RECONSTRUCTING PITTSBURGH'S POLLUTION HISTORY WITH DENDROCHEMISTRY: AN ANALYSIS OF TRACE METAL CONCENTRATIONS IN A SCHENLEY PARK RED OAK TREE

by

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The city of Pittsburgh, Pennsylvania has a rich history of industrial activity, particularly steel manufacturing. This, combined with other urban waste, leaves a legacy of environmental pollution across the landscape. This study compares trace metal concentration data from a Pittsburgh tree to local and national industrial production records and local climatic data. Trace metal concentrations (lead, copper, cadmium, zinc, and nickel) in the annual growth rings of a red oak tree (*Quercus rubra*) from Schenley Park in Pittsburgh were measured. This metal record was used to explore the consequences of pollution over the 126 year life of this tree (1881-2006). Trace metals and wet deposition sulfate concentrations are related (r^2 range of 0.0631 and 0.3458) as are national steel production and regional wet deposition sulfate concentrations ($r^2 = 0.7670$). However, these relationships break down in the 1990s as trace metal concentrations in the tree rings continue to increase and pollution inputs decrease. One potential explanation is the increasing dominance of vehicular traffic in urban systems. Nitrate emissions from vehicles could increase soil acidity and metal bioavailability, facilitating metal uptake by plants. This suggests that Pittsburgh pollution legacy issues should be a continued concern as increased trace metal availability will impact both urban ecosystems and human populations.

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PREFACE

This project would not have been possible without the generosity of an esteemed group of individuals, departments, and organizations. First and foremost, I would like to thank my advisor Dr. Daniel Bain who, through bad times and good times, has patiently and enthusiastically helped me with this project over the course of the last three years. I would also like to thank my thesis committee members: Mr. Mark Collins, Dr. Mark Abbott, and Dr. Geoffrey Buckley. I appreciate all of the time you took out of your busy schedules to sit on my thesis committee. A number of individuals also provided great assistance during my research, including the knowledgeable librarians of the University of Pittsburgh library system, Marion Sikora, Justin Hynicka, Amy Wolfe, and my family: thank you all. Furthermore, this project would not have been possible without the donation of tree material by Mr. Phil Gruszka and Mr. Jake Milofsky of the Pittsburgh Parks Conservancy, or the financial support of the University of Pittsburgh's Honors College and Office of Experiential Learning.

1.0 INTRODUCTION

Environmental science has tended to overlook urban areas in favor of less human-impacted, natural systems as urban areas systems were not considered useful for understanding “natural” processes. However, a majority of our population, and our pollution, is centralized in urban areas requiring a recognition and re-evaluation of this bias (McDonnell and Pickett 1990; Niemelä 1993; Pickett, Cadenasso et al. 2008). Further, understanding urban locations over long time periods is essential as human impacts accumulate. A historical approach is not heavily utilized in urban ecology research, which tends to target more visible ecological characteristics such as invasive species introduction, habitat destruction, and point source pollution (McDonnell and Pickett 1993). These studies tend to approach environmental pollution using a gradient framework over short time spans. National environmental awareness and pollution regulation, and changing American urban culture, including increases in green space development and vehicle miles traveled, have all occurred in the last century and affect pollution emissions. Short-term gradient studies offer important comparative data, but cannot address the origin of legacy pollution and its persistent impacts. Therefore, it is important to study urban ecosystems for extended temporal periods, as historical changes may continue to affect these systems today.

This study synthesizes industrial production records, climate data, and local environmental legislation and pollution events to reconstruct Pittsburgh’s pollution history.

Recent redevelopment in Pittsburgh, an iconic industrial city, includes urban ecosystem restoration projects, urban farming, and brownfield development. Pittsburgh is emerging with proportionally high urban green space, including extensive waterways and parks. Pittsburgh and other industrial cities can only continue to move forward when legacy pollution is considered in revitalization efforts, be it through bioremediation or other means. This is difficult to accomplish without accurate accounting of historical pollution. This study clarifies our understanding of Pittsburgh's pollution history through examination of a tree ring metal contamination record. The tree ring record dates back to 1881, covering a period of significant change in Pittsburgh including, periods of wonton pollution, local and national moves to regulation, and the near-total collapse of the local industrial base in the mid-1970s-early 1980s.

This study uses reconstructed pollution data to analyze interactions among biota and pollution through time. Pollution concentration data reconstructed from a Pittsburgh tree are compared to temporal records of possible source pollutants including industrial production, coal combustion, household energy usage, and transportation sources. Multiple archival records were collected and centralized for a more detailed depiction of local pollution. Trace metal content in annual tree rings are then compared to archival data. Metal analysis is focused on five trace metals: zinc (Zn), cadmium (Cd), copper (Cu), lead (Pb), and nickel (Ni), metals associated with industrial, and transportation emissions (Shaw 1990; Mielke, Gonzales et al. 2000; Mahler, Van Metre et al. 2006). Archival and metal data resulted in a timeline of pollution history and allow exploration of relationships between pollution sources and metal uptake trends in tree rings over more than a century of Pittsburgh history. It is important to note that pollution sources and metal data may not be as closely related as assumed: although a great deal of historical events are accounted for in this study, it is unrealistic to assume that all metal polluting sources are included.

1.1 BACKGROUND

Pittsburgh was the epicenter of American steel manufacturing from the beginning of the steel era in the mid-1800s. The 1880 U.S. Census states that there were fourteen steel mills in the United States during 1850; thirteen of which were in Pennsylvania. These mills produced a total of 6,078 net tons of steel that year. Steel manufacturing though did not occur on a large scale in the United States until the construction of the first Bessemer Converter in 1864 near Detroit, Michigan. National steel production increased drastically from 1870 (42,000 net tons) to 1880 (1,203,173 net tons) with the Bessemer Converter (Hall 1997). Writer James Parton infamously captured Pittsburgh during the rise of this steel era in 1866:

> The entire space lying between the hills was filled with blackest smoke, from out of which the hidden chimneys sent forth tongues of flame, while from the depths of the abyss, came up the noise of hundreds of steam-hammers. There would be moments when no flames were visible; but soon the wind would force the smoky curtains aside, and the whole black expanse would be dimly lighted with dull wreaths of fire... if anyone would enjoy a spectacle as striking as Niagara, he may do so by simply walking up a long hill to Cliff Street in Pittsburg, and looking over into -- hell with the lid taken off.

This landscape and midday darkness continues to haunt Pittsburgh even as industry is becoming local history. The processes surrounding steel manufacturing and the urban development it fueled in Pittsburgh are discussed in the following sections to provide background for subsequent trace metal analysis.

1.1.1 Fuel Sources

Fuel combustion is a major source of trace metal pollution emissions. Fuels are fundamental as they power our industries, homes, and vehicles. Most fuel combustion releases metal particulates to our environmental systems.

Charcoal was the predominant fuel source for steel and iron production in the United States through 1840, but was replaced by coal in the 1860s and 1870s. The introduction of hot air blast furnace technology and the depletion of wood resources both contributed to this transition. The introduction of heated air in blast furnaces in 1828 allowed use of coal fuel in the iron and steel industries, previously precluded by energy limitations caused by coal combustion with cold air. Anthracite coal was the predominant coal used until 1875 when bituminous coal and coke became the main fuels in the steel production process (Hogan 1971). Iron and steel manufacturing became centralized in the Pittsburgh region due to its abundant bituminous coal deposits. The large Connellsville bituminous coal seam, part of the larger Pittsburgh coal seam, produced high quality coke due to its high carbon and low impurity and sulfur content. Coal from this seam was cheaply transported from mines to the mills and coke ovens in and around Pittsburgh on existing river transport infrastructure. Meanwhile, charcoal became increasingly expensive as local forests were consumed. Ultimately, building the mills near the coal resources and water transport centralized industrial activity and its emissions within the city of Pittsburgh (Tarr and Muller 2003).

Local Pittsburgh natural gas reserves were discovered in 1878 and were utilized as a fuel until 1892. These natural gas resources supplied the Pittsburgh steel and glass manufacturers as well as some households and improved Pittsburgh’s poor air quality during that period (Tarr

1980). However, this local natural gas reserve was quickly depleted, causing many industries to switch back to bituminous coal fuel until after World War II. Household fuel usage also increased with population as individual uses are multiplied by this growth. Pittsburgh population density increased from the 1880s until 1920, when it reached its peak (Figure 1). Pittsburgh had a relatively stable population density between 1930 and 1950, but has been decreasing since due to suburbanization and declines in industrial production.

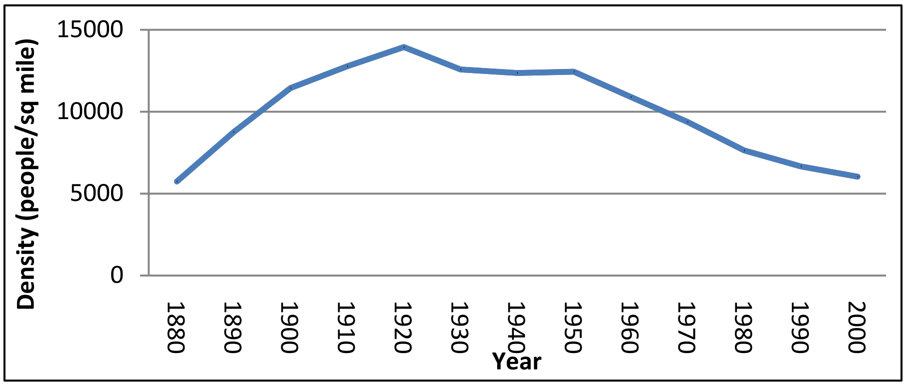

Figure 1. Pittsburgh population density (people per square mile) from census years 1880 to 2000.

1.1.2 Transportation Sources

It is important not to just consider what type of fuels are being utilized, but what forms of transportation are present and at what levels. For example, cars do not simply emit exhaust. They also generate toxic metal-laden dust from brake and other part wear. It is assumed that as vehicular use increases, trace metal emissions from these sources increase as well. For this reason, considering patterns of vehicular use is essential in assessing patterns of trace metal emissions and plant uptake in this study.

The mining and manufacturing industries heavily utilized local water and train transportation networks from the beginning of the industry's establishment around Pittsburgh. This land-use pattern concentrated industry, and its pollution, around the city of Pittsburgh (Tarr and Muller 2003; Longhurst 2005). Coal combustion in the transportation sector increased with the gradual replacement of horse-drawn carriages by electric streetcars in the 1890s. Gasoline fueled automobiles followed in the early 1900s. Vehicular pollution was exacerbated with the introduction of leaded gasoline as an antiknock agent in 1924. Leaded gasoline was used in the United States until it was phased out between 1976 and 1986 (Table 1). The interstate highway system was begun under President Eisenhower with the passing of the National Interstate and Defense Highways Act of 1956, which led to increased connectivity across the country and catalyzed suburbanization and sprawl development. Vehicle ownership in the United States increased to 70% of families in the 1950s (Hall 1997). Vehicular usage has continued to increase: the total vehicle miles traveled in the United States increased by 178 percent between 1970 and 2005 (EPA 2000).

