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PLANT UPTAKE, TIME TRENDS, AND NATURAL ATTENUATION OF
SELECTED METALS IN AN ABANDONED MINING DISTRICT

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PLANT UPTAKE, TIME TRENDS, AND NATURAL ATTENUATION OF
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Abstract

Soils, vegetation, and water in the abandoned Tri-State mining district are contaminated by lead, zinc, and other metals. To investigate trends in lead and zinc concentrations in the environment for past periods when little environmental monitoring occurred, 32 tree cores were sampled in the mining district and 6 reference tree cores were sampled at a reference site in Norman, Oklahoma. The hypotheses of this work were that lead and zinc contents in tree growth rings would have decreased after mining ceased ca. 1970, increased with rising water tables and seepage of groundwater from the mine workings starting in late 1979, again increased with short-term disturbance of tailings caused by reclamation activities in the late 1990s and early 2000s, and that tree growth rings sampled from trees in the reference area would have different periods of significant changes of lead and zinc contents than tree growth rings sampled in the mining district. Except for lack of significant decreases in lead and zinc contents of tree growth rings after the mines closed ca. 1970 to 1980 and lack of significant decreases of zinc in the 2000s, content of lead and zinc in tree rings corroborated those hypotheses.

Tissues from 32 upland and 32 wetland trees in the abandoned mining district, and 6 reference site trees were sampled to test the hypotheses that wetland tree tissues have greater lead and zinc concentrations than upland trees and that mining district trees have elevated concentrations of those metals compared to trees at a reference site. Those hypotheses were only partially supported by lead and zinc concentrations of tree tissues in the three sample groups. Bole wood of upland trees had greater lead concentrations than bole wood of wetland trees and similar lead concentrations as those

in bole wood of reference trees. Similar lead concentrations in samples of bole wood and other tissues in trees from both the mining district and the reference site, despite much smaller lead concentrations in soils at the reference site, may indicate natural limits to lead uptake by trees. Commercial nut samples had similar lead and zinc concentrations as nuts sampled from reference trees and wetland and upland trees in the mining district, refuting the hypothesis that nut tissues of trees in the mining district would have greater lead concentrations. Concentrations of zinc in bole wood, twigs, and leaves of wetland trees were 5-10 times greater than in upland trees in the mining district, supporting the hypothesis of greater zinc concentrations in wetland trees. However, zinc concentrations in nut and hull tissues were similar in upland and wetland trees. Zinc concentrations in reference tree bole wood samples were similar to those in bole wood samples from upland trees, but zinc concentrations of other types of reference tree tissues ranged from one-tenth about half of those in upland tree tissues.

Comparison to lead and zinc concentrations of tree tissues at other mining and commercial areas and estimates of lead and zinc concentrations in biomass of selected trees in the mining district indicate that trees may be useful for phytostabilization in this mining district, refuting the hypothesis that very large lead and zinc contents of trees in the mining district would preclude planting of trees for phytoremediation. Reference soil samples supported the hypothesis of having less total lead and zinc concentrations than mining district soils. Unlike soils in the mining district, zinc concentrations were not substantially greater than lead concentrations in the reference soils. Nearly half of the upland soil samples collected in the mining district had lead concentrations exceeding a residential clean-up standard of 500 mg/kg, with none of the reference soil

samples having lead concentrations exceeding that standard.

At a stream site receiving drainage from most of the Oklahoma part of the mining district, total concentrations of iron, manganese, and zinc significantly decreased from the mid-1980s to the mid-2000s. Natural attenuation and long-term effects of reclamation activities probably are causing gradual decreases in metals concentrations in the aquatic environment of this abandoned mining district, similar to gradual decreases with time of lead and zinc contents in many, but not all of the tree cores.

