-.2688
8	1	.5238	.28725	.605	-.3584	1.4060
	2	.7442	.27794	.137	-.1094	1.5978
	3	1.6207*	.32647	.000	.6181	2.6234
	4	.2849	.36936	.994	-.8495	1.4193
	5	1.4705*	.29380	.000	.5681	2.3728
	6	.9933	.32647	.054	-.0094	1.9959
	7	1.2714*	.32647	.004	.2688	2.2741

Based on observed means.
The error term is Mean Square(Error) = .796.
*. The mean difference is significant at the 0.05 level.

OneWayFactor designations as follows: 1 = Lowellville silver maple, 2 = Lowellville sycamore, 3 = Struthers silver maple, 4 = Struthers sycamore, 5 = Girard silver maple, 6 = Girard sycamore, 7 = Kirwan silver maple, 8 = Kirwan sycamore.

Table 7. Post-hoc (Tukey) results for PCA2 for Site x Species interaction term from MANCOVA. OneWayFactor designations as follows: 1 = Lowellville silver maple, 2 = Lowellville sycamore, 3 = Struthers silver maple, 4 = Struthers sycamore, 5 = Girard silver maple, 6 = Girard sycamore, 7 = Kirwan silver maple, 8 = Kirwan sycamore.

Multiple Comparisons

Dependent Variable: PCA2

Tukey HSD

(I) OneWayFactor		Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	.7657*	.20096	.005	.1485	1.3829
	3	.3818	.25709	.814	-.4078	1.1713
	4	.2618	.30373	.989	-.6710	1.1946
	5	.3903	.21985	.638	-.2849	1.0655
	6	1.1927*	.25709	.000	.4032	1.9823
	7	.3299	.25709	.904	-.4597	1.1194
	8	2.1496*	.26892	.000	1.3237	2.9756
2	1	-.7657*	.20096	.005	-1.3829	-.1485
	3	-.3839	.24795	.780	-1.1454	.3776
	4	-.5039	.29603	.686	-1.4131	.4052
	5	-.3754	.20909	.624	-1.0175	.2668
	6	.4270	.24795	.673	-.3345	1.1885
	7	-.4358	.24795	.649	-1.1973	.3257
	8	1.3839*	.26020	.000	.5848	2.1831
3	1	-.3818	.25709	.814	-1.1713	.4078
	2	.3839	.24795	.780	-.3776	1.1454
	4	-.1200	.33666	1.000	-1.1540	.9140
	5	.0085	.26349	1.000	-.8007	.8178
	6	.8110	.29527	.117	-.0959	1.7178
	7	-.0519	.29527	1.000	-.9587	.8549
	8	1.7679*	.30564	.000	.8292	2.7065
4	1	-.2618	.30373	.989	-1.1946	.6710
	2	.5039	.29603	.686	-.4052	1.4131
	3	.1200	.33666	1.000	-.9140	1.1540
	5	.1285	.30916	1.000	-.8210	1.0780
	6	.9310	.33666	.111	-.1030	1.9649
	7	.0681	.33666	1.000	-.9659	1.1021
	8	1.8879*	.34579	.000	.8259	2.9499

5	1	-.3903	.21985	.638	-1.0655	.2849
	2	.3754	.20909	.624	-.2668	1.0175
	3	-.0085	.26349	1.000	-.8178	.8007
	4	-.1285	.30916	1.000	-1.0780	.8210
	6	.8024	.26349	.054	-.0068	1.6117
	7	-.0604	.26349	1.000	-.8697	.7488
	8	1.7593*	.27505	.000	.9146	2.6041
6	1	-1.1927*	.25709	.000	-1.9823	-.4032
	2	-.4270	.24795	.673	-1.1885	.3345
	3	-.8110	.29527	.117	-1.7178	.0959
	4	-.9310	.33666	.111	-1.9649	.1030
	5	-.8024	.26349	.054	-1.6117	.0068
	7	-.8629	.29527	.075	-1.7697	.0440
	8	.9569*	.30564	.042	.0182	1.8956
7	1	-.3299	.25709	.904	-1.1194	.4597
	2	.4358	.24795	.649	-.3257	1.1973
	3	.0519	.29527	1.000	-.8549	.9587
	4	-.0681	.33666	1.000	-1.1021	.9659
	5	.0604	.26349	1.000	-.7488	.8697
	6	.8629	.29527	.075	-.0440	1.7697
	8	1.8198*	.30564	.000	.8811	2.7584
8	1	-2.1496*	.26892	.000	-2.9756	-1.3237
	2	-1.3839*	.26020	.000	-2.1831	-.5848
	3	-1.7679*	.30564	.000	-2.7065	-.8292
	4	-1.8879*	.34579	.000	-2.9499	-.8259
	5	-1.7593*	.27505	.000	-2.6041	-.9146
	6	-.9569*	.30564	.042	-1.8956	-.0182
	7	-1.8198*	.30564	.000	-2.7584	-.8811

Based on observed means.
The error term is Mean Square(Error) = .697.
*. The mean difference is significant at the 0.05 level.

OneWayFactor designations as follows: 1 = Lowellville silver maple, 2 = Lowellville sycamore, 3 = Struthers silver maple, 4 = Struthers sycamore, 5 = Girard silver maple, 6 = Girard sycamore, 7 = Kirwan silver maple, 8 = Kirwan sycamore.

Table 8. Principle Components Analysis of 7 trace metals (i.e. NOT including environmentally conservative trace elements Ca, Mg, P, an S) from Mahoning River silver maple and sycamore tree core segments (total of 173 core segments). The sole PC axis represent 45.58% of data variance.

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.261	46.582	46.582	3.261	46.582	46.582
2	.977	13.951	60.533			
3	.857	12.241	72.773			
4	.727	10.388	83.161			
5	.456	6.509	89.670			
6	.402	5.741	95.411			
7	.321	4.589	100.000			

Extraction Method: Principal Component Analysis.

Table 9. “Loadings” of trace elements on PCA axis 1 (components). These are equivalent to correlation coefficients, and range from -1.0 to 1.0.

Component Matrix[a]

	Component
	1
Cd	.790
Cu	.795
Fe	.669
Mn	.472
Pb	.634
Sn	.759
Zn	.597

Extraction Method: Principal Component Analysis.

a. 1 components extracted.

Table 10. Results from two-factor ANCOVA of trace element Principle Components Analysis scores (PCA presented in Table 8).