1.1.3 Manufacturing Technology

Steel is a metal alloy, predominantly iron with a carbon content below two percent combined with small amounts of strengthening metals such as nickel, chromium, and vanadium (Hall 1997). Steels can have anti-corrosive (galvanized) coatings, which are mainly made of zinc with either iron or aluminum. Steel is manufactured from iron ore and/or scrap iron and steel. Iron ores are refined with blast furnace technology to remove impurities before steel production. Blast furnace technology allowed manufacturers to replace charcoal with anthracite and bituminous coal and produce purer and stronger iron products. These furnaces are named for the hot oxygen that blasted through the furnaces to ignite the coke fuel. Iron ores (or sinter, which is a combination of crushed iron ore, coke, and limestone) were placed in blast furnaces and, in the presence of the hot coke, the iron melted allowing the oxygen in the iron ore to combine with the carbon in the coke as carbon dioxide and form reduced, "pig" iron. The remaining coke ash, limestone flux, and iron ore impurities form slag. The pig-iron, with impurities removed, becomes a steel production feedstock (Hall 1997).

Steel manufacturing advanced through three major technological innovations: the Bessemer Converter, the open hearth furnace, and the Basic Oxygen Process (Adams and Dirlam 1966). Bessemer Converters were the first technology allowing steel manufacture on a large scale and were invented in 1855. Bessemer converters work by inserting molten pig-iron through an opening in the top and forcing atmospheric air through the bottom of the converter and through the molten pig-iron. The oxygen in the air reacts with any impurities present in the iron and the carbon. These impurities then either escape as a gas or are incorporated into the slag waste.

Steel made from the Bessemer process contained relatively high levels of nitrogen, which left the steel brittle. The invention of open hearth furnaces (1880) solved this issue. The open hearth furnace process was slower than Bessemer Converters (i.e. eight hours versus one hour to make one batch of steel), but the steel emerged almost entirely free of nitrogen (Adams and Dirlam 1966). Open hearth furnaces could also use a mixture of scrap material and pig-iron, rather than just pig-iron, reducing production costs. Steel was primarily manufactured using open-hearth furnaces from 1908 until 1969 and accounted for 89% of steel manufacture in the United States (Adams and Dirlam 1966). The last remaining open hearth furnace closed in 1991.

Coke is a processed coal material that is used as a fuel in steel manufacturing. Coke is formed when coal is baked at very high temperatures (1000°C). The amount of coke necessary for blast furnaces decreased following World War II through the 1970s. During the mid-1900s, blast furnaces burned around 1,700 pounds of coke per ton of steel produced. This had decreased by about 500 pounds of coke by 1970 when only 1,200 pounds of coke was burned per ton of steel (Hogan 1971). The reduced need for coke was due to improvements in iron ore purity and higher blast furnace temperatures, which were as high as 1093° Celsius in 1970, an increase of around 427° Celsius since World War II. The introduction of a septum valve on top of furnaces, increasing the internal pressure, as well as blowing equipment improvements, which increased the volume air blown into the furnace, all contributed to these improvements.

The Basic oxygen process (BOF) was introduced in Austria following World War II and were first used in the United States in 1954. These furnaces use molten pig-iron and steel scrap material to produce steel products in the presence of oxygen. Basic oxygen furnaces and electric arc furnaces (another similar process invented in 1900), require significantly less energy to produce a given volume of steel. By 1970, 48% of United States steel was produced with basic oxygen furnaces (Hogan 1971). Coal consumption declined in the steel industry starting in the 1970s due to changes in blast furnace technology as well as improved efficiency in coke consumption: 90.3 million tons of coal were consumed by the steel industry in 1973 while only 27.8 million tons were consumed in 1993 (Hall 1997).

The United States steel industry produced 57% of world steel in 1947. However, with increased global competition, the United States only produced 23% of world steel in 1969 (Hogan 1971). Due to the depletion of domestic supplies, the U.S. steel industry began importing iron ore. Cold War military contracts and U.S. economic growth increased demand for steel products. As national production could not meet this demand, a variety of replacement products were developed for specific purposes, including reinforced concrete, aluminum, and plastics. United States steel imports in 1957 totaled 1.1 million tons and exports totaled 5.3 million tons. However, this had reversed by 1968 with 2.2 million tons of steel exports and 18 million tons imported. The decline of U.S. steel production was further exacerbated in the 1960s by increases in coal exports to other steel producing regions, mainly in Europe, Russia, and Japan, beginning in the 1960s (Hogan 1971).

1.1.4 Other Metal Refining

Significant zinc smelting also occurred in the Pittsburgh region. Zinc smelters process zinc ore, usually found in the form of zinc sulfide. Processing involved the removal of sulfides from the ore through either zinc roasting in furnaces or electrothermic distillation retort. Roasting furnaces are heated as high as 690°C and the sulfides in the zinc ore react with oxygen in the furnaces and are released as sulfuric acid. Electrothermic distillation retort, a technology invented in 1930, uses electrolysis to purify zinc ores. Heated air reacts with the ores to release impurities, which are then collected in bag filters. After zinc ores are purified, zinc is reduced in the presence of carbon monoxide. Energy and carbon monoxide for zinc reduction often is co-produced in coke combustion in furnaces, which can have temperatures as high as 1,400°C. Otherwise, energy for zinc ore processing is obtained from coke combustion (EPA Background Report).

Regional Pennsylvania zinc smelters include the Donora Zinc Works and the Monaca Zinc Corporation of America and the Horsehead Corporation zinc smelters. Donora and

Monaca, Pennsylvania are about twenty miles south of Pittsburgh and the Horsehead Corporation about twenty-five miles north of Pittsburgh. The famous 1948 air inversion in Donora produced a smog that killed twenty people over six days and sickened over 7,000 individuals (Snyder 1994). Zinc smelting emits a wide variety of materials to the atmosphere, particularly trace metals commonly found in sulfide forms including zinc, copper, lead, and cadmium.

1.1.5 Changes in Smoke Pollution Perspectives

Pittsburgh air quality was considered to be as poor in the 1940s as it was during the 1800s (Tarr 1980): the daytime skies were darkened by smoke pollution even in the early 1940s (Figure 2. This was most likely because the Pittsburgh industrial sector was still thriving and burning bituminous coal. However, smoke was no longer considered necessary for economic success or as healthy, viewpoints that had been developing since the late 1800s. Prior to the late-1800s, it was believed that smoke could prevent malaria and protected eyesight. Smoke was also viewed as a positive symbol of Pittsburgh's labor force and industrial base (Gugliotta 2003).

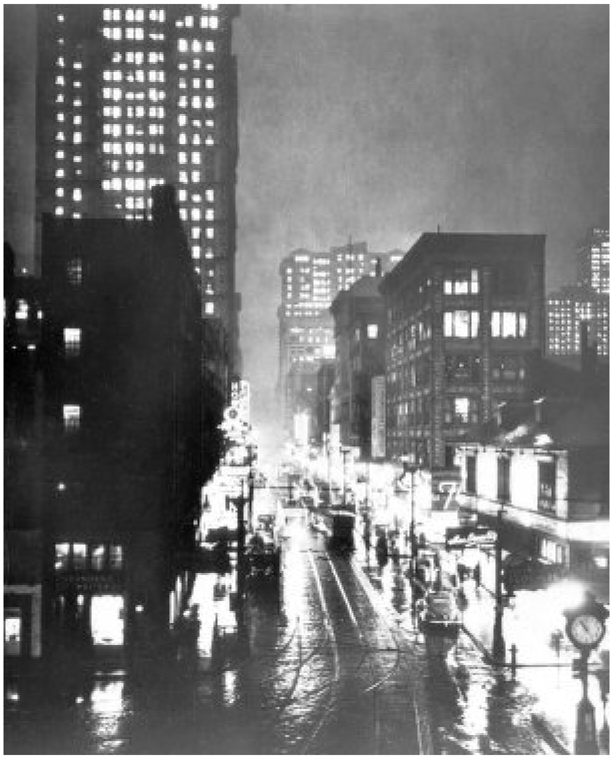

Figure 2. Corner of Liberty and Fifth Avenues 10:55 AM (Unknown 1940) [Smoke Control Lantern Slide Collection, ca. 1940-1950, AIS.1978.22 (Archives Service Center, University of Pittsburgh)].

However, during a period of brief natural gas usage in the city from 1884-1892, citizens' perspectives on smoke began to change. It was argued that natural gas produced superior iron and steel, as well as cleaner working and living conditions, than when bituminous coal was used as a fuel (Gugliotta 2003). Smoke began to be viewed as a health rather than simply an aesthetic problem around the same time period. The Ladies Health Protective Association, a women's group established in 1889 to address health concerns, argued that smoke was an enemy to public health. Local newspapers also began targeting smoke pollution in their articles around the same time (Gugliotta 2003). Smoke was also detrimentally affecting Pittsburgh's real estate and civic pride through its darkening of the skies and buildings. The city was considered to be a poor area of investment for these reasons (Schreibeis, Grove et al. 1961).

1.1.6 Pittsburgh Renaissance-Local Regulatory Effects

Local health and economic concerns realized from the late-1800s through early-1900s led to environmental legislation by the city. The Pittsburgh City Council passed an ordinance in 1941 with the goal of reducing smoke pollution in the city by requiring the use of “smokeless fuels” or “mechanical solid fuel-burning equipment” in all households and by prohibiting open air trash burning (Schreibeis, Grove et al. 1961). This ordinance targeted industry, transportation, business and domestic heating plants. Due to World War II, the ordinance was not enforced until 1946. Industry was targeted in this antismoke enforcement campaign in 1946 and households were added in 1947.

Major reductions in smoke occurred from 1946 through 1958 mainly due to households switching to natural gas for heating and cooking and river and train transportation switching from coal to diesel fuels (Figure 3). Natural gas became readily available to Pittsburgh with the opening of a natural gas pipeline in 1946. This pipeline facilitated the switch from coal to natural gas. Consider these numbers: 81% of Pittsburgh households burned coal for heating in 1941 and only 17% used natural gas. In 1950, only 31% of Pittsburgh households used coal and 65% used natural gas (Tarr 1980). The number of households relying on coal further decreased by 1961, with only 9% of households burning coal that year. Further, all trains and boats switched from coal to diesel by 1961 (Schreibeis, Grove et al. 1961).

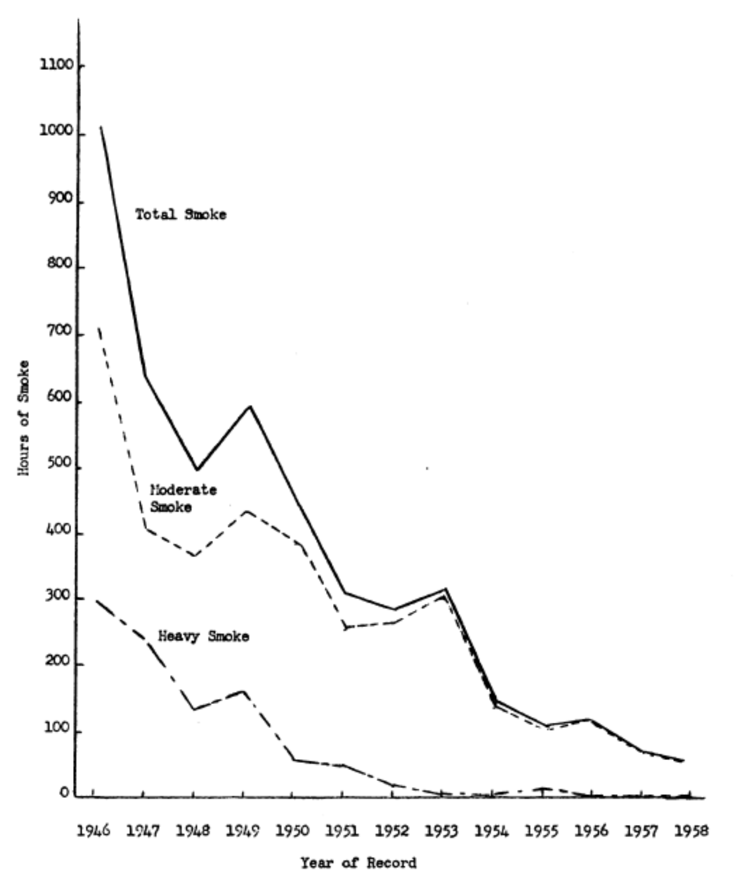

Figure 3. Smoke Reduction Based on U.S. Weather Bureau Visibility Observations, Pittsburgh, PA, 1946-1958. From (Schreibeis, Grove et al. 1961).