Data collected from terrestrial and aquatic environments of the mining district in this dissertation indicate that metals concentrations have decreased gradually since cessation of mining ca. 1970. Natural events, such as filling of the mine workings with groundwater and subsequent seepage to local streams starting in 1979, and short-term disturbance and dissemination effects of reclamation activities in the late 1990s through early 2000s temporarily increased metals concentrations in the local environment.

Several different types of reclamation methods can be used to reclaim large metals-contaminated sites such as this mining district. Treatment of groundwater seepage from the mine workings, whether by passive or active systems, is being done at one site in the district to reduce quantities of metals discharging to a local stream. Phytoremediation, particularly with high-value hardwood trees, is likely to reduce erosion of fine tailings particles by wind and water, minimize bioavailability of metals to local wildlife, and improve the local economy by producing high-value agricultural products and forming a potential basis for industries using those materials. Better management of metals-rich fine tailings particles during excavation and transport of the

millions of tons of tailings remaining in the mining district would minimize dissemination of fine tailings to the local environment and improve the quality of terrestrial and aquatic environments of the mining district during reclamation activities.

Monitoring of the media described in this dissertation and other environmental media such as growth rings in freshwater mussel shells from local rivers, age-dated cores from Grand Lake (the downstream recipient of most drainage from the mining district) metals in terrestrial wildlife and livestock, regular periodic water-quality sampling of local streams, and collecting air-quality and atmospheric deposition samples in the mining district would augment knowledge of trends of metals and the short- and long-term effects of natural attenuation and reclamation projects on the recovery of metals-contaminated terrestrial and aquatic systems in the past and the future.

CHAPTER 1

Introduction

1.1 Description of the Setting of the Mining District

The abandoned Tri-State mining district (Figure 1.1) is a 3,100 km² area including parts of Jasper and Newton Counties in southwest Missouri, Cherokee County in southeast Kansas, and Ottawa County in northeast Oklahoma. This mining district was a major source of zinc and lead to industry in the U.S. and elsewhere from the early 1800s to 1970, producing 11.7 million tons of zinc, and 2.8 million tons of lead (Table 1.1; Figure 1.2; Stewart, 1986). Investigation of metals presence and distribution in the terrestrial and aquatic environments of this district should provide information useful not only for reclamation of this abandoned mining district, but for reclamation of millions of other metals-contaminated sites around the world.

The abandoned Tri-State mining district is situated on the Osage Plains on the northwest side of the Ozark Uplift, and is drained by numerous creeks and the Neosho, Spring, and Elk Rivers (McKnight and Fisher, 1970; Gibson, 1972). The district has a warm, humid, continental climate, with large seasonal variations in temperature and precipitation and annual average of 45 inches of precipitation (Oklahoma Climatological Survey, 2010). Summers in the district are warm, with daytime high temperatures of 38 °C or more and average daily temperatures of 25 °C (Oklahoma Climatological Survey, 2010).