Tests of Between-Subjects Effects

Dependent Variable: PCA1

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	30.217[a]	8	3.777	4.382	.000
Intercept	1.241	1	1.241	1.439	.232
Age	1.913	1	1.913	2.220	.138
Site	12.075	3	4.025	4.669	.004
Species	2.665	1	2.665	3.091	.081
Site * Species	14.188	3	4.729	5.486	.001
Error	138.783	161	.862		
Total	169.000	170			
Corrected Total	169.000	169			

a. R Squared = .179 (Adjusted R Squared = .138)

Table 11. .056. OneWayFactor designations as follows: 1 = Lowellville silver maple, 2 = Lowellville sycamore, 3 = Struthers silver maple, 4 = Struthers sycamore, 5 = Girard silver maple, 6 = Girard sycamore, 7 = Kirwan silver maple, 8 = Kirwan sycamore.

Multiple Comparisons

Dependent Variable: PCA1

Tukey HSD

					95% Confidence Interval	
(I) OneWayFactor		Mean Difference (I-J)	Std. Error	Sig.	Lower Bound	Upper Bound
1	2	.53890	.22424	.247	-.1497	1.2275
	3	1.17741*	.28687	.002	.2964	2.0584
	4	-.03955	.33892	1.000	-1.0804	1.0013
	5	1.02903*	.24532	.001	.2757	1.7824
	6	.96119*	.28687	.022	.0802	1.8422
	7	.69559	.28125	.215	-.1681	1.5593
	8	.43682	.30009	.829	-.4847	1.3584
2	1	-.53890	.22424	.247	-1.2275	.1497
	3	.63851	.27668	.296	-.2112	1.4882
	4	-.57846	.33033	.654	-1.5929	.4360
	5	.49013	.23331	.419	-.2264	1.2066
	6	.42229	.27668	.792	-.4274	1.2720
	7	.15669	.27085	.999	-.6751	.9884
	8	-.10209	.29035	1.000	-.9937	.7896
3	1	-1.17741*	.28687	.002	-2.0584	-.2964
	2	-.63851	.27668	.296	-1.4882	.2112
	4	-1.21696*	.37567	.031	-2.3706	-.0633
	5	-.14838	.29402	1.000	-1.0513	.7545
	6	-.21622	.32949	.998	-1.2281	.7956
	7	-.48182	.32461	.815	-1.4787	.5150
	8	-.74059	.34105	.375	-1.7880	.3068
4	1	.03955	.33892	1.000	-1.0013	1.0804
	2	.57846	.33033	.654	-.4360	1.5929
	3	1.21696*	.37567	.031	.0633	2.3706
	5	1.06858*	.34499	.046	.0091	2.1280
	6	1.00075	.37567	.142	-.1529	2.1544
	7	.73514	.37140	.499	-.4054	1.8757
	8	.47637	.38586	.920	-.7086	1.6613
5	1	-1.02903*	.24532	.001	-1.7824	-.2757

	2	-.49013	.23331	.419	-1.2066	.2264
	3	.14838	.29402	1.000	-.7545	1.0513
	4	-1.06858*	.34499	.046	-2.1280	-.0091
	6	-.06784	.29402	1.000	-.9708	.8351
	7	-.33344	.28854	.943	-1.2195	.5527
	8	-.59221	.30692	.533	-1.5348	.3503
6	1	-.96119*	.28687	.022	-1.8422	-.0802
	2	-.42229	.27668	.792	-1.2720	.4274
	3	.21622	.32949	.998	-.7956	1.2281
	4	-1.00075	.37567	.142	-2.1544	.1529
	5	.06784	.29402	1.000	-.8351	.9708
	7	-.26560	.32461	.992	-1.2625	.7312
	8	-.52438	.34105	.786	-1.5717	.5230
7	1	-.69559	.28125	.215	-1.5593	.1681
	2	-.15669	.27085	.999	-.9884	.6751
	3	.48182	.32461	.815	-.5150	1.4787
	4	-.73514	.37140	.499	-1.8757	.4054
	5	.33344	.28854	.943	-.5527	1.2195
	6	.26560	.32461	.992	-.7312	1.2625
	8	-.25877	.33634	.994	-1.2917	.7741
8	1	-.43682	.30009	.829	-1.3584	.4847
	2	.10209	.29035	1.000	-.7896	.9937
	3	.74059	.34105	.375	-.3068	1.7880
	4	-.47637	.38586	.920	-1.6613	.7086
	5	.59221	.30692	.533	-.3503	1.5348
	6	.52438	.34105	.786	-.5230	1.5717
	7	.25877	.33634	.994	-.7741	1.2917

*. The mean difference is significant at the 0.05 level.

OneWayFactor designations as follows: 1 = Lowellville silver maple, 2 = Lowellville sycamore, 3 = Struthers silver maple, 4 = Struthers sycamore, 5 = Girard silver maple, 6 = Girard sycamore, 7 = Kirwan silver maple, 8 = Kirwan sycamore.

DISCUSSION

Even though there was a reasonable expectation for metal concentrations in cores from riparian trees along the Lower Mahoning River to be linked to the spatial and temporal patterns of industrial legacies from the past, our results mostly suggested otherwise. In general, river site, and thus proximity to historical industrial facilities, did not significantly influence metal concentrations in the tree cores. This could reflect the possibility that the trees were not present at the sites closest to historical industrial facilities at the time they were actively discharging. For example, the historical photographs of the Struthers river segment (Figure 11) indicate an absence of trees at the sampling site early in the 20th century. Interestingly, Dickinson et al. (1991) studied sycamore maple (*Acer pseudoplatanus*) seedling survival at a heavily copper-contaminated (up to 4000 mg/kg dry weight in upper soil layers) site in the North of England, and reported a severe inhibition of their growth. (Note that this European tree is a different genus from the American sycamore, despite its similar common name.) Although there are no such data from the early-to-mid 20th century industrial era of the Mahoning River, it is possible that some river banks were too contaminated for the species studied in this thesis to have established at the time. Also, even at sites where we suspected trees actually dated to the industrial era, it was sometimes difficult to identify those oldest trees, or to obtain a long enough core when we did.

However, and despite such drawbacks, a number of interesting patterns did emerge from the research reported here. The Lowellville tree cores seemed to display higher non-dietary trace metal (e.g. cadmium and lead, which act as contaminants) concentrations compared to the other sites along the river. An interesting observation was made at this site. There is a small side creek entering the Mahoning River in which a boom had been placed ~100 m upstream, suggesting there may have been a recent spill or leakage from some sort of industrial source. This led to an interesting possibility that this side creek could influence trace metal concentrations in the trees along the Mahoning itself. More observations would be needed here to investigate this possibility.

The present study also suggested there may be trace element accumulation differences between the two species studied – silver maple and American sycamore. Sycamores displayed higher concentrations of dietary essential elements, but lower concentrations of the non-dietary metals than did silver maples.