Despite these household and transportation improvements, there were no standards for industrial operation emissions established in the Allegheny County Smoke Control Ordinance. Open hearth furnaces, Bessemer converters, electric furnaces, coke ovens, sintering plants, and nonferrous foundries were not regulated under this ordinance (Schreibeis, Grove et al. 1961). In 1961, 102 open-hearth furnaces operated in Allegheny County and only twelve had dust collecting equipment installed (Schreibeis, Grove et al. 1961). So although smoke was significantly decreased following World War II due to legislation, infrastructure, and technology changes, particulate and other forms of pollution were still present with continued industrial activities.

The national economic and population boom following World War II is also essential to understanding pollution history. Although Pittsburgh may have been burning cleaner fuels, they were burning substantially more fuel as electrical appliances, vehicles, and population all increased. Seventy percent of American families owned cars in the 1950s and more than a quarter of their income was spent on these vehicles and other gasoline and electricity consuming technology, such as refrigerators and televisions (Hall 1997).

Beginning in the 1970s, the United States steel industry began to decline. The 1973 Oil Embargo and deferred capital investments raised the cost of manufacturing steel in Pittsburgh and allowed foreign manufacturers to outcompete American operations. The 1980-1982 national economic recession further reduced American steel companies' ability to compete and, in the Pittsburgh region, almost all the remaining operations closed down. The Pittsburgh economy became dominated by service industries, including its large academic and medical community. While Pittsburgh today is not the industrial city it once was, legacy pollutants from its industrial past continue to impact its urban ecosystems.

1.1.7 National Air Quality Legislation

Several important national environmental standards were established during the 1970s. This included the Clean Air Act, Motor Vehicle Act, National Ambient Air Quality Standards (NAAQS), as well as other stationary, mobile, and fuel regulations. All of these air quality standards required industry and households to regulate their emission sources, reducing ambient air pollution. The Clean Air Act focuses on six main air pollutants, including lead and particulate emissions, and has been reducing environmental levels of these pollutants since its original enactment in 1970 through stricter emission standards. Particulate pollution includes soot, dust, and smoke and is formed by industry, households, and vehicles from coal combustion and other fuel sources. Stricter regulation of these pollutants was introduced with amendments to the National Ambient Air Quality Standards (NAAQS) in the 1990 Clean Air Act amendments.

The Clean Air Act Amendments of 1990 also target acid deposition and toxic air pollutants. Acid deposition is addressed by regulating sulfuric acid and nitrogen oxide emissions. Sulfuric acid emissions are limited to 50 percent of 1980 national emission levels under the 1990 amendments. The acid deposition program officially began in 1995, targeting major industrial polluters and then coal-fired powered plants in 2000. Industrial sulfuric acid emissions were seven million tons in 2005, only 41 percent of 1980 levels (EPA 2000). Toxic air pollutants are also defined and controlled under the Clean Air Act 1990 amendments. This list of 187 toxins includes nickel, lead, and cadmium compounds. Main sources are industrial and vehicular and are addressed through cleaner vehicle gasoline, parts, and industrial emission controls. According to the EPA, national sulfur dioxide and lead emissions peaked around 1970 and decreased through 1998. Particulate emissions 10 micrometers or less (PM_{10}) peaked around 1950 and steadily decreased until the 1980s, and have remained stable since (EPA 2000).

1.1.8 Trace Metal Cycling

In order to understand environmental contamination through materials in tree rings, it is necessary to understand trace metal cycling. Trace metal cycling is controlled by factors as varied as climate and metal bioavailability. These factors are briefly explored in the following section.

1.1.9 Pollution Sources

Sources of the five metals studied, cadmium, copper, nickel, lead, and zinc, include industrial plant air emissions, vehicular emissions, and household pollution (Table 1). Factors affecting these sources include of the production of steel, pig-iron, and coal, as well as soil pH values, pollutant deposition amounts, and soil and plant processes.

Table 1. Metals and major pollution sources considered in this study.

	Industrial Sources:		**Vehicular Emissions**	
Metals:	**Coke Ovens and Steel Mills**	**Zinc Smelters**	**Fuel**	**Part Wear**
Zinc	Coal Combustion	zinc ore & coal/coke combustion	-	tires, brake pad linings
Nickel	Coal Combustion	coal/coke combustion	-	tires, engines
Copper	Coal Combustion	coal/coke combustion	-	tires, engines, brake pad linings
Cadmium	Coal Combustion	coal/coke combustion	-	tires, brake pad linings
Lead	Coal Combustion	zinc ore & coal/coke combustion	tetraethyl leaded gasoline	brake pad linings

Trace metals in the Pittsburgh region are strongly influenced by coal combustion. Coal arises from plant and animal carbon generally thought to have been deposited in ancient bog environments. Bogs are stratified systems with anaerobic bottoms, which are a reducing chemical environment. Pyrite (FeS_2) is formed within bogs once concentrations of sulfur anions (S^{2-}) and iron (Fe^{2+}) cations reach or exceed saturation. Zinc, copper, cadmium, and lead have characteristics (e.g., atomic radius, etc.) causing relatively stronger affinities for sulfides than iron, allowing substitution for iron within sulfide crystal structures. Therefore, while concentrations of these trace metals were likely much less than iron in bog environments, they were more likely to precipitate to the sulfide phase. Over time, sediment layers buried these reduced organic sediments. Subsequent exposure to high pressures transformed the materials to coal. While nickel does not have as strong an affinity for sulfides they are also incorporated into coal seams as all trace metals associate with organic ligands and thus are also incorporated into the massive organic matter layers that become coal. When coal is burned (i.e., oxidized) these metals are remobilized to the environment.

1.1.10 Source to Sink Model

To understand the metal concentration data recorded in tree ring material, the following conceptual model is used. Coal combustion, whether for metal refining or household energy production, releases trace metals in coal to the Pittsburgh ecosystem. The subsequent fate and transport can take a variety of paths (Figure 4). Emission sources include steel manufacturing facilities and their utilized feed stocks (e.g., coke), zinc smelting, vehicle emissions, and household energy use. Emissions from these sources form gaseous and particulate pollution

(Figure 4.1), which is then deposited back on the surface in the form of wet and dry deposition (Figure 4.2). Pollution can then remain on biotic surfaces, in the soil, dissolve in water, or be assimilated by vegetation via root systems (Figure 4.3). We assume that the metals measured in the red oak were assimilated via the root system based on past studies (Watmough and Hutchinson 2003).

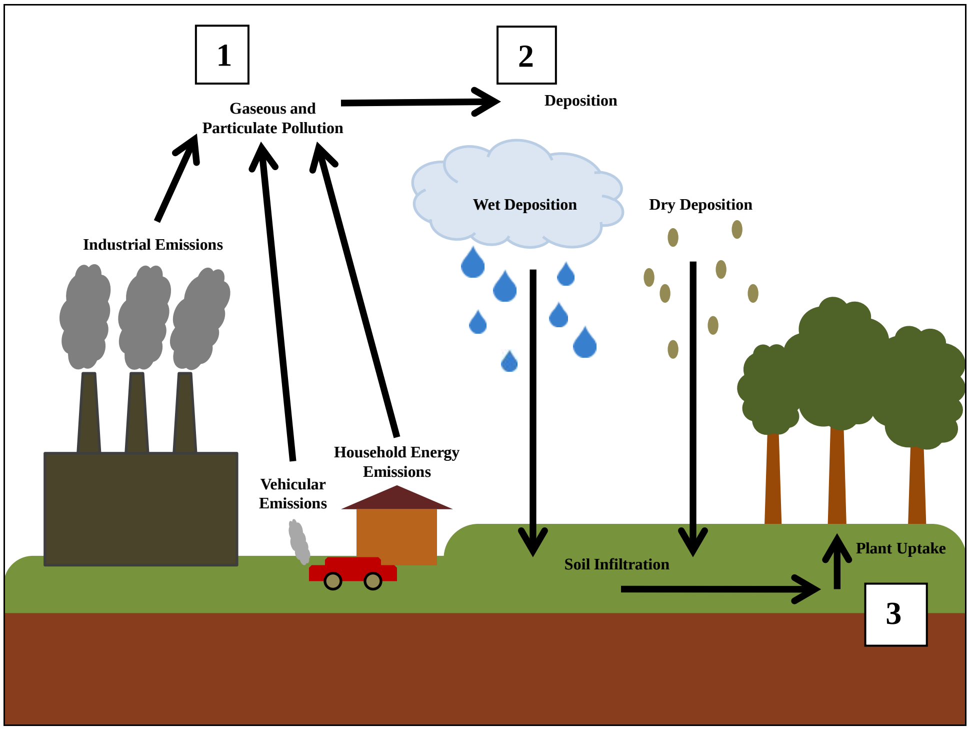

Figure 4. Source to Sink model showing metal emission pathway from source to soil and plant sinks.

1.1.11 Plant and Soil Uptake

Trace metals can be deposited onto soil via wet and dry deposition and can enter plants through normal uptake processes like transpiration. Plants absorb water and any associated dissolved materials through their root hairs and pull water and other molecules through their xylem vessels, which are used for water transport. Trace metals dissolved in soil water can be directly incorporated into the tree material through this process. Such metal uptake is dependent upon trace metal mobility and solubility in the soil matrix. This mobility is dictated by a complex mixture of soil and solution characteristics. For example, high metal mobility is observed in acidic or weakly acidic environments relative to neutral and alkaline environments (Fortescue 1980).

Three of the metals in this study are plant micronutrients, copper, zinc, and nickel. The following is a list of the chemical and physical characteristics of these elements in plant systems as described in Mineral Nutrition of Higher Plants (Marschner 1995):

1. Copper is found mainly in plant proteins and ligands. It is found in a complexed form about 98% of the time within plants rather than as a free cation. Uptake occurs through plant roots, especially when soil copper levels are high.
2. Zinc uptake mainly occurs with Zn as a divalent cation (Zn^{2+}), although it can also be bound to organic acids for long-distance xylem transport. Zinc is also found in high concentrations in plant phloem. Zinc is necessary in plants for its catalytic or co-catalytic role in plant enzymes. It also is used structurally and is found in biomembranes.
3. Nickel is a micronutrient for plant-associated bacteria in both legumes and non-legumes. It is also necessary for structural and catalytic functions in plants. Nickel occurs both as a cation and as part of ligand complexes in plant systems. It is mainly found as Ni(II), but also as Ni(I) and Ni(III) in its cation state. It is found in both xylem and phloem.

Trace metal accumulation occurs in annual growth rings, or xylem tissue. Xylem tissue is formed through annual secondary growth and secondary plants (including trees) use new xylem vessels for water transport each year. Older xylem tissue eventually forms what is known as the heartwood section of trees. Heartwood can be used as waste storage by trees, and must be carefully examined during annual trace metal data analysis as translocation to heartwood is a possibility.