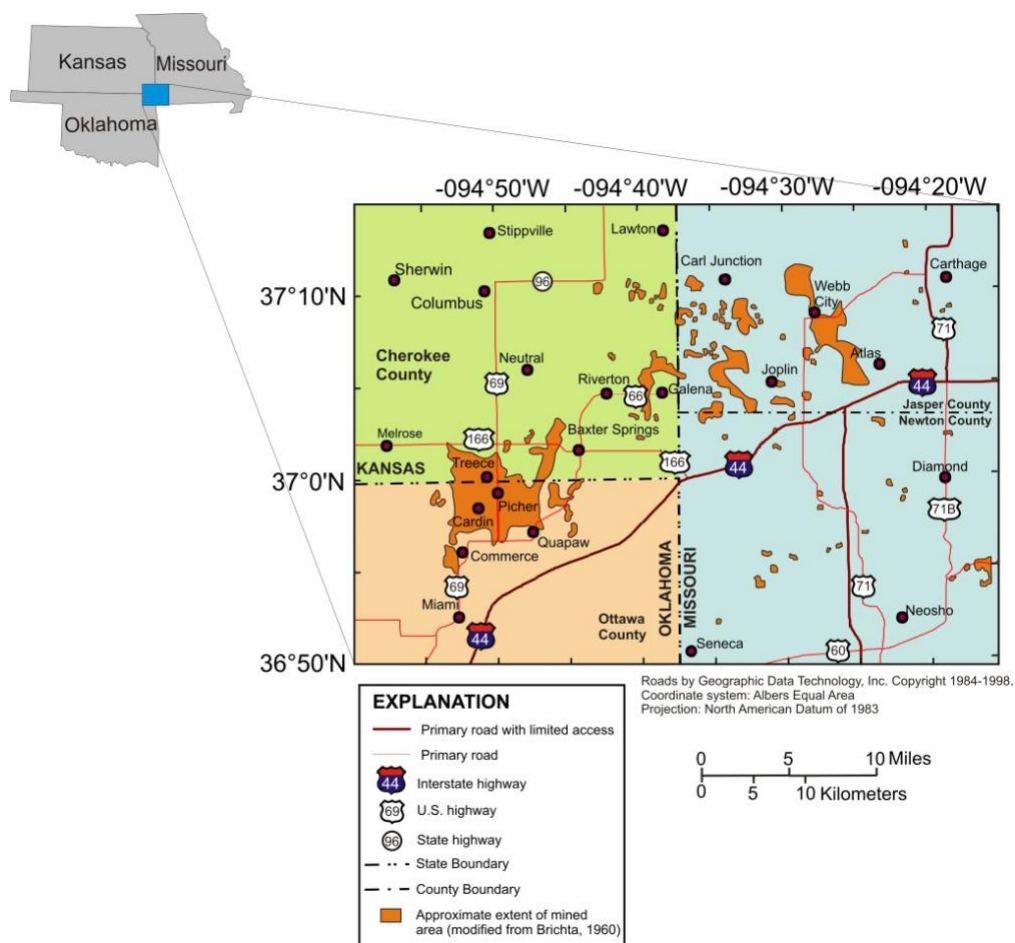


Figure 1.1 Location of the Tri-State mining district and mined areas in the district.

Table 1.1 Total production of lead and zinc from the Tri-State mining district.

[modified from Stewart (1986)]

State	Operating Period	Estimated Tons of Rock Mined	Recoverable Metal (tons)	
			Lead	Zinc
Missouri	1850-1957	196,000,000	885,390	3,618,930
Kansas	1876-1970	115,000,000	691,338	2,900,000
Oklahoma	1891-1970	187,000,000	1,306,679	5,219,998
Totals	1850-1970	498,000,000	2,883,407	11,738,928

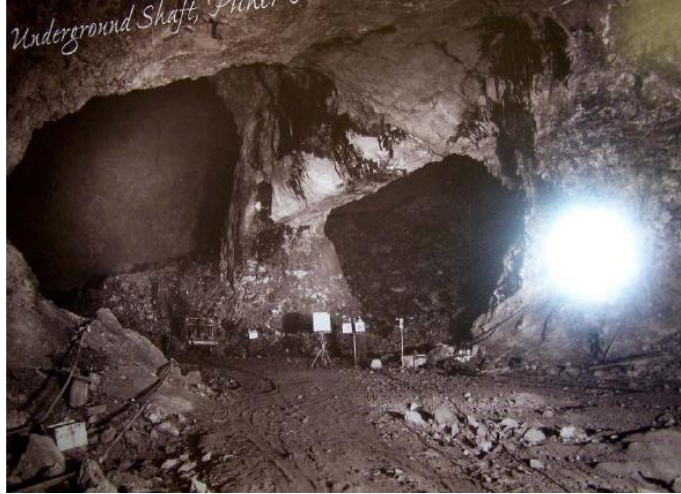


Figure 1.2 Underground mine workings near Picher, Oklahoma ca. 1925 (Northeast Oklahoma A&M College photo)