Although dendroanalysis is a relatively recent application of biomonitoring, a growing number of quantitative studies have investigated spatial and temporal patterns of contaminant bioaccumulation by trees in relation to industrial sources (Watmouth et al. 1999, Watmouth and Hutchinson 2002, Madeiros 2008, Bilo et al. 2017, Jung and Ahn 2017). Most such studies have been done in Europe and Asia, with fewer conducted in eastern North America.

Observational studies of trace element bioaccumulation in trees have typically focused on either soil or atmospheric exposure pathways. Some have investigated both. Jung & Ahn (2017) have shown that the Japanese cedar trees (*Cryptomeria japonica*) can accumulate non-dietary metals when near industrial locations, apparently in contrast to the minimal amount of such evidence in the present thesis on the Mahoning River. In their study of a phosphate fertilizer plant in South Korea, mercury levels in tree rings and soil samples were elevated closer to the plant, but decreased gradually moving away from the site. Mercury concentrations in different aged core segments also indicated greater accumulation near the time of discharge. Although the uptake pathway to the trees was via soil contamination, the ultimate source of the mercury was atmospheric emissions (Jung & Ahn, 2017). Similarly, a study by Medeiros et al. (2008) in the State of Sao Paulo, Brazil, showed that lead was at highest concentrations in *Araucaria columnaris* (Chilean pine) tree rings during the 1980's when tetraethyl lead was commonly used as a gasoline additive. The results indicated that absorption of lead was via both the roots and leaves of the Chilean pine trees – i.e. exposure via both soil and the atmosphere.

In a study by Patrick & Farmer (2007) of sycamore maple throughout Scotland, lead concentrations and isotopic ratios near a local mine gave evidence that the trees were directly accumulating atmospheric lead through the bark, and possibly the leaves. Much as for soil/root accumulation trends reported above (Jung and Ang 2017, Madeiros 2008), bark and leaf accumulation from the atmosphere was greater nearer to lead sources (Patrick & Farmer, 2007). A similar observational study in England of sycamore maples adjacent to a metal refinery (Watmough & Hutchinson, 2002) suggested that the trees can accumulate lead through their foliage and bark, and subsequently can translocate metals within the tree. Lead concentrations in trees generally decreased after 1950, coinciding with a number of factors reducing lead emissions, such as the enactment of the Clean Air Act and the introduction of unleaded gas. (Watmough & Hutchinson, 2002). In Brazil, Locosselli et al. (2018) reported a temporal decrease in cadmium, copper, lead, and nickel in tree rings of *Tipuana tipu* (tipa trees) from the central region of São Paulo, which coincided with deindustrialization patterns and increasing efficiency of vehicles.

Some studies have been conducted on bioaccumulation strictly via absorption from the soil through the roots. In an experimental study by André et al. (2006), sycamore maples were grown in metal contaminated soils (lead, zinc, copper, cadmium), and were compared to trees growing in uncontaminated soils. Additionally, an observational study by Nkongolo et al. (2017) was conducted on nickel tolerance and exclusion in silver maples near Sudbury, Ontario, where nickel smelting has been a major industry for many decades. This study revealed that silver maple is tolerant to high doses of nickel, which it stores in its roots without translocating to other plant parts. Silver maple likewise was shown to exclude iron, manganese, zinc, and copper (Nkongolo et al. 2017).

In contrast to the findings of Dickinson et al. (1991) of severe seedling growth inhibition, Andre et al. (2006) found that sycamore maples were able to grow in contaminated soils in their study, but within which lead, cadmium, and copper were at concentrations ~5 – 10 times less than in the Dickinson et al. (1991) study. However, these soils were still quite highly contaminated, and trees displayed oxidative stress in older foliage, with necrotic spots and flecks next to the leaf veins (André et al. 2006).

Interestingly, Labidi et al. (2017), in an experimental study of several tree species in northern France, reported that trace metals were absorbed from the soil through the roots, but ultimately accumulated in the leaves. This seems to contrast with the findings of Nkongolo et al. (2017) that silver maples did not translocate contaminants from the roots to other plant parts. Black locust (*Robinia pseudoacacia L.*), black alder (*Alnus glutinosa L.*), sycamore maple (*Acer pseudoplatanus L.*), white willow (*Salix alba L.*) and pedunculate oak (*Quercus robur L.*) were planted near a former lead and zinc smelter. Subsequent trace metal concentrations (Cd, Zn and Pb) in leaves varied among species, with the highest levels in white willow (Labidi et al. 2017).

In the present study, I likewise observed interspecific differences in tree ring trace element concentrations from the same sites. Perhaps American sycamores along the Mahoning River may accumulate trace elements more in their leaves than in wood, as compared to silver maple. To test this hypothesis, leaf samples could be collected in the future from cored trees, and analyzed by ICP as for the wood samples. It is apparent that tree species can differ notably in their physiological responses to environmental contamination, so it is reasonable to suggest the same may be true of silver maple and American sycamore growing along the Mahoning River. Future research in this new field of dendroanalysis could clarify such trends.

Trees at different Mahoning River sites may also have been exposed to different amounts of the trace elements studied here, which I hypothesized at the beginning of the study may be a reflection of their industrial histories. As mentioned previously, silver maple cores from the Lowellville site yielded the highest concentrations of potential contaminant trace metals. Lowellville was formerly heavily industrialized itself, and is also located *downstream* from major discharges to the river (e.g. Youngstown Sheet & Tube, J&L Steel/Cold Metal Products, Sharon Steel's Lowellville Works), so there may be a greater cumulative exposure of trees here to contaminants. The interesting observation of a spill-capture boom on a side creek near Lowellville raises the possibility that trace element sources from tributaries may be more important than I initially anticipated, and could be studied in the future.

CONCLUSIONS

Interestingly, considering the long industrial legacy of the Mahoning River, metal concentrations in tree cores did not significantly reflect sampling sites, and thus proximity to historical manufacturing facilities. Several Lowellville trees did tend to display higher concentrations of non-dietary metals (e.g. cadmium and lead, which act as contaminants) than other sites along the river. As suggested earlier, this raised an interesting possibility that highly localized sources such as side creeks may influence trace metal availability within the Mahoning River riparian zone.

There also was no statistical evidence of temporal patterns of trace elements within cores. Difficulties in identifying trees dating to the industrial era and of extracting long enough cores pose a real but not insurmountable challenge to such research. Another potential confounding factor could be trace element translocation inside trees that might obscure detailed temporal patterns within cores. This factor likely varies among tree species, sampling locations, and elements targeted, and seems to be an inherent limitation of dendroanalysis that may be beyond the control of the researcher.

The present study definitely suggested trace element accumulation differences between the two species examined. Sycamores displayed higher concentrations of dietary essential elements, such as phosphorus, sulfur, and magnesium, but lower concentrations of the dietary-non-essential metals than did silver maples. These bioaccumulation differences between the two species could reflect unexplored physiological differences between them that might affect trace element dynamics.