1.1.12 Precipitation

Precipitation affects biota growth patterns as well as the availability of soil material, including metals. Acidic deposition tends to increase metal mobility (displacing metals bound to soil substrates). However, these data do show a decrease in sulfate values, suggesting that environments have become less acidic in the last thirty years. Data used in this study are from National Atmospheric Deposition Program (NADP) station PA42, a collection site located at Leading Ridge in central Pennsylvania, southeast of Pittsburgh (Figure 5).

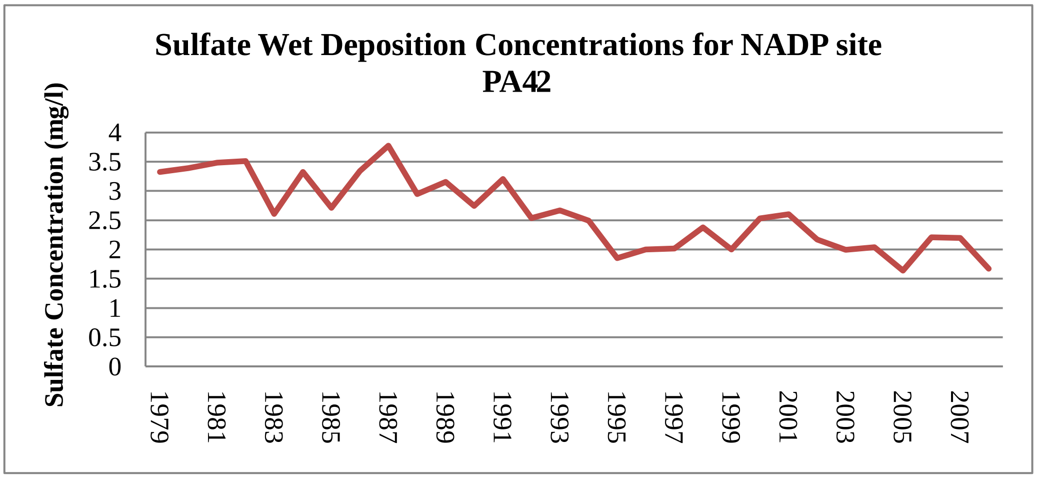

Figure 5. Sulfate wet deposition concentrations for National Atmospheric Deposition Program (NADP) site PA42 (Leading Ridge, Pennsylvania). Values are precipitation-weighted means. Years are 1978-2008, sulfate values are mg/L.

These climate and biological factors play important roles in pollution availability. Therefore, considering these factors provides essential information for interpretation of historical pollution trends recorded in tree ring metal concentration data.

2.0 METHODS

This investigation utilized annular tree rings from a red oak (*Quercus rubra*) that grew in Schenley Park, a 456 acre park that was established in 1889 when Mary Schenley donated 300 acres to the city. The tree was collected after it blew down in a January 2007 storm (Figure 6). Tree rings were organized based on their year of growth: 1881 (ring 1) through the final year of complete growth, 2006 (ring 126) and concentration data were then compared to historical data.

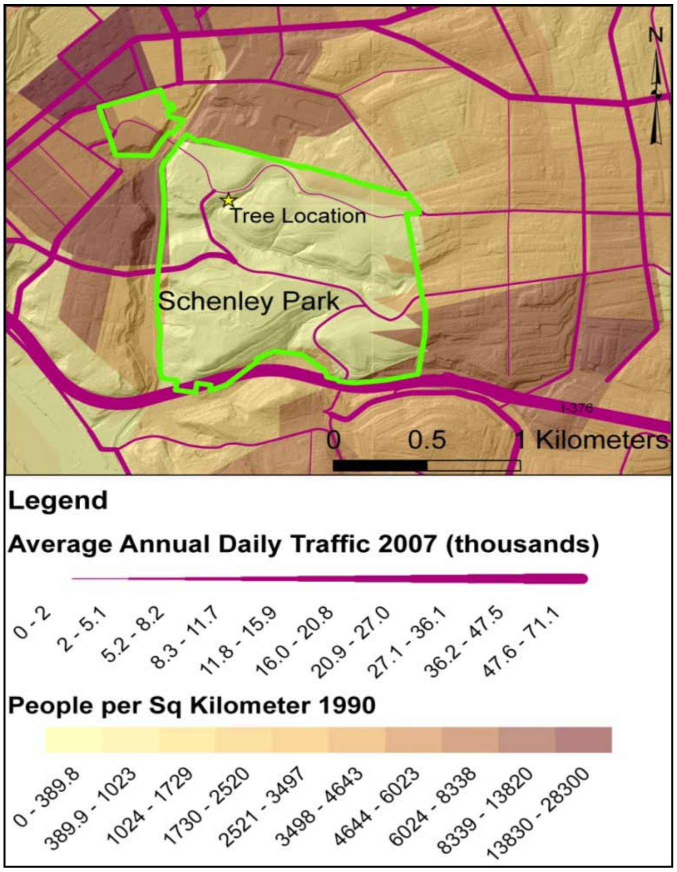

Figure 6. Map of Schenley Park (outlined in green) in Pittsburgh, Pennsylvania. Yellow star indicates tree location. Road width is proportional to average annual daily traffic (2007) and shading indicates population density (1990) in the surrounding neighborhood.

2.1 ACID CLEANING PROCEDURES

Crucibles and 7mL Teflon vials for sample storage were all acid-cleaned in order to remove any contamination. The following procedure was utilized:

1. Materials were first rinsed three times in Milli-Q water (MQW).
2. Materials were soaked for a minimum of eight hours separately in each of the following: MQW, 50% hydrochloric acid (HCl), 50% nitric acid (HNO_3), and MQW again.
3. All materials were rinsed with MQW between soaks.

4. Washed labware was dried before use in sample processing.
    a. Porcelain crucibles: dried at 100˚C to drive off residual water attached to the ceramic material.
    b. Teflon: air-dried in a HEPA fume hood.

2.2 SAMPLE PREPARATION AND ANALYSIS

Tree rings were sampled from a block cut (about 9 cm by 33 cm) from the *Q. rubra* trunk roughly two meters above the ground. Annual rings, containing both earlywood and latewood were separated with an Exacto blade. Latewood was used as a guide to separate rings based on its darker shade and its formation at the end of the growing season (fall-winter). Individual years were stored in plastic bags until further processing. These separation methods were developed through a preliminary data procedure using the ten most recent tree rings (1996-2005 or rings 117-126) and were utilized for all ring separation.

The following procedure was utilized for processing ring material in this study:

1. Ring material was dried in acid washed porcelain crucibles.
2. Rings were dried for a minimum of one week at 60˚C in a drying oven and then weighed before being ashed.
3. One laboratory blank accompanied each batch of prepared rings except for the first two batches of analyzed rings: rings 117-126 and rings 1, 4, 10, 12, 13, and 16-20.
4. Tree material was ashed in a muffle furnace at 400˚C for 12 hours (temperature was increased and then decreased at a rate of 1˚C per minute during this ashing).

5. Ashed samples were then reweighed and transferred to acid cleaned 7mL Teflon vials.
6. Ashed samples were digested in *aqua regia*, (1:1 $HCl:HNO_3$, concentrated trace metal grade acids) as follows: refluxing for a minimum of 12 hours followed by drop wise addition of optima 30% hydrogen peroxide during dry down . This process was repeated until the ashed material was completely digested.
7. Digested samples were dissolved into 2% trace metal grade nitric acid solution and stored in centrifuge tubes and weighed again. Analyzed solution volumes are between 6 and 7 mL.
8. These solutions were analyzed on the Specetroflame Modula (FTM 08) axial inductively-coupled plasma atomic emission spectrometer (ICP-AES) to determine zinc, nickel, copper, cadmium, and lead concentrations in solution (mg/l). Samples were run in sets of ten with standards run between each set to check for drift from calibration. These metal concentrations were used to obtain metal concentrations in dry ring material samples (ppm).

2.3 HISTORICAL RESEARCH

Historical data were collected to provide context and improve understanding of metal concentration trends. Historical research was focused on local steel and other manufacturing products production rates, climate data, population density, and local and national technology and policy changes during the study period (1880-2005). Data collected and sources are listed below (Table 2).

Table 2. List of data, sources, and manipulation of data for this study.

Data	Source	Description of Data Processing
Pittsburgh Precipitation Data	Precipitation Data: (Brotzman 1936; Rockwood 1952; NOAA 1977; NOAA 2006) Snowfall conversion: (Roebber, Bruening et al. 2003)	Annual precipitation and snowfall values were summed. Snowfall values were converted to rainfall equivalents using a 12:1 (snow to rainfall) ratio. This ratio is the average of the medium snow fall density conversion range (9:1 to 15:1) in Roebber, Bruening et al. (2003).
Sulfate Concentrations in Wet Deposition	(Husar, Sullivan et al. 1991), (NADP 2010)	Sulfate in kg/hectare/year. Continuous Husar West Virginia estimates were digitized and linear interpolation was used for any missing years (1881-1985). NADP data dates 1979-2008.
Population Density	Pittsburgh Population: (Gibson 1998); Pittsburgh area: (Briem 2008)	Population density was determined by dividing population by Pittsburgh city area (square miles).
National Vehicle Miles Traveled	(Federal Highway Administration 2010)	Monthly total vehicle miles traveled (VMT) in million miles from 1970-2008. VMT data is national.
Coal (local)	(Pennsylvania Department of Mines 1905-1930; Pennsylvania Department of Environmental Resources 1985)	Annual production rates for Allegheny County.
Coal (national)	(Singer and Small 1993)	US energy production in coal equivalents.
Pig-Iron	(Pittsburgh Business Review 1930-1961)	Annual Pittsburgh District and Pittsburgh-Youngstown District production values.
Steel (local)	(Cassidy 2009)	US Steel Company annual steel production.
Steel (national)	(Singer and Small 1993)	United States annual steel production.
Zinc	(United States Geological Survey Bureau of Mines 1932-1978)	National and Pittsburgh annual zinc production values.

3.0 RESULTS

Ninety-five of 126 rings (1881-2006) were analyzed. Although this is not yet a complete record, there are no gaps larger than four years (1904-1907) and points represent individual years. In contrast, typical dendrochemical studies often group rings into sets of 3 to 5 years due to sample size limitations (Baes and Ragsdale 1981; Watmough, Hutchinson et al. 1999). Some sample measurements were discarded due to problems in individual metal calibrations or with high blank concentrations. Total samples sizes plotted are 94 samples for zinc, 89 for nickel, 93 for copper, 92 for cadmium, and 64 for lead. Metal concentration values (ppm of dry wood sample) are shown for each metal in Figure 5.1-5.5 along with moving seven-sample average trendlines.

High zinc and nickel concentrations were found in the laboratory blank for samples 11 through 20. To account for the high blank values, concentrations of zinc and nickel in the blank were subtracted from samples 11 through 20 and any samples with concentrations below the blank were omitted (samples 17 for zinc and samples 12 and 17 for nickel). The two other blanks analyzed at this point, B4 and B5, had values for zinc above instrument detection level but well below all samples they were controlling for (i.e., blanks were roughly 1% of the tree ring value). All blank values (mg/l) and samples they were controlling for are listed below in Table 3. Blanks not run at this point are B2 (samples 21-30), B3 (samples 31-40), B6 (81-97), B7 (61, 74, 98-115), and B8 (122-126). These blanks have not been run as some samples in the sets these blanks are controlling for have not been completely processed.

Table 3. Measured blanks and instrument detection limits per metal. Concentrations in mg/l. Rings listed are minimum and maximum metal concentration (mg/l) for controlled samples.