Topographic relief in the mining district ranges from nearly flat in the Oklahoma part of the district to gently rolling prairie with small hills and incised stream valleys in other areas (McKnight and Fisher, 1970; Gibson, 1972). Hills in the district are heavily wooded. White and blackjack oaks (*Quercus alba* L., and *Quercus marylandica*) are the predominant native tree species (Gibson, 1972). In the Oklahoma part of the Tri-State mining district, also known as the Picher mining district, predominant trees near streams and wetlands include: black willow (*Salix nigra*), river birch (*Betula nigra*), and southern catalpa (*Catalpa bignonioides*). On drier uplands away from stream valleys, predominant trees include plains cottonwood (*Populus deltoides* var. *occidentalis*), green ash (*Fraxinus pennsylvanica*), box elder (*Acer negundo* L.), sycamore (*Platanus occidentalis*), eastern red cedar (*Juniperus virginiana* L.), Osage Orange (*Maclura pomifera* (Raf.) Schneid), and various species of elms. The trees that have invaded the more recently mined Picher mining district are those that propagate by spreading small windblown seeds, such as cottonwoods and elms. There

are relatively few trees that bear larger seeds or nuts, such as oak or hickory, in the mined upland areas of the Picher mining district. Greater numbers of those types of trees can be found in older parts of the mining district, undisturbed stream valleys, and areas surrounding the mining district in Kansas and Missouri.

The mining district is underlain by approximately 360 m of sedimentary rocks ranging in age from Ordovician (445 to 490 million years before present) to Mississippian (299 to 359.2 million years before present) (Christenson, 1995). Much of the district is underlain by a sequence of almost 90 m of cherty limestones of the “Boone Chert” or Boone Formation of early Mississippian age (Table 1.2). The base of that sequence of limestone units is the Chattanooga Shale, which consists of up to 21 m of black, fissile shale of late Devonian age (360-415 million years before present). The Chattanooga Shale forms a basal confining unit, separating the near-surface Boone aquifer, from which the metallic sulfide minerals were mined, from the underlying Roubidoux aquifer, which is now the sole-source water supply aquifer in much of the district. Despite confinement by the Chattanooga Shale, parts of the Roubidoux aquifer have become contaminated by metals-rich mine water from the overlying Boone Aquifer (Christenson, 1995). The Boone Formation is overlain by as much as 16 m of the calcareous Hindsville Formation of late Mississippian age (330-320 million years before present). Beneath most of the Oklahoma part of the mining district, the Hindsville Formation is overlain by several meters of black, fissile shale of the Fayetteville Formation of late Mississippian age (Huffman, 1958), which are, in turn, overlain by several meters of the MacAlester and Hartshorne Formations of Pennsylvanian age (Marcher and Bingham, 1971). In most of the mining district, the

water table is several meters below the land surface, but in areas underlain by shales of the Fayetteville, MacAlester, and Hartshorne Formations, there is a perched water table near or above the land surface that causes soils in some areas to be perennially waterlogged. Areas underlain by this shale, including the City of Miami, Oklahoma, are subject to periodic flooding due to this low-permeability unit.

Numerous carbonate and metallic-sulfide and metallic-disulphide minerals precipitated in local karstic, fractured cherty dolomites and limestones. Precipitation of those minerals was caused by supersaturation of carbonate minerals and reactions between metal-bearing hydrothermal water and natural asphalt. In the late 1800s, asphalt was reported to seep from the headwaters of Tar Creek (Keheley et al., 2003; Gibson, 1972; McKnight and Fisher, 1970). Reducing conditions caused by the chemical and biological oxygen demand created by the organic compounds in asphalt and the sulfide solubilized from the asphalt combined with metals dissolved in groundwater to precipitate metallic sulfide and disulphide minerals. Such minerals included sphalerite (ZnS), galena (PbS), marcasite and pyrite (FeS₂), and lesser amounts of other metallic minerals in voids in the cherty dolomitic limestone host rocks.