An expansion of sampling sites should be considered in the future to further investigate accumulation of trace metals in trees along the Mahoning River. Ideally, one or more sites immediately adjacent to previous or active industrial facilities could provide tree cores with higher concentrations of contaminant metals. A site adjacent to Valourec Steel has already been identified, and future studies will be able to be conducted here.

Soil samples from the vicinity of cored trees, some of which have already been collected, can be analyzed in the future to determine if soil composition acts as a pathway for bio-accumulation of trace elements along the Mahoning. Also, as previously discussed, foliage and bark might be analyzed for trace element concentrations, as both can be sites of accumulation via atmospheric deposition.

Lastly, future work should be done on maintaining and updating the ICP apparatus, specifically installing a new camera, which could improve resolution and “method” detection limits. Additional cores may be required from trees to get more wood mass if detection limits still present an obstacle to evaluating non-essential metals. Also, if available, additional standard reference materials could be incorporated to enhance QA/QC in future studies.

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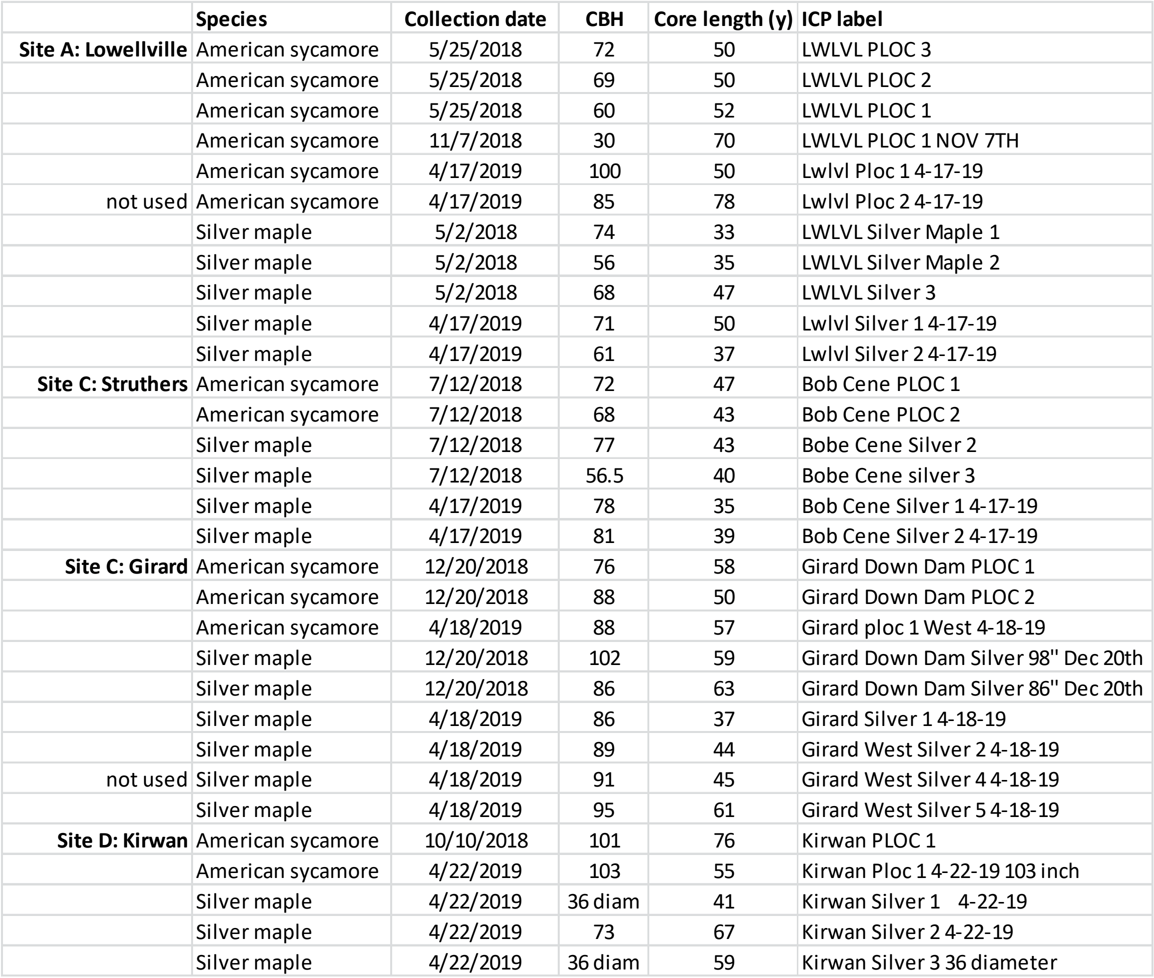
Appendix 1. Tree cores analyzed by ICP.



	Species	**Collection date**	**CBH**	**Core length (y)**	**ICP label**
Site A: Lowellville	American sycamore	5/25/2018	72	50	LWLVL PLOC 3
	American sycamore	5/25/2018	69	50	LWLVL PLOC 2
	American sycamore	5/25/2018	60	52	LWLVL PLOC 1
	American sycamore	11/7/2018	30	70	LWLVL PLOC 1 NOV 7TH
	American sycamore	4/17/2019	100	50	Lwlvl Ploc 1 4-17-19
not used	American sycamore	4/17/2019	85	78	Lwlvl Ploc 2 4-17-19
	Silver maple	5/2/2018	74	33	LWLVL Silver Maple 1
	Silver maple	5/2/2018	56	35	LWLVL Silver Maple 2
	Silver maple	5/2/2018	68	47	LWLVL Silver 3
	Silver maple	4/17/2019	71	50	Lwlvl Silver 1 4-17-19
	Silver maple	4/17/2019	61	37	Lwlvl Silver 2 4-17-19
Site C: Struthers	American sycamore	7/12/2018	72	47	Bob Cene PLOC 1
	American sycamore	7/12/2018	68	43	Bob Cene PLOC 2
	Silver maple	7/12/2018	77	43	Bobe Cene Silver 2
	Silver maple	7/12/2018	56.5	40	Bobe Cene silver 3
	Silver maple	4/17/2019	78	35	Bob Cene Silver 1 4-17-19
	Silver maple	4/17/2019	81	39	Bob Cene Silver 2 4-17-19
Site C: Girard	American sycamore	12/20/2018	76	58	Girard Down Dam PLOC 1
	American sycamore	12/20/2018	88	50	Girard Down Dam PLOC 2
	American sycamore	4/18/2019	88	57	Girard ploc 1 West 4-18-19
	Silver maple	12/20/2018	102	59	Girard Down Dam Silver 98" Dec 20th
	Silver maple	12/20/2018	86	63	Girard Down Dam Silver 86" Dec 20th
	Silver maple	4/18/2019	86	37	Girard Silver 1 4-18-19
	Silver maple	4/18/2019	89	44	Girard West Silver 2 4-18-19
not used	Silver maple	4/18/2019	91	45	Girard West Silver 4 4-18-19
	Silver maple	4/18/2019	95	61	Girard West Silver 5 4-18-19
Site D: Kirwan	American sycamore	10/10/2018	101	76	Kirwan PLOC 1
	American sycamore	4/22/2019	103	55	Kirwan Ploc 1 4-22-19 103 inch
	Silver maple	4/22/2019	36 diam	41	Kirwan Silver 1 4-22-19
	Silver maple	4/22/2019	73	67	Kirwan Silver 2 4-22-19
	Silver maple	4/22/2019	36 diam	59	Kirwan Silver 3 36 diameter

Appendix 2. Trace element concentrations used in analyses, by site, species, and core segment.