Blank:	**Controlled Samples**	**Zinc**		**Nickel**		**Copper**		**Cadmium**		**Lead**	
		Blank	rings	Blank	Rings	Blank	rings	Blank	rings	Blank	rings
B	11-20	.0243	.0228-.0702	.0184	.0471-.0674	.0014	.0014	.0026	.0043-.0051	0	0
B4	41-67	.0031	.0361-.1284	.0009	.0363-.1020	.0034	.0249-.0346	.0016	.0044-.0084	.0024	.001-.0264
B5	68-80	.0020	.0364-.0974	.0195	.0020-.0588	.0014	.0309-.1453	.0015	.0035-.0078	.0133	.0011-.0194

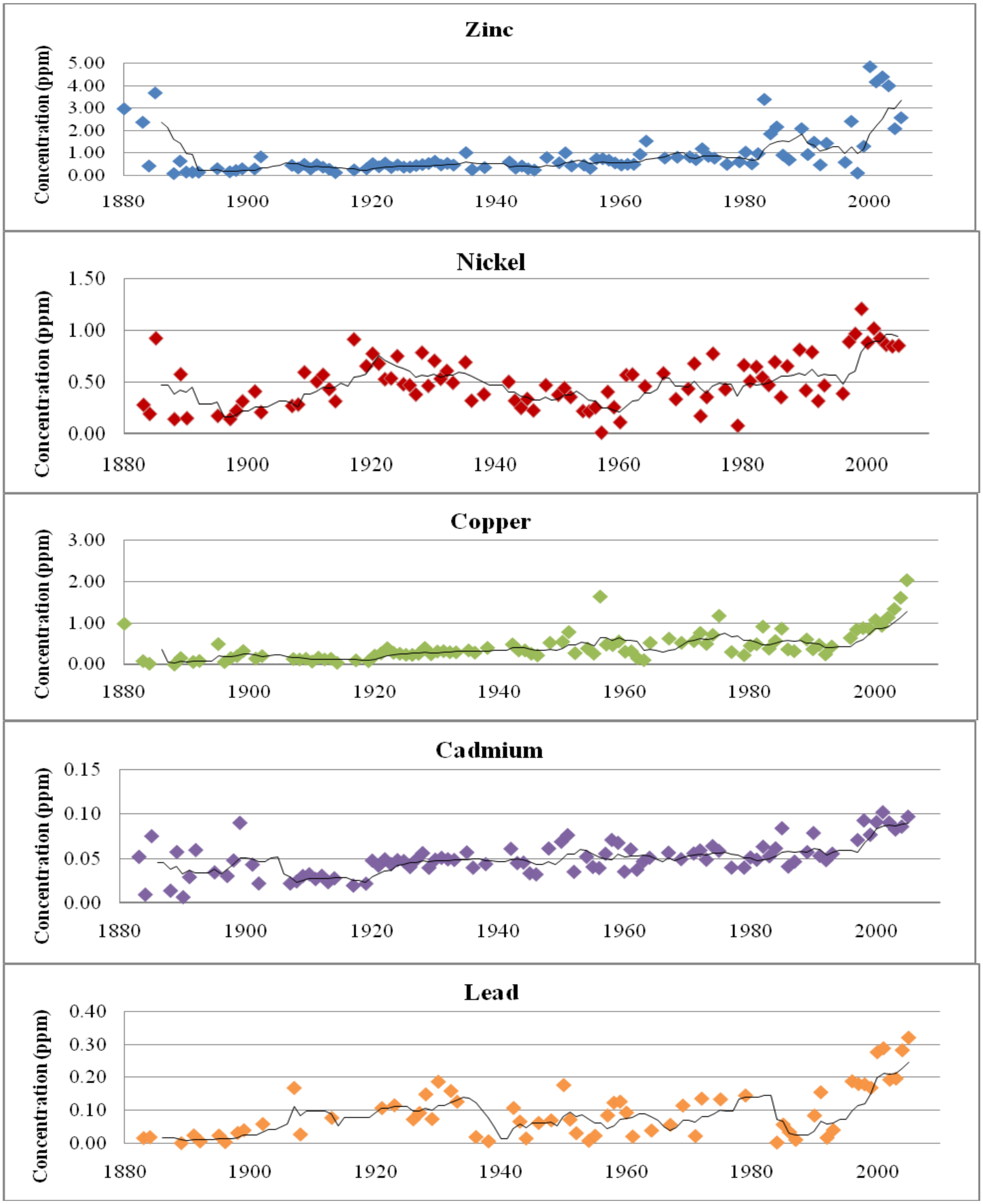

Figure 7.1-7.2. Concentration values (ppm trace metal per dried ring sample) for all metals analyzed. Ring values listed in years (1881-2006). Trendlines are the running seven-sample averages of concentration data.

3.1 DESCRIPTION OF METAL DATA

There are several similarities across all reconstructed metal records (Figure 7). All records have two periods of high metal concentrations, one in the first two decades of data (1881-1900) and one in the last decade of data (1996-2006). Of these two periods, the most recent decade of metal concentrations is the maximum in the record for all metals. There are several other trends that are apparent in some of the metal records. Lead and nickel records both have additional periods of elevated concentrations: nickel has a 1920 peak and a 1960 trough in concentration not found in the other data sets. In general, the lead is more variable in concentrations than the other metals. Copper, cadmium, and zinc have fairly consistent concentration patterns, with increasing concentrations from around 1900 until 1980 where they all exhibit a slight decrease before rapidly increasing from around the late 1990s through 2006.

In order to understand the temporal structure in inter-ring concentration variability, seven-sample relative deviations were calculated for each metal (Figure 8.1-8.5). High rates of variability in metal values occur in the earliest rings (1881 through the early 1900s) for all metals. Overall, the metal records have decreasing variability in concentrations over time. As expected, lead is more variable than the four other metals, with periods of elevated variability between 1930 and 1960 and between 1980 and the 1990s. Copper and Cadmium have periods of increased variability during 1910-1920 and 1940-1950. Zinc is the only metal other than lead with increasing variability from 1980-2006, though zinc has multiple, distinct peaks in variability (e.g., around 1990).

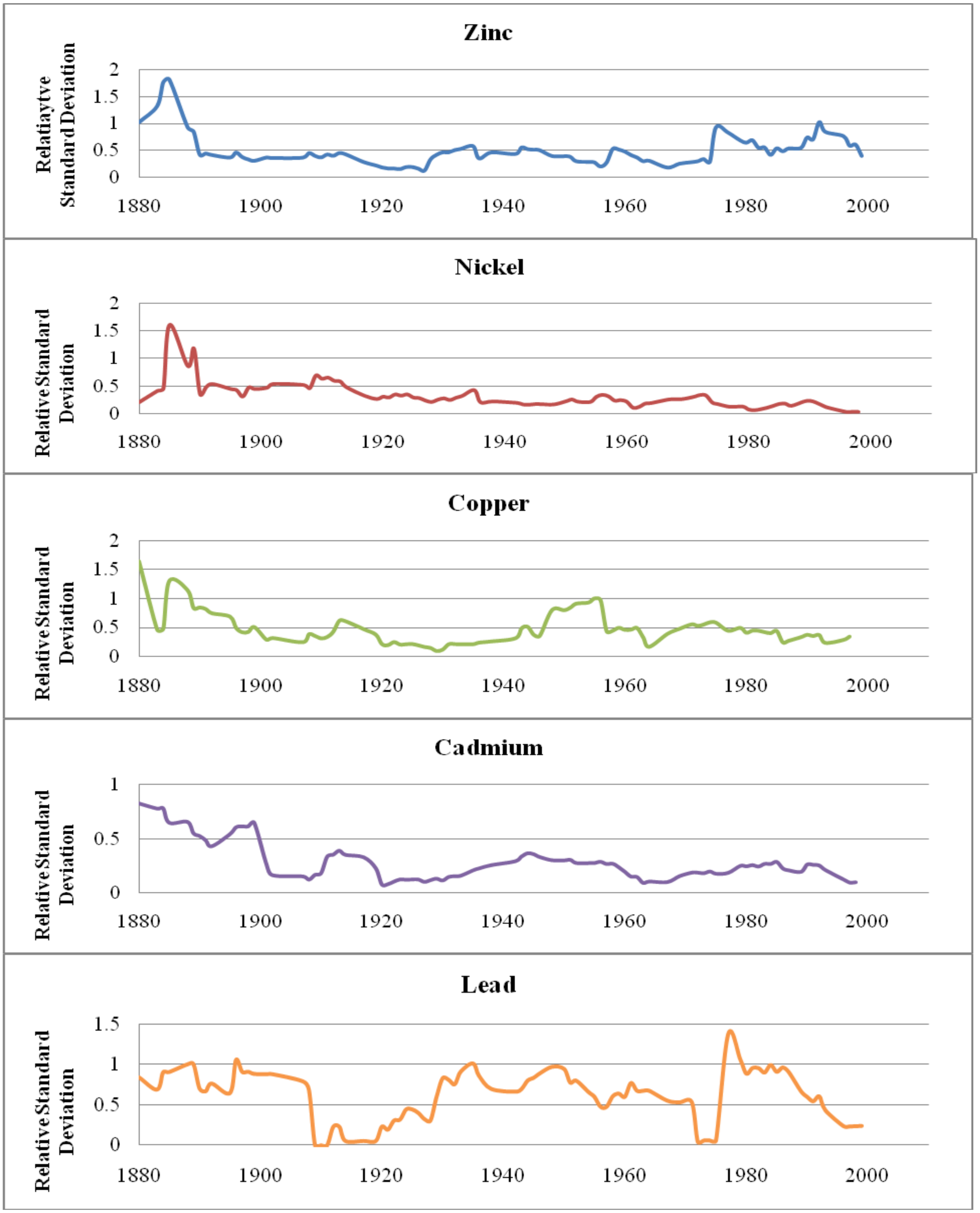

Figure 8.1-8.5. Seven sample relative standard deviations of metal concentration data for each metal. Ring numbers listed as years.

3.2 HISTORICAL DATA

National and local technological, social, and legislative changes were researched to provide a better picture of events that could possibly affect trace metal pollution levels with the Pittsburgh region. These events were organized into a timeline for the lifespan of the red oak tree (Figure 9).