Development of the mining district proceeded from east to west. Mining started in the Missouri portion of the district, gradually progressing westward in the late 1800s and early 1900s to the Kansas and Oklahoma parts of the district (Table 1.3). Initially, mining was concentrated on recovery and smelting of the lead-sulfide mineral galena (PbS) due to its ready identification, easy separation from the host rock due to its great density, the ease (low temperatures) at which it can be smelted, and the demand for

lead for bullets, paints, plumbing fixtures, and other uses (Keheley et al., 2003). When zinc smelters opened in 1872 in St. Louis, the zinc sulfide mineral sphalerite (ZnS), which had been discarded as waste rock, became a profitable commodity. As the price of zinc rose from \$3 per ton in 1872 to \$27 per ton in 1888, zinc mining surpassed lead mining in the district. Mines were increased in depth from the water table to more than 100 meters below the land surface, with zinc being the primary metal mined below the water table (Gibson, 1972).

Mining below the water table required continuous pumping. Even during times of mine shutdowns, pumping had to be continued to prevent flooding of mines. Water from the mines was pumped out into sludge ponds, which also were used as reservoirs for washing and milling of ores. When those ponds were full, excess water was pumped to local creeks. Those creeks became discolored and contaminated by deposits of iron oxides, oxyhydroxides, and acids (Figure 1.3). Those deposits clogged local creeks, destroying vegetation and habitat for aquatic wildlife (Gibson, 1972).

From 1850-1950, the Tri-State mining district produced 50 percent of the zinc and 10 percent of the lead in the United States (Kansas Geological Survey, 2003). From the early 1900s to 1950, the Oklahoma (Picher) part of the mining district produced 5.2 million tons of zinc and 1.3 million tons of lead (Stewart, 1986). By 1926, the peak year of production, the Picher mining district was the world's largest source of lead and zinc for industries in the U.S. and elsewhere (Everett, 2004). From 1908 through 1930, district mines produced more than 50 percent of the zinc and 45 percent of the lead needed for World War I (McKnight and Fisher, 1970; Everett, 2004). After 1915, more than 90 percent of ores produced in the Tri-State mining district came from the Picher

mining district (Everett, 2004). From 1908-1950, the entire Tri-State mining district had produced metals with value exceeding \$1 billion (McKnight and Fisher, 1970). Although many mines ceased production in the 1950s, the Tri-State Ore Producers' Association (1954) estimated that reserves of 2,402,433 tons of zinc concentrates; 312,649 tons of lead concentrate, and substantial quantities of germanium and cadmium remained in the district.



Figure 1.3 Water seeping from mines staining the bed and banks of Tar Creek near Douthat, Oklahoma with goethite and other iron oxides and hydroxides (W.J. Andrews photo).

Table 1.2 Stratigraphic column for the Tri-State mining district.

[modified from Huffman, 1958; Marcher and Bingham, 1971; McKnight and Fisher, 1970; Luza, 1986; Christensen, 1995]