Site	Species	Age mid-point		Ca3179	Cd2265	Cu3247	Fe2598	Mg2802	Mn2576	P_1859	Pb2203	S_1820	Sn1899	Zn2138
A	American sycamore	5		1230.4	0.0122	2.3959	116.9	483.4	2.215	422.9	0.0467	121.3	0.0386	1.865
A	American sycamore	15		992.1	0.0146	1.3296	87.7	457.3	1.371	91.3	0.1440	139.2	0.0104	1.467
A	American sycamore	25		1069.4	0.0160	1.5194	36.0	452.2	0.845	119.1	0.0000	158.0	0.0439	2.008
A	American sycamore	35		1050.1	0.0209	1.8421	72.0	394.3	1.456	77.5	0.1548	196.4	0.0383	2.449
A	American sycamore	45		1154.4	0.0108	1.4039	96.1	216.1	1.449	19.2	0.0705	136.8	0.0174	1.863
A	American sycamore	2.5		427.5	0.3184	2.9453	102.6	132.7	2.090	559.7	0.3184	164.4	0.2189	13.463
A	American sycamore	7.5		757.2	0.0242	2.7522	155.4	263.0	3.632	573.2	0.0888	646.3	0.1937	62.107
A	American sycamore	17.5		581.2	0.0316	3.2628	94.6	144.9	2.808	165.2	0.1105	182.9	0.1990	9.545
A	American sycamore	22.5		592.8	0.0297	2.2212	121.0	111.7	2.779	166.8	0.3648	219.7	0.1097	12.085
A	American sycamore	27.5		675.1	0.0462	2.7091	122.6	105.2	2.277	154.9	0.1387	266.9	0.2042	14.173
A	American sycamore	32.5		585.6	0.0113	2.5310	120.8	79.8	2.185	96.6	0.0000	195.8	0.1580	8.176
A	American sycamore	37.5		877.7	0.0669	3.0900	371.0	171.2	3.236	104.3	1.0341	351.1	0.2981	12.743
A	American sycamore	42.5		1066.7	0.0292	4.5497	347.1	196.5	3.316	21.5	0.3801	312.0	0.2807	30.918
A	American sycamore	47.5		979.1	0.0232	2.7964	374.6	179.8	2.278	25.8	0.1328	233.0	0.1793	8.589
A	American sycamore	51		1107.0	0.0294	5.9200	415.6	229.5	2.563	16.8	0.3410	290.9	0.1529	12.322
A	American sycamore	2.5		864.8	0.0395	2.9960	366.4	554.5	2.636	825.3	0.1581	171.6	0.1383	15.360
A	American sycamore	7.5		1329.5	0.0684	2.2778	357.0	567.5	3.778	447.9	0.9957	303.3	0.2009	16.423
A	American sycamore	12.5		1260.2	0.0266	1.2015	295.9	303.4	3.037	157.4	0.1328	194.4	0.0929	12.237
A	American sycamore	17.5		1101.6	0.0353	1.8419	228.8	226.9	1.807	91.0	0.0928	1005.7	0.1458	160.203
A	American sycamore	22.5		776.9	0.0336	2.1194	277.6	210.4	1.716	71.3	0.2649	167.9	0.1493	15.690
A	American sycamore	27.5		922.1	0.0449	2.4038	465.6	257.1	2.371	55.1	0.2763	223.2	0.1157	10.153
A	American sycamore	32.5		912.1	0.0210	2.5729	319.5	218.0	1.846	21.5	0.0000	164.8	0.0420	10.580
A	American sycamore	37.5		354.5	0.0521	1.3799	125.7	72.8	0.643	6.4	0.2781	66.6	0.0070	10.626
A	American sycamore	42.5		1024.0	0.0244	3.4148	212.2	271.8	1.834	18.2	0.1385	168.6	0.0570	14.389
A	American sycamore	47.5		1174.3	0.0205	5.8713	304.8	359.1	2.099	18.3	0.0000	270.4	0.1886	23.506
A	American sycamore	2.5		1283.9	0.0711	4.4028	1824.6	332.7	8.081	305.2	0.6114	95.7	0.1137	23.972
A	American sycamore	7.5		1321.3	0.0713	5.3387	1581.1	233.3	10.428	151.6	0.4768	115.6	0.0267	23.200
A	American sycamore	12.5		1217.3	0.0649	4.7135	1010.3	190.7	6.778	101.7	0.4324	133.8	0.0919	27.254
A	American sycamore	17.5		932.6	0.0457	6.2229	590.3	107.1	3.457	64.3	0.4400	118.5	0.1086	28.960
A	American sycamore	22.5		1354.7	0.0541	4.7905	630.1	145.3	3.480	76.3	0.3919	152.9	0.0000	34.905
A	American sycamore	32.5		1033.2	0.0385	5.5577	363.7	117.5	2.514	60.0	0.3125	172.8	0.0096	28.990
A	American sycamore	42.5		1146.9	0.0300	3.6336	628.4	192.5	3.931	39.7	0.2512	134.3	0.0519	6.508
A	American sycamore	47.5		1049.2	0.0347	1.7861	563.4	176.3	3.027	35.7	0.3037	128.0	0.0165	4.561
A	American sycamore	5		3203.6	0.0124	3.0966	263.7	330.5	3.452	408.0	0.1156	260.2	0.2023	4.310
A	American sycamore	15		669.6	0.0174	3.4086	245.1	187.2	2.778	83.3	0.1968	154.6	0.1389	2.616
A	American sycamore	25		747.3	0.0235	2.3153	234.0	161.3	3.002	45.0	0.0800	191.8	0.2588	2.028
A	American sycamore	35		514.2	0.0127	2.2062	166.8	127.2	1.723	24.8	0.1146	137.2	0.1061	1.383
A	American sycamore	45		766.1	0.0327	1.6962	310.9	228.2	2.881	19.8	0.1749	275.7	0.0576	2.512
A	American sycamore	55		632.3	0.0225	2.7884	190.9	131.5	1.190	13.6	0.1697	113.8	0.0675	1.349
A	American sycamore	65		1101.4	0.0600	3.7722	524.7	226.0	2.227	17.3	0.1352	210.7	0.0498	1.902
A	Silver maple	5		737.8	0.0097	3.8499	92.3	142.2	4.376	258.8	0.0000	77.0	0.0000	5.497
A	Silver maple	15		1049.6	0.0304	1.4037	34.8	132.5	4.149	77.2	0.0000	29.5	0.0304	5.112
A	Silver maple	25		483.3	0.0115	0.8530	28.0	59.8	1.716	24.6	0.0645	16.0	0.0299	3.268
A	Silver maple	35		838.7	0.0173	0.5912	46.6	95.8	2.794	25.0	0.0272	23.1	0.0236	5.061
A	Silver maple	45		749.2	0.0216	2.6699	33.4	77.9	2.470	25.0	0.0000	43.1	0.0270	7.001
A	Silver maple	5		591.3	0.0191	1.3282	53.3	141.5	2.553	147.3	0.0000	25.1	0.0339	1.598
A	Silver maple	15		703.6	0.0269	1.0387	55.4	120.0	2.878	102.8	0.0000	30.3	0.0051	2.628
A	Silver maple	25		745.9	0.0314	1.4998	69.8	104.0	3.035	82.7	0.2283	22.0	0.0524	3.574
A	Silver maple	33.5		749.3	0.0277	1.3436	68.4	113.4	3.313	48.6	0.0000	17.6	0.0179	3.531
A	Silver maple	2.5		327.9	0.1660	1.9923	1275.0	50.1	4.292	127.2	0.1854	68.6	0.2269	4.917
A	Silver maple	7.5		637.4	0.0906	3.5702	758.3	76.9	4.601	80.9	0.2055	105.8	0.1881	8.830
A	Silver maple	12.5		623.6	0.0658	1.4004	291.9	58.5	2.680	64.7	0.5765	101.0	0.1132	11.071
A	Silver maple	17.5		615.2	0.0863	2.6987	170.5	54.8	2.375	51.7	0.0996	594.2	0.0686	66.881
A	Silver maple	22.5		610.1	0.0753	1.7906	200.9	51.8	2.412	48.4	0.2565	79.1	0.1365	15.911
A	Silver maple	27.5		566.0	0.0842	1.6461	432.5	56.3	2.867	38.8	0.1112	94.8	0.0541	18.566
A	Silver maple	31.5		533.0	0.0688	1.4682	316.7	54.6	2.334	36.6	0.0718	77.0	0.0314	9.795