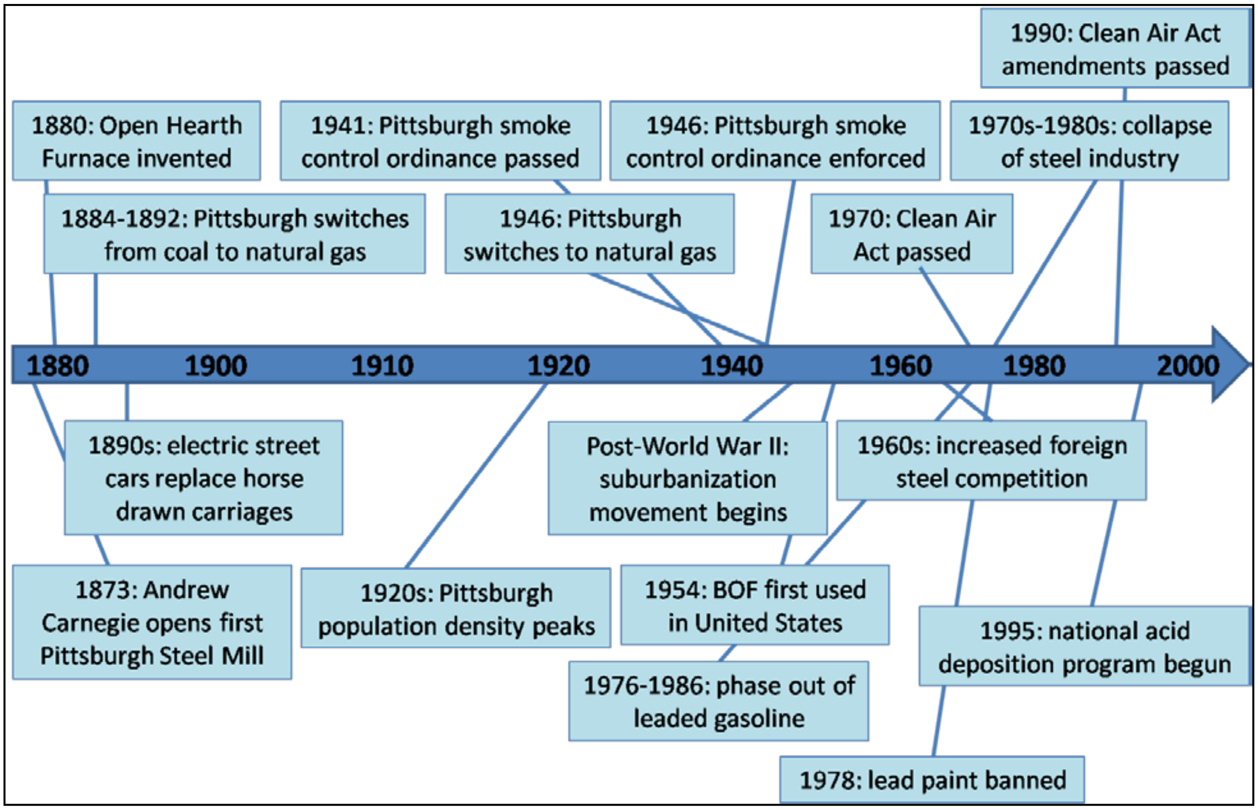

Figure 9. Timeline of possible metal pollution affecting events for lifespan of studied tree (1881-2006). National and local production records exhibit similar patterns in manufacturing activity.

National production of steel, coal, and zinc (Figure 10.2) is relatively low from the 1880s through 1910, likely due to lower demand for manufactured goods during this period. Production increases quickly for steel, coal, and zinc between the 1920s and the 1960s, though two periods of decreased production occur during the 1930s and the 1960s. The Great

Depression is likely the reason for decreased production during the 1930s. The decrease in all three goods during the 1960s might result from the advent of foreign competition in the global and United States manufacturing markets. Decreases in production begin in the 1970s for zinc and in the 1980s for steel and coal. Stricter emission standards during this time period from the Clean Air Act in 1970 and 1990 may drive part of this decreased production, though increased competition for foreign manufacturers with is probably the ultimate driver.

Local production records reflect environmental legislation and local events discussed earlier in this study (Figure 10.3). Local steel production climbs steadily until the Great Depression (1930) before continuing to increase through World War II and the late 1950s, driven by increased war-time and post-WWII consumer demand. Production remains generally consistent during the 1960s and 1970s before plummeting in the 1980s and remaining low through the end of available data in 2000. Allegheny County coal production increases until it peaks in the late 1940s and then decreases through 1985. Sudden drops in local coal production following World War II could be due to the enforcement of the 1941 Pittsburgh Ordinance as well as the depletion of easily accessible local coal deposits. Local pig-iron data were difficult to obtain for the Pittsburgh area and thus only a brief period of data is shown (Figure 10.3). The monthly Pittsburgh Business Review only listed production for the Pittsburgh District from 1919 to 1941 and then switched to recording pig-iron production for the larger Pittsburgh-Youngstown District (also shown in Figure 10.3).

Overall, national and local production plots (Figure 10.2 and 10.3) exhibit increasing production rates from the beginning of recorded data (1880s) until the 1980s. Local and national steel production rates are similar ($r^2 = 0.7653$), likely resulting from the dominance of the US Steel Company in national steel manufacturing.

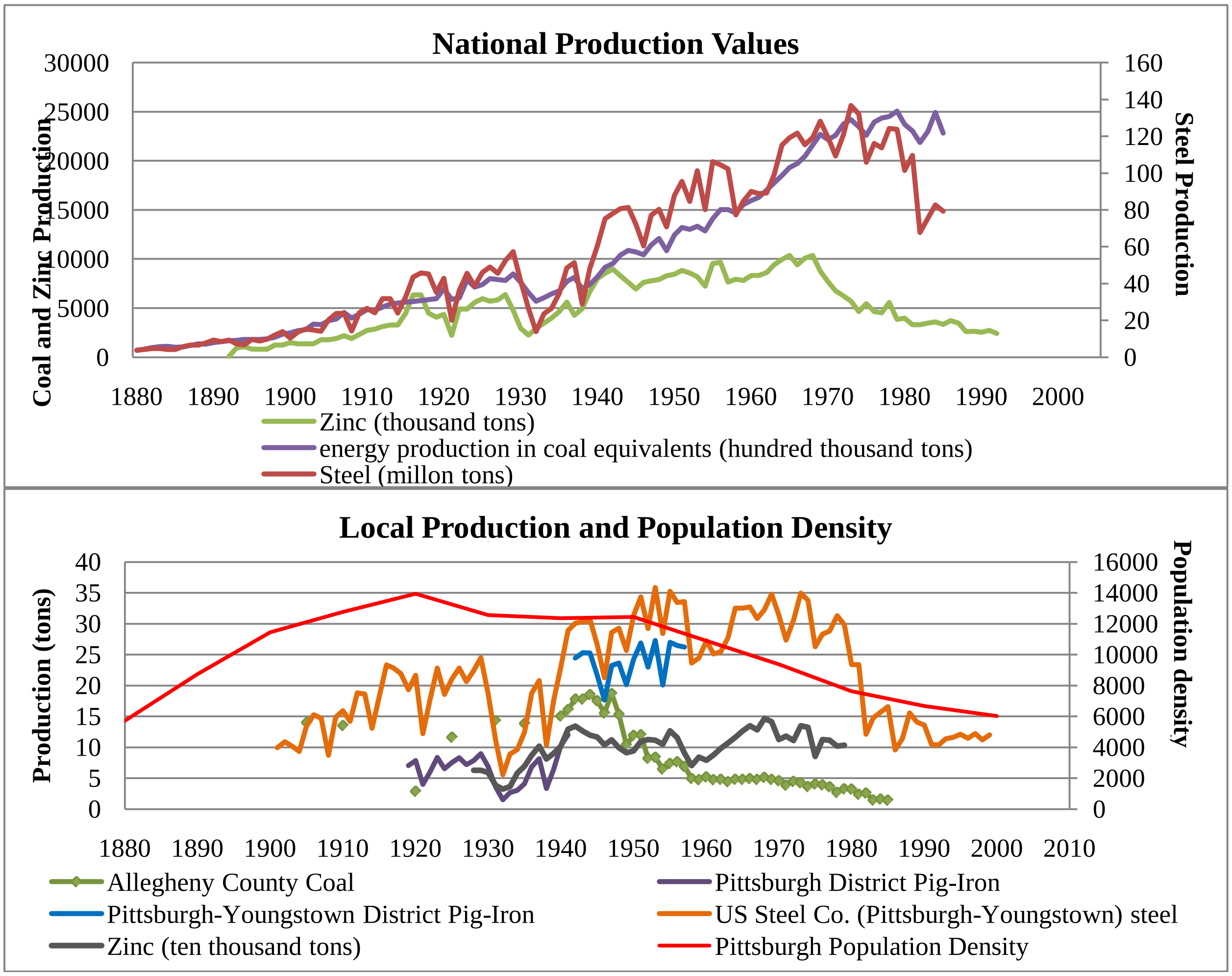

Figure 10.1-10.2. National and local production graphs. Local graph includes Pittsburgh population density as well. Production units selected to allow for optimal display on plots.

Vehicles account for a large amount of trace metal emissions, including tire, brake pad, and engine wear. Vehicles have played an increasingly dominant role in American culture since World War II. Considering vehicle miles traveled (VMT) is therefore important when analyzing metal concentration trends, especially during the period of interest in this study. Long-term VMT reports are not readily available as national data sets were only collected beginning in 1970, with the advent of environmental legislation. National VMT rapidly increased from 1970 to 2007 (Figure 11.3).

In addition, acidity plays a large role in determining metal bioavailability, and thus metal uptake by plants. Although there are no major fluxes in Pittsburgh annual precipitation records since the 1880s (Figure 12), there have been fluxes in wet deposition acidity. Wet deposition sulfate values are a good indicator of acidity trends due to the dominance of acidic deposition from coal combustion in this area. Industry is a major contributor to sulfate emissions and, through the Clean Air Act, has faced stricter emission regulations since the 1990s. Sulfate air emission trends are therefore used in this study as a proxy for soil acidity conditions (Figure 13.5).

Local precipitation records were also collected to examine possible correlations between annual wetness and metal uptake patterns. Deposition data include Pittsburgh precipitation data collected at the Pittsburgh Airport (Brotzman 1936; Rockwood 1952; 1977; 2006), a reconstructed deposition loading for West Virginia (Husar, Sullivan et al. 1991), and wet deposition sulfate concentration observations from the NADP site at Leading Ridge, Pennsylvania (NADP 2010). Annual wet deposition sulfate concentrations for the West Virginia reconstruction increase from 1881 until the late 1970s, with two depressed periods in the 1930s and late 1950s-1960s. The Leading Ridge data set (PA42) only includes data for 1979-2008 and has higher wet deposition sulfate concentrations than West Virginia concentrations in overlapping periods (1979-1985). PA42 sulfate wet deposition peaks in 1986 and then decreases through the present. While these data sets do not match precisely that is not unexpected. The West Virginia data set is based on an empirical model of sulfate deposition developed by Husar et al. (1991) based on anthropogenic sulfate emissions. The PA42 site is located east of Pittsburgh and may have higher sulfate concentrations due its downwind location from Ohio and Pennsylvania industries as well as its higher elevation, causing increased precipitation and associated contaminate deposition due to the orographic effect. However, the combination of these records provides a good indicator of sulfate emissions in the Pittsburgh region in general, as they follow similar trends in periods of overlapping data.

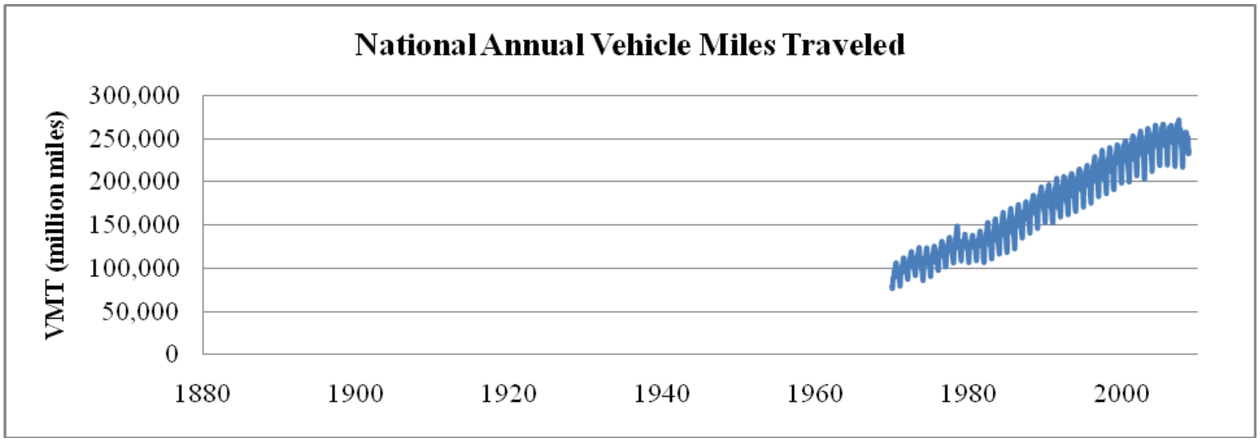

Figure 11. National Monthly Vehicle Miles Traveled (VMT) values (in millions of miles) from 1970-2008 on axis dating from 1880-2010.