System	Series	Geologic Unit		Range in Thickness (meters)	Lithology	
Pennsylvanian	Desmonian	Krebs Subgroup of Cherokee Group	Boggy Formation, Savanna Formation, McAlester and Hartshorne Formations	0-80	Interbedded black shales, fine-grained sandstones, and coals	
Mississippian	Chesterian	Fayetteville Shale		5-20	Black, fissile shale with some thin interbeds of blue-black limestone	
		Batesville Sandstone		0-12	Tan to gray, medium to fine-grained, oolitic calcareous sandstone.	
		Hindsville Limestone		0-12	Light gray, medium, crystalline limestone, with abundant crinoid fossils	
	Meramecian	Quapaw Limestone		0-8	Medium to coarse-grained light-gray to brownish-gray crinoidal limestone	
		Boone Formation	Moccasin Bend Member		0-40	Alternating chert, tripoli, and fine to medium-grained limestone
			Baxter Springs Member		0-20	Glauconitic, phosphatic cherty crinoidal limestone
			Short Creek Oolite Member		0.3-3	Brown to light brown massive oolitic cherty limestone
			Joplin Member		0-25	Medium to light gray stylolitic, crinoidal, fossiliferous thick-bedded limestone.
	Grand Falls Chert Member		8-30	Flint to porous tripoli containing minor amounts of interstitial calcite		
	Reeds Spring Formation		0-32	Blue-white to tan, thin-bedded flint and blue-gray fine fossiliferous limestone		
Osagean	St. Joe Member		2-10	Gray, fine to medium crystalline limestone with small crinoid stem plates and green calcareous shale at the base		
	Upper Devonian					
Devonian	Kinderhookian & Upper Devonian	Chattanooga Shale		0-20	Black, fissile shale with basal sandstone	

Table 1.3 A history of mining in the Tri-State mining district.

[modified from Keheley et al., 2003; Gibson, 1972]

Dates	Location	Involved Parties	Ores Mined	Ore Processing
1700s	Throughout the district	French traders and Native Americans	Galena	Surface mining above the water table with crude and inefficient furnaces
1848	Confluence of Leadville Hollow and Turkey Creek, 3.2 km northwest of the current location of Joplin, Missouri	William Tingle	Galena	First discovery of “commercial” ore deposit
1850	Spurgeon, Newton County, Missouri	Mr. Spurgeon	Galena	First lead smelted in Newton County in crude log furnace
1852	Neosho, Newton County, Missouri	J.W. Moseley	Galena	First use of blast furnace to smelt lead in the district.
1854	Granby, Newton County, Missouri	--	Galena	--
1855	Oronogo, Jasper County Missouri	--	Galena	Mines had produced 419,000 pounds of lead. Erected 6 “Scotch hearth” blast furnaces for smelting lead, Production in entire region was 4,000 tons
1856	Granby, Missouri	Blow & Kennet	Galena	300 mineshafts had been sunk near Granby
1860	Granby, Missouri	--	Galena	Production had reached 35,414,014 pounds of refined lead
1861	Granby, Missouri	Blow & Kennet	Galena	Local miners left due to skirmishing at onset of Civil War
1861-1862	Southwest Missouri	All	Galena	Operation of mines and smelters by Confederate troops produced 200,000 pounds per month of lead—to supply Confederate ammunition
1861-1862	Granby, Missouri	Confederate troops	Galena	Union troops occupied area and conducted limited mining and smelting of lead.
1863-1865	Granby, Missouri	U.S. troops	Galena	Mines reopened throughout Southwest Missouri
1865	Southwest Missouri	All	Galena	

Table 1.3 A history of mining in the Tri-State mining district, continued.

[modified from Keheley et al., 2003; Gibson, 1972]

Dates	Location	Involved Parties	Ores Mined	Ore Processing
1869	Granby Missouri	--	Zinc silicate hydrate	First shipment of zinc ores for smelting in St. Louis and central Illinois
1870-1877	Southwest Missouri	--	Zinc ores	Expansion of railroads facilitates shipment of zinc ores to St. Louis and central Illinois smelters
1870-1877	Quapaw Territory	--	Galena	Limited surface mining by Quapaw tribe to produce lead shot near Peoria
1874	Joplin, Missouri	--	Galena	200 tons of lead produced weekly
1876	Webb City, Carterville, and Galena, Jasper County, Missouri	--	Galena	New discoveries and commencement of mining
1876	Jasper County, Missouri	--	--	Interurban electric trolleys enabled many miners to live in the rapidly growing City of Joplin, limiting the growth of surrounding mining towns.
1880-1890	Southwest Missouri	--	Lead and zinc ores	Joplin becomes center of mining industry and support industries. Major consolidations and mergers of mining companies. Development of large scale mining of sheet-ground ore deposits between Duenweg to Oronogo and expansion of prospecting and mining
1891	Peoria Reservation, Oklahoma	--	Lead and zinc ores	First commercial ore production in Oklahoma
1893-1894	Peoria, Oklahoma	--	Lead and zinc ores	1,400 tons of galena, 56 tons of sphalerite, and 332 tons of silicate produced
1897	Lincolnville, Oklahoma (Maud Abrams Farm)	--	Galena	Beginning of Lincolnville mining camp
1904	Quapaw, Oklahoma	--	Galena	Mining commenced, producing more than \$1 million by 1914.