Site	Species	Age mid-point		Ca3179	Cd2265	Cu3247	Fe2598	Mg2802	Mn2576	P_1859	Pb2203	S_1820	Sn1899	Zn2138
A	Silver maple	2.5		956.0	0.1206	8.6193	1423.6	154.0	5.214	247.9	1.1260	278.2	0.6568	10.161
A	Silver maple	7.5		1105.0	0.1072	7.9491	490.3	166.5	4.772	120.0	0.1206	293.2	0.3485	10.804
A	Silver maple	12.5		2182.3	0.1206	9.0080	831.9	337.4	13.271	360.9	3.2306	397.2	0.2547	21.971
A	Silver maple	17.5		2951.7	0.2547	8.7534	613.3	415.7	15.483	389.8	1.0724	457.5	0.4826	35.362
A	Silver maple	22.5		3424.9	0.2949	11.1394	1253.4	503.9	20.174	416.9	0.0402	598.0	0.7507	50.201
A	Silver maple	27.5		2465.1	0.1877	14.1421	617.6	374.5	16.180	138.1	0.7775	423.1	0.5496	32.105
A	Silver maple	32.5		3195.7	0.3351	8.8740	872.9	481.9	21.702	207.1	1.5684	486.1	0.4155	38.753
A	Silver maple	2.5		691.3	0.0393	1.0307	201.4	117.9	4.005	211.2	0.0000	147.0	0.2360	42.502
A	Silver maple	7.5		725.7	0.0393	2.8379	253.3	116.9	5.519	131.2	0.1907	138.1	0.1122	32.524
A	Silver maple	12.5		640.5	0.0000	4.1924	155.3	76.1	3.195	67.7	0.0000	156.9	0.1412	38.429
A	Silver maple	17.5		633.0	0.0000	2.6945	157.8	73.8	3.153	71.0	0.0697	106.6	0.1278	28.873
A	Silver maple	22.5		1216.1	0.1839	4.3423	180.8	122.6	5.177	94.7	0.5799	233.2	0.7214	84.371
A	Silver maple	27.5		1041.9	0.0111	0.6423	188.9	109.6	4.972	79.4	0.0000	158.4	0.2326	57.386
A	Silver maple	37.5		620.1	0.0321	2.4342	114.3	69.9	4.441	37.0	0.0000	64.7	0.1156	19.573
A	Silver maple	42.5		456.6	0.0178	0.8990	81.1	56.9	1.729	36.0	0.0218	46.9	0.0475	15.578
A	Silver maple	46		682.1	0.0375	0.9178	151.1	93.7	2.930	55.3	0.1284	69.1	0.1151	24.766
B	American sycamore	5		1418.9	0.0709	6.1442	879.9	534.8	11.772	477.7	0.6169	140.6	0.0459	25.565
B	American sycamore	15		2008.3	0.0413	3.1244	579.7	424.4	7.950	159.7	0.3996	142.3	0.1309	20.107
B	American sycamore	25		1765.2	0.0599	3.6415	611.9	300.0	7.752	48.7	0.7549	145.9	0.0200	18.181
B	American sycamore	35		1517.1	0.0741	4.7577	791.4	398.8	13.460	56.3	0.2222	170.5	0.0262	11.582
B	American sycamore	41.5		851.5	0.0957	5.6689	819.1	272.0	6.292	33.6	0.0991	103.5	0.0222	7.581
B	American sycamore	5		765.4	0.0458	7.5985	1411.5	323.8	9.977	575.6	0.3529	160.7	0.0550	21.604
B	American sycamore	15		779.5	0.0356	3.7068	884.8	243.3	7.913	192.6	0.2027	155.3	0.0401	12.152
B	American sycamore	25		616.9	0.0320	3.8262	825.7	225.8	7.361	59.3	0.2128	194.0	0.0240	9.054
B	American sycamore	35		647.8	0.0257	4.2060	708.4	194.4	6.786	48.6	0.1454	162.4	0.0122	7.437
B	American sycamore	43.5		846.2	0.0211	6.9153	536.9	307.8	5.607	22.3	0.1285	153.6	0.0021	10.457
B	Silver maple	5		813.1	0.0349	1.4526	104.5	175.8	5.004	152.0	0.0134	37.8	0.0188	4.633
B	Silver maple	15		860.1	0.0534	1.1287	52.7	112.6	6.373	66.5	0.0865	34.0	0.0000	6.073
B	Silver maple	25		891.9	0.0388	0.8210	58.9	94.7	7.794	47.0	0.1932	30.4	0.0473	6.849
B	Silver maple	32.5		187.0	0.0082	0.1416	9.8	19.3	1.396	3.5	0.0057	5.3	0.0065	1.322
B	Silver maple	5		726.4	0.0916	2.9853	58.4	138.8	17.894	183.2	0.3571	108.2	0.0641	8.269
B	Silver maple	15		845.1	0.0352	0.8601	32.3	119.4	7.926	62.7	0.0000	35.4	0.0220	4.520
B	Silver maple	25		692.9	0.0230	0.8462	26.0	96.4	2.510	55.1	0.1228	23.2	0.0000	5.173
B	Silver maple	34.5		797.3	0.0316	0.7070	89.7	102.5	4.667	55.9	0.0323	26.5	0.0191	4.926
B	Silver maple	5		680.0	0.0587	3.0211	273.3	106.0	12.196	113.2	0.1334	48.1	0.0160	5.255
B	Silver maple	15		692.1	0.0466	0.9245	119.6	115.8	9.444	70.7	0.0992	36.3	0.0616	5.301
B	Silver maple	25		742.4	0.0381	1.3508	72.4	97.0	6.337	56.0	0.1389	40.5	0.0545	6.944
B	Silver maple	35		1098.4	0.0660	1.2273	134.9	119.5	5.548	47.4	0.0387	39.2	0.0290	7.508
B	Silver maple	15		291.7	0.0250	2.3642	158.9	37.5	4.321	48.9	0.2000	26.3	0.0000	2.426
B	Silver maple	25		204.9	0.0151	1.1004	115.9	23.0	3.033	25.7	0.0904	18.9	0.0241	2.085
B	Silver maple	35		548.8	0.0364	1.7036	379.6	61.4	5.438	41.6	0.0785	29.8	0.0032	5.580
B	Silver maple	41.5		337.0	0.0281	2.1186	208.8	40.9	2.016	23.6	0.2153	30.0	0.0187	2.459
C	American sycamore	5		1147.8	0.0779	5.5051	69.0	613.4	2.138	1076.8	0.3895	199.5	0.1385	5.938
C	American sycamore	15		5915.2	0.0161	2.2320	42.2	645.3	2.926	286.5	0.1302	201.7	0.0836	2.314
C	American sycamore	25		645.3	0.0043	1.4242	35.4	234.7	1.106	56.7	0.1152	193.6	0.0000	2.368
C	American sycamore	35		1671.2	0.0140	3.5680	58.5	219.0	1.854	108.5	0.4123	201.4	0.0365	4.530
C	American sycamore	45		827.6	0.1113	3.0936	46.4	213.9	1.339	84.1	0.1745	246.9	0.0000	3.587
C	American sycamore	53.5		1114.8	0.0081	2.6462	109.7	253.4	1.582	31.1	0.2587	246.6	0.1213	2.781
C	American sycamore	5		418.6	0.0350	2.8272	267.2	116.0	2.375	178.1	0.2572	85.5	0.0475	2.473
C	American sycamore	25		621.7	0.0250	2.4698	351.0	144.7	2.604	79.8	0.2140	171.1	0.0182	3.606
C	American sycamore	35		447.2	0.0585	2.7714	287.3	115.1	2.008	49.5	0.1756	118.1	0.0527	2.608
C	American sycamore	45		788.7	0.0187	1.8992	301.5	163.2	2.175	42.3	0.3753	162.6	0.0187	2.339
C	American sycamore	54		1175.8	0.0262	2.3688	420.6	236.2	2.791	29.4	0.2433	227.6	0.0286	3.170
C	American sycamore	5		977.5	0.0309	3.8422	642.8	272.4	4.607	362.4	0.2019	109.0	0.0000	4.164
C	American sycamore	15		737.0	0.0200	2.9097	269.0	234.0	2.599	74.6	0.9647	92.4	0.0399	3.817
C	American sycamore	25		3620.6	0.0148	3.1546	251.1	286.1	2.341	64.4	0.2385	182.4	0.0111	3.180
C	American sycamore	35		744.9	0.0252	1.9518	366.5	219.3	2.346	79.2	0.1616	165.8	0.0139	3.357
C	American sycamore	45		693.3	0.0395	1.8231	154.7	129.8	1.159	34.9	0.0906	151.7	0.0527	4.733