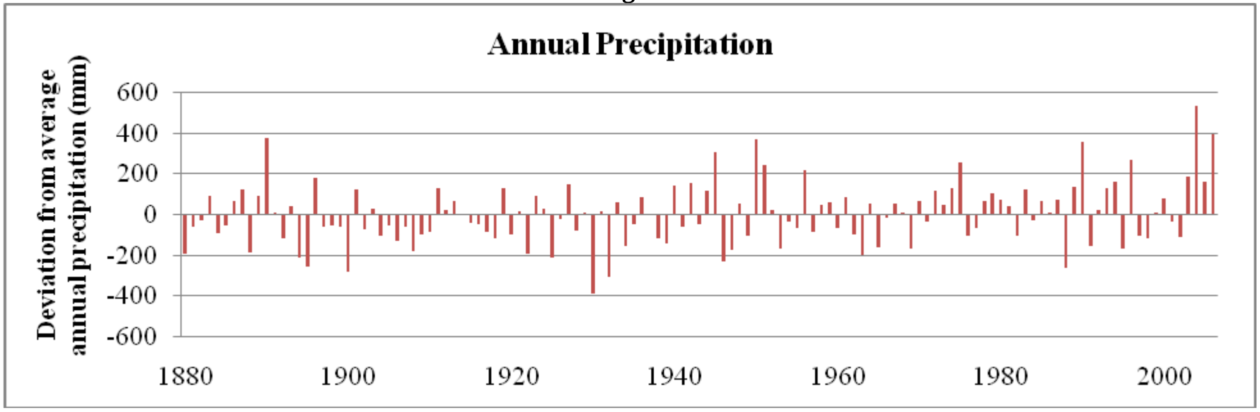

Figure 12. . Relative Annual Pittsburgh Wet Deposition (mm) for years 1880-2006.

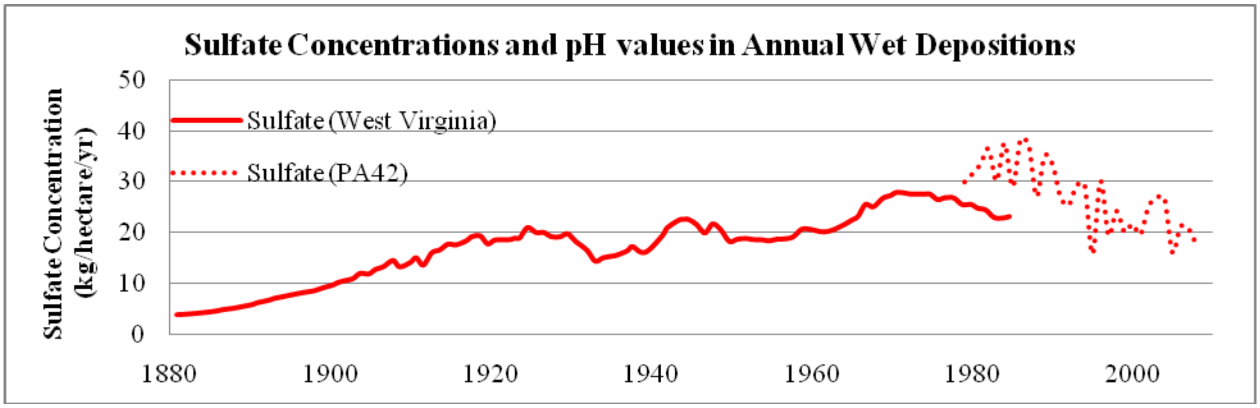

Figure 13. Sulfate Concentrations in Annual Wet Deposition from West Virginia (1881-1985) and NADP site PA42 at Leading Ridge, PA (1979-2008). All annual sulfate values in kg/hectare.

3.3 HISTORICAL DATA: CORRELATION WITH TRACE METAL DATA

Data sets were examined via regression analysis to explore similarity in sources and in environmental regulating factors. Wet deposition sulfate concentrations and local steel production values have the highest correlation to metal concentration values out of all environmental parameters tested (Table 4). National and local steel production are related (r^2=0.7653) as are national steel production and sulfate deposition (r^2= 0.7670). However, correlation between sulfate concentrations and steel production is not unexpected since the West Virginia sulfate data set (1881-1985) is calculated from anthropogenic emission estimates, which includes industrial steel production (Husar 1991). In contrast, local steel production and sulfate deposition are not clearly related (Table 4: r^2 = 0.0769). Precipitation values are regressions of deviation from the overall sample average (precipitation 1880-2006). The highest linear r^2 value between a metal and precipitation data was 0.1137 for copper (Table 5), suggesting a closer relationship between precipitation and copper bioavailability than with other metals.

Table 4. Correlations (r^2) for environmental parameters. National coal (an energy equivalent calculation) not included.

	National Steel	**Local Steel**	**Local Coal**	**Precipitation**	**Sulfate Wet Deposition Concentrations**
National Steel	-	0.7653	0.3073	.0699	0.7670
Local Steel	0.7653	-	0.0025	.0413	0.07690
Local Coal	0.3073	0.0025	-	.0017	0.2625
Precipitation	.0699	.0413	.0017	-	.0025
Sulfate Wet Deposition Concentration	0.767	0.0769	0.2625	.0025	-

Table 5. Metal concentration and industrial production and environmental parameter regressions (resulting r^2 listed).

	Precipitation	Sulfate Wet Deposition Concentrations	National Steel	Local Steel	National Coal	Local Coal	National Vehicle Miles Traveled
Zinc	0.0278	0.1501	0.1320	0.0115	0.0532	0.1981	0.3360
Nickel	0.0003	0.0631	0.0069	0.1385	0.0026	0.0387	0.4281
Copper	0.1137	0.3458	0.3398	0.0462	0.2880	0.0538	0.3342
Cadmium	0.0421	0.1734	0.1698	0.0049	0.1609	0.0472	0.5582
lead	0.0330	0.1185	0.0907	0.017	0.0471	0.0006	0.4272

4.0 DISCUSSION

The highest concentrations for all five trace metals measured were found in the most recently formed rings, 2000 through 2006 (Figure 8). This is surprising as it was expected that trace metal concentrations should be more tightly related to metal pollution loading inferred from production records. Based on both national and local industrial production data sets, it was therefore assumed that trace metal concentrations would peak between the 1950s and 1970s and then decrease until present. A number of studies have found this direct relationship between biota and sources to be the case for tree rings (Baes and Ragsdale 1981; Watmough 1999; Watmough and Hutchinson 2003). These studies typically observed this association when looking directly at air transport from a specific point source, such as highway traffic or an industrial operation. The tree in this study though is not adjacent to a specific point source. Instead, the tree was likely subject to more general pollution patterns occurring across the Pittsburgh region. The relationship between metal pollution loading and tree ring concentrations may therefore not be as simple or directly related to industrial sources as is the case in the studies cited above. This makes comparisons between pollutants and tree ring metal concentrations more challenging. Potential explanations for this unexpected trend will be discussed in the following sections.

4.1 EXPLAINING THE METAL RECORD

Translocation is the movement of metals through tree rings via normal plant processes and is an important factor to consider in tree ring analysis. Such active transport of metals potentially makes analysis of concentrations per specific years that assume passive recording of environmental conditions inaccurate. However, previous studies have found ring-porous tree species, especially red oaks, to have very low translocation rates and to therefore be accurate historical recorders (Hagemeyer 1993; Watmough and Hutchinson 2003). Lack of high variability throughout the entire record (Figure 6.1-6.5) combined with the unique patterns of concentration and variability among the five trace metals that can be related to dated events (e.g. higher levels of lead beginning in the 1920s when tetraethyl leaded gasoline was introduced) provides further evidence that translocation is not likely the dominant process.

The only location where translocation may be a factor are the earliest rings (1881-1900), which have high metal concentrations and variability despite being formed during a time period with much lower emission sources. However, this period was also marked by apparent contamination in the laboratory and must be re-analyzed before any conclusions can be made.

4.2 COMPARING TRACE METAL AND HISTORICAL DATA

The metal concentration record suggests that there were increases in metal inputs from the mid-1900s onward. This is supported by industrial production records until the 1980s when production drops off. This discrepancy between trace metal data and manufacturing rates suggests that other environmental parameters are affecting tree trace metal uptake increases in the last two decades. Factors possibly affecting metal uptake dynamics beyond industrial production are increases in national vehicle miles traveled, and changes in wet deposition sulfate concentrations. These factors will be discussed more fully in the following sub-sections.

4.3 ACIDITY

In general, trace metal mobility increases in more acidic solutions. Metal uptake patterns are affected by mobility and, because of this, it is important to consider local environmental acidity trends. Acidity in regional precipitation has been decreasing since the enactment of the Clean Air Act in 1970. According to the EPA, national sulfur dioxide emissions peaked in 1970 before decreasing through 1998 (EPA 2000) and this pattern is found in both the NADP PA42 and reconstructed West Virginia wet deposition of sulfate data set. Metal data were compared to sulfate wet deposition data and the resulting r^2 values show relatively clear relationships, particularly when compared with other environmental parameters (Table 2), suggesting acidity is a major factor affecting metal loading.

It is important to consider that sulfate is not the only source of environmental acidification. The Fernow Watershed Acidification Study found that nitrogen deposition controlled the forest acidification process rather than sulfate (Adams, Kochenderfer et al. 2007). This was due to the longer residence time of nitrates compared to sulfates in soils, causing continued acidification for periods extending beyond initial deposition. Acidification also caused initial cation depletion in the soils by increasing cation mobility and therefore leaching.

Similar soil acidity processes may be occurring in Schenley Park, particularly due to heavy traffic and associated nitrate deposition in and near the park (Figure 6). This acidity could be increasing metal bioavailability, and metal uptake by the tree, beyond what is expected given the sulfate wet deposition data.

4.4 SOIL COMMUNITY FACTORS

Simple acidity is an important control on metal mobility. However, available data do not indicate acidity is the only control on tree ring metal concentrations. Therefore, we must examine other potential controls on metal assimilation. For instance, metal storage in the soil ecosystem and variation in the bioavailability of these metals could be causing this recent high metal uptake. Possible changes in soil microbial community structures could have occurred during these recent periods as improving environmental conditions should allow changes in soil acidity, soil microbial community, and plant chemistry affecting bioavailability of the metals.

While changes in soil acidity remain indeterminate, they do affect biological community structure in the soil environment due to differences in acidity tolerances across species. Decreasing wet deposition sulfate concentrations from the late 1970s onward may have changed species richness and diversity in the Pittsburgh regional microbial community and therefore metal processing in these communities. Beyond the microbial community, plants rooted in these soils may have changed soil chemistry via root exudates. Such changes can impact plant uptake patterns (Stone 1997). For instance, plant nutrients like zinc and copper may have been less readily available in less acidic soil environments, causing plants to work harder to assimilate these metals. This study does not focus on microbial communities or plant chemistry characteristics, but these are factors to consider in continued research.