Table 1.3. A history of mining in the Tri-State mining district, continued.

[modified from Keheley et al., 2003; Gibson, 1972]

Dates	Location	Involved Parties	Ores Mined	Ore Processing
1907	Commerce, Oklahoma (Emma Gordon Allotment)	Commerce Mining and Royalty Company	Lead and zinc ores	Beginning of the Miami mining camp
1908-1914	Commerce Oklahoma	--	Lead and zinc ores	Production of \$1,702,472 of lead concentrates and \$3,095,816 of zinc concentrates
1914	Picher, Oklahoma (Ethel Crawfish Allotment)	O.S. Picher and A.E. Bendelari	Lead and zinc ores	Discovery of Picher Field. 90 percent of production after 1915 came from this field.
1916	Picher, Oklahoma	Picher Company	Lead and zinc ores	Four large mills to process ores in operation
1916	Picher, Oklahoma	Picher Lead Company, Eagle White Lead Company	Lead and zinc ores	Companies combine to form the Eagle-Picher Lead Company
1916	Treece, Blue Mound, and Baxter Springs, Kansas	--	Lead and zinc ores	Outbreak of World War I and expansion of mining district into southeast Kansas, Mining industry migrates from Joplin, Missouri to Oklahoma and Kansas fields
1920	Ottawa County, Oklahoma and Cherokee County, Kansas	--	Lead and zinc ores	90 percent of ore production occurred in the Oklahoma and Kansas portions of the district
1925-1926	Tri-State mining district	--	Lead and zinc ores	Peak of mine production, with \$74,009,833 of lead and zinc concentrates produced
1929-1942	Tri-State mining district	--	Lead and zinc ores	Metals prices less than the cost of production, many mines shut down
1942-1944	Tri-State mining district	--	Lead and zinc ores	Government institutes "Premium Price Plan" to encourage metals production, 9 million tons of ore concentrates produced annually, total historic production of district exceeded \$1 billion

Table 1.3. A history of mining in the Tri-State mining district, continued.

[modified from Keheley et al., 2003; Gibson, 1972]

Dates	Location	Involved Parties	Ores Mined	Ore Processing
1945-1957	Tri-State mining district	--	Lead and zinc ores	Mining gradually declines until closure of most mines, pumping about 30 million gallons of water per day to keep mines dry tapered off after 1957
1960-1965	Tri-State mining district	--	Lead and zinc ores	Some smaller mines reopened under Federal subsidy program
1965-1970	Picher field	--	Lead and zinc ores	Some “Gougers” continue to mine out support pillars
1979	Picher field	--	--	Mines filled with water and acidic, metals-rich water begins seeping out near Commerce, Oklahoma

1.2 Environmental Legacies of the Mining

After abandonment ca. 1970, the mining district continued to be affected by severe environmental degradation. Soils and streams in more than 180 km² of the mining district and downstream areas were contaminated by metals. Little environmental monitoring was conducted in the district until late 1979, when metals-laden water started to flow from the abandoned mines to local streams. Parts of this mining district are affected by some of the most severe and widespread environmental degradation of any of the tens of thousands of abandoned mining sites in the U.S. (Robertson, 2006; State of Oklahoma 2000a; Ferderer, 1996). Tar Creek, which drains much of the Picher mining district, also is the name for the Superfund site at this location. The Tar Creek Superfund site, included in the initial National Priority List of Superfund sites by the U.S. Environmental Protection Agency in 1983, is one of the largest in the U.S.