Site	Species	Age mid-point		Ca3179	Cd2265	Cu3247	Fe2598	Mg2802	Mn2576	P_1859	Pb2203	S_1820	Sn1899	Zn2138
C	Silver maple	5		599.4	0.0339	44.6132	77.3	171.4	3.012	266.0	3.1624	50.0	0.1751	29.605
C	Silver maple	15		615.8	0.0129	1.0624	23.7	93.5	2.556	136.5	0.0821	41.5	0.0228	6.003
C	Silver maple	25		736.0	0.0229	2.8869	28.8	86.5	3.572	57.9	0.0535	37.4	0.0699	7.941
C	Silver maple	33.5		796.6	0.0210	1.1782	56.7	97.4	4.722	43.4	0.0026	38.1	0.0341	5.977
C	Silver maple	5		638.0	0.0367	1.5855	37.4	173.5	2.545	134.1	0.0000	32.8	0.0355	4.805
C	Silver maple	15		738.2	0.0323	1.3325	54.4	187.4	2.397	73.9	0.1267	29.4	0.0000	4.806
C	Silver maple	25		795.4	0.0234	1.1184	59.4	152.6	2.320	54.5	0.0640	35.5	0.0328	5.317
C	Silver maple	35		853.7	0.0329	1.4895	79.1	118.1	3.045	45.5	0.1283	29.9	0.0000	5.476
C	Silver maple	42		975.0	0.0742	1.8242	384.1	152.6	4.473	42.4	0.1703	36.3	0.0769	5.525
C	Silver maple	5		614.2	0.0590	2.6475	105.8	153.3	4.867	245.9	0.0221	87.7	0.0442	5.428
C	Silver maple	15		610.1	0.0321	1.4965	40.4	114.1	3.570	97.6	0.4035	57.9	0.0454	5.283
C	Silver maple	25		326.2	0.0168	0.7941	20.6	44.0	2.046	30.8	0.0318	22.9	0.0354	4.312
C	Silver maple	35		729.7	0.0177	2.2603	31.6	90.2	4.613	46.8	1.1001	46.8	0.0743	8.019
C	Silver maple	45		847.9	0.0312	1.1799	28.2	87.5	4.510	21.5	0.1105	29.5	0.0132	7.575
C	Silver maple	55.5		946.7	0.0334	1.2134	41.9	110.5	3.782	20.6	0.0000	34.1	0.0350	7.834
C	Silver maple	5		455.1	0.0387	3.3959	257.8	150.3	5.224	266.4	0.2430	75.5	0.1712	5.897
C	Silver maple	15		328.8	0.0073	3.7856	149.6	73.0	3.501	75.1	0.1459	63.8	0.3136	2.954
C	Silver maple	25		474.0	0.0456	1.2361	149.4	69.9	4.219	59.6	0.2629	54.4	0.0456	5.264
C	Silver maple	35		333.2	0.0252	0.9689	130.4	45.8	2.907	39.4	0.1624	45.8	0.0840	3.601
C	Silver maple	45		510.0	0.0626	1.6149	77.1	66.0	7.735	18.1	0.1396	49.8	0.0481	4.284
C	Silver maple	55		457.0	0.0886	1.1035	67.7	56.2	13.494	13.3	0.2459	36.4	0.0313	4.075
C	Silver maple	61.5		430.7	0.0540	2.9671	261.6	56.7	12.323	12.2	0.0000	51.8	0.1306	2.359
C	Silver maple	5		567.0	0.0373	4.9099	379.9	158.4	6.010	388.1	0.1802	104.7	0.2672	6.333
C	Silver maple	15		474.3	0.0260	2.5736	181.0	82.3	4.896	165.8	0.0721	71.1	0.1356	6.241
C	Silver maple	25		512.8	0.0420	1.5001	262.9	76.7	5.462	104.5	0.0187	90.7	0.0684	7.894
C	Silver maple	35		570.6	0.0464	1.1238	260.5	97.8	6.789	83.7	0.0000	73.1	0.0890	7.820
C	Silver maple	45		568.1	0.0508	2.4567	271.1	89.5	6.611	62.4	0.0747	64.6	0.0448	8.751
C	Silver maple	54.5		645.3	0.0613	1.2601	242.7	108.9	5.554	78.3	0.0911	115.4	0.0824	7.964
D	American sycamore	5		3566.1	0.0000	0.0000	86.0	573.3	3.749	1005.6	0.0000	1138.7	0.2437	4.817
D	American sycamore	15		2160.4	0.0504	0.0000	55.3	381.0	3.223	398.3	0.0000	60.9	0.0576	2.453