4.5 TRANSPORTATION PATTERNS

Metal data are clearly correlated to VMT data (Table 5). However, vehicle data only date back to 1970, which may be causing an artificially high correlation due to the relatively small period of overlap. National vehicle miles traveled increases steadily from the 1970s until present. This parallels the found metal concentration increases in tree rings during this same period.. Although VMT data are only available for this forty-year period, it is unlikely there were earlier peaks in VMT as increased consumption, road infrastructure, suburbanization, and national population increases have all occurred over similar periods. For example, a U.S. Geological Survey study (Mahler, Van Metre et al. 2006) analyzed lake sediments beginning in the 1970s and found that zinc concentrations increased through this period, especially in urban lakes and concluded that increased VMT over this time period was causing increased zinc emissions from tires. Vehicle emissions include the trace metals analyzed (Table 1), and increases in VMT could be causing the recent increases in tree ring concentrations. As noted above, nitrogen oxide is also a vehicle emission and, like sulfate, causes acidification. Thus, increases in VMT may be increasing acidity in Pittsburgh soils and metal uptake by plants. Vehicle emissions should impact the tree as it grew in close proximity to several major commuter routes including Boulevard of the Allies and Interstate Highway 376 (Figure 1). Nickel, copper, cadmium, and lead are also associated with vehicular wear (Table 1) and increased traffic close to the tree may contribute to increased concentrations in the later years.

4.6 LEAD

Lead emissions are regulated under the Clean Air Act and are of special interest in this study due to the introduction and phase out of tetraethyl leaded gasoline and the toxic effects on humans and ecosystems. Previous tree ring studies have found lead concentration levels to increase following this introduction of leaded gasoline and increased vehicular traffic (Baes and Ragsdale 1981; Watmough 1999; Watmough and Hutchinson 2003).

Lead is present in low concentrations with low variability before 1900. However, it does peak before the 1920s, suggesting that gasoline is not the only source of lead in this study. A peak in the 1920s and decrease during the 1980s though do suggest some influence by the introduction and phase out of tetraethyl leaded gasoline. The sudden drop in lead values in 1940 could also be due to reduced availability of gasoline following World War II. The increasing lead concentration values from the 1940s until the early 1980s may be due to increasing urban traffic. Peak usage of leaded gasoline in the United States occurred from the late 1960s to the early 1970s (Mielke et al. 2000), and national vehicle miles traveled increased through 2006.

4.7 SUMMARY OF METAL AND HISTORICAL RELATIONSHIPS

Overall, the five metals analyzed are nominally related to historic pollution sources and air quality changes until the 1980s. However, these industrial parameters cannot explain the elevated metal concentrations observed from the 1980s until 2006. Metals during this later time period may instead be representing accumulated soil pollution rather than air pollution, (Figure 3). Changes in soil metal bioavailability, directly related to acidity, also seem to be an important control on trace metals assimilated into tree materials. Based on these two important observations, acidity and trace metal emissions resulting from vehicular traffic is a bigger pollution source in recent decades of data than originally assumed.

4.8 SUGGESTIONS FOR FUTURE WORK

As with any study, this work does not reconstruct the complete picture of historical pollution. A number of continuations are suggested. Examination of urban biota, especially soil communities, is suggested in order to better understand the relationship between soils and metal bioavailability. Comparing other local red oak trees not located in highly trafficked or historically manufactured areas is also suggested. This will allow for comparison of recent decadal data trends among trees and for improvement of conclusions drawn on trace metal sources.

5.0 CONCLUSIONS

The aim of this study was to examine the role of historical pollution in Pittsburgh's environment through studying trace metal concentrations in a Pittsburgh red oak tree. Trace metal concentrations were found to be related to steel, sulfate wet deposition concentrations, and vehicle miles traveled. However, as steel production declined beginning in the early 1980s and sulfate concentrations followed, the tree ring record indicates a period of increasing concentrations of all metals examined. This pattern may indicate a stronger influence from vehicular traffic than previously considered. Vehicle emissions from fuel, engine, tire, and brake pads may cause increases in metal concentrations and metal availability in soils close to roads. Nitrate and acidity changes in the last two decades may be increasing metal mobility and metal retention and uptake in urban ecosystems. In particular, nitrates from car emissions may also be playing a bigger role in soil acidity than commonly recognized.

This study found trace metal legacy pollution is incorporated into vegetation in even higher amounts in the last two decades than during the peak of the Pittsburgh manufacturing era. While this pattern may result in part due to vehicle traffic, legacy pollution likely also plays a significant role. It is important to realize that although Pittsburgh is visibly less polluted, emissions of pollutants continue and may interact with legacies in the Pittsburgh urban ecosystem.

APPENDIX A

TRACE METAL CONCENTRATION VALUES PER ANNUAL TREE RINGS

Table 6. Trace metal concentration values per annual growth ring (ppm) calculated in this study. Rings without a value have not yet been analyzed. Rings with dashes (-) were below the detection limit of the ICP-AES used in this study.

	Metal Concentration in Annual Tree Ring (ppm)				
Ring (Year)	**Zinc**	**Nickel**	**Copper**	**Cadmium**	**Lead**
1881	2.960219	-	0.983158	-	-
1882					
1883					
1884	2.362652	0.286477	0.086974	0.052005	0.015691
1885	0.412306	0.200573	0.023964	0.009192	0.018383
1886	3.66779	0.924985	-	0.075433	-
1887					
1888					
1889	0.072483	0.149734	0.004451	0.01367	-
1890	0.626672	0.579416	0.1605	0.057473	0.000426
1891	0.141728	0.158486	-	0.006323	-
1892	0.134259	-	0.066337	0.02909	0.023955
1893	0.133808	-	0.091047	0.059764	0.005651
1894					
1895					
1896	0.292883	0.181075	0.494429	0.034391	0.023434
1897	-	-	0.063899	-	0.003444
1898	0.153442	0.151494	0.159252	0.030288	-
1899	0.212559	0.230902	0.206865	0.047999	0.031404
1900	0.287617	0.321257	0.328309	0.090542	0.039427
1901					
1902	0.281462	0.415796	0.145529	0.043179	-
1903	0.818986	0.215796	0.206436	0.02184	0.058239
1904					
1905					

1906					
1907					
1908	0.438459	0.27685	0.137061	0.021821	0.167747
1909	0.324202	0.290032	0.125014	0.024169	0.02667
1910	0.485595	0.599162	0.141958	0.03035	-
1911	0.279346	-	0.07593	0.03234	-
1912	0.471066	0.512084	0.16984	0.026918	-
1913	0.357116	0.574373	0.124244	0.030552	-
1914	0.266311	0.438319	0.141831	0.023387	0.076951
1915	0.116274	0.321399	0.044974	0.027697	-
1916					
1917					
1918	0.237381	0.91489	0.104621	0.019481	-
1919					
1920	0.29012	0.658892	0.084304	0.021665	-
1921	0.515648	0.777452	0.220234	0.047762	-
1922	0.377029	0.682327	0.272056	0.041989	0.106723
1923	0.539682	0.532643	0.398113	0.049275	-
1924	0.342472	0.540669	0.288551	0.04372	0.115129
1925	0.460949	0.753981	0.2634	0.04829	-
1926	0.359279	0.484799	0.238306	0.047297	-
1927	0.366404	0.475047	0.235038	0.040475	0.072429
1928	0.432068	0.386184	0.26077	0.048942	0.091767
1929	0.474059	0.787465	0.401195	0.056185	0.148363
1930	0.522579	0.469313	0.250492	0.039589	0.07342
1931	0.623413	0.709298	0.316889	0.048866	0.18658
1932	0.455076	0.537181	0.325873	0.050918	-
1933	0.526895	0.612808	0.299795	0.049265	0.158609
1934	0.454302	0.49904	0.298038	0.048518	0.12602
1935					
1936	1.004232	0.695297	0.344129	0.057094	-
1937	0.247142	0.326784	0.289492	0.039821	0.018962
1938					
1939	0.34182	0.387948	0.403916	0.043762	0.005914
1940					
1941					
1942					
1943	0.589737	0.508194	0.487079	0.061158	0.107026
1944	0.314837	0.32692	0.34236	0.044977	0.065787
1945	0.411385	0.257874	0.342821	0.045507	0.014562

1946	0.284501	0.344093	0.262715	0.03332	-
1947	0.232133	0.233419	0.222488	0.032151	0.061731
1948					
1949	0.787635	0.475492	0.526438	0.061458	0.069545
1950					
1951	0.55678	0.383923	0.550411	0.069143	0.176496
1952	0.999291	0.447795	0.783642	0.076597	0.071883
1953	0.413839	0.361772	0.277389	0.03501	0.030522
1954					
1955	0.450794	0.227066	0.389352	0.052092	0.007346
1956	0.307614	0.224795	0.266205	0.040565	0.022818
1957	0.729459	0.26301	1.633134	0.039339	-
1958	0.737828	0.020581	0.481595	0.055569	0.084382
1959	0.670913	0.411477	0.470604	0.071194	0.123081
1960	0.547473	0.264215	0.559375	0.067839	0.126157
1961	0.456508	0.120619	0.311598	0.03518	0.092977
1962	0.486927	0.572417	0.319662	0.060401	0.020443
1963	0.485448	0.577666	0.153986	0.037409	-
1964	0.931003	-	0.110431	0.046752	-
1965	1.520924	0.464308	0.524543	0.051032	0.038483
1966					
1967					
1968	0.766059	0.588731	0.62597	0.056745	0.055858
1969					
1970	0.803306	0.341793	0.526398	0.04935	0.114236
1971					
1972	0.818834	0.44062	0.565431	0.055787	0.021747
1973	0.695032	0.682805	0.762748	0.059252	0.135432
1974	1.1812	0.179371	0.499262	0.048769	-
1975	0.840692	0.361392	0.717032	0.064226	-
1976	0.759936	0.777096	1.171772	0.058834	0.133193
1977					
1978	0.484438	0.435669	0.303993	0.039828	-
1979					
1980	0.596486	0.087798	0.228095	0.039826	0.144822
1981	1.030219	0.667686	0.453818	0.051294	-
1982	0.506171	0.514142	0.491225	0.048824	-
1983	0.961949	0.651749	0.914099	0.063525	-
1984	3.378197	0.548764	0.383722	0.052607	-
1985	1.842985	0.477496	0.570017	0.061681	0.002127

1986	2.151709	0.697216	0.86521	0.084432	0.056578
1987	0.897891	0.360948	0.366708	0.040959	0.033919
1988	0.685544	0.65866	0.325711	0.04653	0.01034
1989					
1990	2.076019	0.815579	0.605011	0.057338	-
1991	0.921806	0.425449	0.371761	0.079012	0.084077
1992	1.474331	0.792235	0.474375	0.053138	0.154583
1993	0.459118	0.324357	0.248147	0.048328	0.016729
1994	1.425105	0.473438	0.43702	0.055586	0.040252
1995					
1996					
1997	0.575578	0.394576	0.642115	-	0.187982
1998	2.40127	0.891681	0.843614	0.071056	0.179729
1999	0.095993	0.968185	0.878181	0.093219	0.178722
2000	1.290958	1.206948	0.863328	0.077039	0.168141
2001	4.832354	0.883825	1.071479	0.091396	0.276135
2002	4.157133	1.018905	0.934581	0.102593	0.288104
2003	4.383007	0.922944	1.131193	0.090926	0.192606
2004	3.986064	0.862106	1.335605	0.083004	0.196191
2005	2.075189	0.847594	1.605019	0.086304	0.282103
2006	2.562722	0.854713	2.026031	0.097509	0.320216

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