D	American sycamore	25		1666.7	0.0745	0.0000	58.8	355.0	2.897	167.7	0.6603	70.6	0.0000	2.737
D	American sycamore	35		1835.8	0.0150	0.0000	55.7	353.2	2.708	70.3	0.4505	99.9	0.1902	2.543
D	American sycamore	45		1598.6	0.0053	0.8844	51.6	324.6	2.387	65.9	0.0000	136.7	0.0000	4.388
D	American sycamore	52.5		9767.1	0.1087	0.8851	505.9	1075.9	12.422	275.2	0.5590	598.3	0.5901	24.177
D	American sycamore	5		1045.7	0.0360	1.7523	422.5	390.0	4.697	497.6	0.0000	219.7	0.2107	35.334
D	American sycamore	15		1508.7	0.0411	4.0853	421.4	521.6	6.264	290.3	0.0719	271.3	0.0976	35.031
D	American sycamore	25		1069.9	0.0257	1.6701	203.5	316.8	3.587	125.6	0.0000	271.8	0.1850	35.010
D	American sycamore	35		2271.3	0.0206	4.5529	427.5	633.6	9.039	278.0	0.2210	649.5	0.1439	39.872
D	American sycamore	45		1385.9	0.0154	1.9527	402.4	288.3	6.161	121.0	0.1182	356.5	0.1387	34.399
D	American sycamore	55		838.6	0.0206	1.2744	166.0	145.7	3.212	57.3	0.4368	257.8	0.2775	36.192
D	American sycamore	65		2730.7	0.0719	6.0432	980.0	507.9	11.881	114.9	0.0360	668.0	0.2569	43.145
D	American sycamore	73		1653.1	0.0514	2.7030	612.5	295.7	6.079	40.7	0.1182	477.1	0.1696	33.900
D	Silver maple	5		736.5	0.0742	7.8245	137.8	191.2	16.749	264.9	0.0000	5.5	0.2349	3.350
D	Silver maple	15		13268.1	0.0815	14.1320	137.6	2749.0	45.599	113.3	0.3749	1500.4	0.1548	7.954
D	Silver maple	25		1499.1	0.0506	2.8151	78.5	163.7	38.583	81.0	0.0000	30.3	0.1518	5.087
D	Silver maple	35		1074.6	0.0547	1.8796	134.1	162.5	17.890	68.5	0.5885	32.7	0.1095	7.032
D	Silver maple	45		1276.1	0.0493	1.2203	105.4	178.9	14.923	54.4	0.0057	33.7	0.0133	6.286
D	Silver maple	55		3248.3	0.0620	2.1569	60.8	587.4	18.483	49.0	0.1110	284.3	0.0360	8.254
D	Silver maple	63.5		1202.2	0.0373	0.7209	53.3	159.1	12.648	43.5	0.1119	34.7	0.0478	4.848
D	Silver maple	5		450.6	0.0371	0.0000	102.5	127.8	10.614	184.0	0.3748	30.3	0.0453	2.780
D	Silver maple	15		462.8	0.0390	0.0000	21.7	99.0	10.267	89.7	0.0694	22.7	0.0976	3.368
D	Silver maple	25		550.3	0.0495	0.0000	36.6	107.1	13.252	68.7	0.0000	22.3	0.0797	3.917
D	Silver maple	35		859.9	0.0351	0.4523	30.4	113.2	17.816	64.2	0.2195	26.4	0.1054	4.259
D	Silver maple	45		614.3	0.0418	0.2635	24.2	96.9	8.950	51.9	0.0274	24.9	0.1310	4.911
D	Silver maple	54.5		582.5	0.0313	0.3253	40.5	79.2	5.520	47.6	0.0127	22.4	0.0733	4.719
D	Silver maple	5		429.8	0.0249	0.0000	64.3	104.6	10.154	130.6	0.0748	22.5	0.2993	3.599
D	Silver maple	15		433.0	0.0194	0.0000	22.3	85.8	12.768	75.3	0.0552	21.5	0.0701	3.758
D	Silver maple	25		451.8	0.0464	0.7491	19.1	93.3	13.708	69.8	0.2675	24.8	0.1641	5.950
D	Silver maple	35.5		544.3	0.0512	0.6276	23.2	96.5	15.726	61.3	0.0892	22.7	0.0541	6.704