Legacies of nearly a century of mining in the Picher mining district as of 2000 included more than 480 km of underground tunnels, 165 million tons of metals-contaminated mine tailings (Figures 1.4 and 1.5), 1,320 vertical mineshafts, and tens of thousands of 10- to 20-cm-diameter test holes, extending down to 120 m below the land surface (State of Oklahoma, 2000a; Gibson, 1972). Subsidence is an ongoing problem in the district, with hundreds of sinkholes reported in Kansas, Oklahoma, and Missouri in areas underlain by mine workings (Figure 1.6; Luza, 1986; Subsidence Evaluation Team, 2006). The large piles of mine tailings that remain in the district only represent part of the material originally removed by miners. From 1942-50, more than 4 million tons of tailings were removed annually from the mining district for use in railroad ballast and concrete (Gibson, 1972). Removal of mine tailings has continued intermittently since the 1940s; tens of millions of tons of tailings have been removed for the aforementioned uses and for use on unpaved roads and driveways and as sub-grade and paving materials for paved roads (Figure 1.7). When mining stopped in the late 1960s, between 165-300 million tons of metals-rich mine tailings remained in the district (State of Oklahoma, 2000a). As of 2000, as much as 75 million tons of mine tailings remained (State of Oklahoma, 2000a).



Figure 1.4 Tailings pile in Douthat, Oklahoma, July 2004 (W.J. Andrews photo)



Figure 1.5 Tailings piles surrounding houses in Picher, Oklahoma (Associated Press, 2008).



Figure 1.6 Sinkhole about 4 miles west of Picher, Oklahoma, August 2004 (U.S. Geological Survey photo).

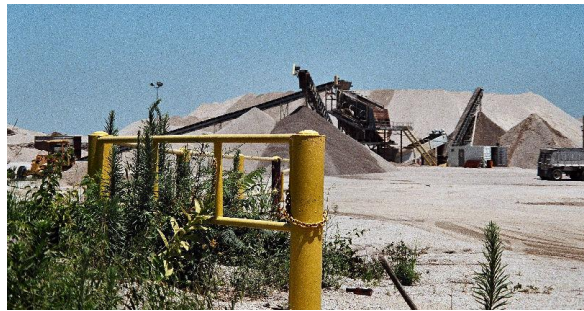


Figure 1.7 Tailings mining operation at Douthat, Oklahoma, July 2004 (W.J. Andrews photo).

Mine tailings remaining in the Picher mining district (Figures 1.4 and 1.5) contain thousands to tens of thousands of milligrams per kilogram (mg/kg, or parts per million) of aluminum, iron, and zinc and can up to several thousands of mg/kg of lead and tens of mg/kg of cadmium. Finer particles in tailings, which are more likely to be transported by air and water, contain the greatest metals concentrations (Table 1.4; Datin and Cates, 2002; Schaider et al., 2007). Although the number of samples analyzed for metals concentrations listed on Table 1.4 is small, similar concentrations were reported for cadmium, lead, and zinc in the 56 tailings samples collected from a local tailings pile (Datin and Cates, 2002) and from 6 tailings piles sampled in the Tar Creek Basin in the Picher mining district (Schaider et al., 2007). Leachate and runoff

from tailings and metals-contaminated soils and seepage of metals-contaminated groundwater from flooded underground mine workings discharge to streams draining the Picher mining district, with Tar Creek being the primary stream draining the district. Along Tar Creek, about 8 km upstream from a streamflow-gaging station at the 22nd Street Bridge at Miami, Oklahoma, as much as 99 percent of iron loading was from mine outflows, with lesser proportions of zinc (19 percent), lead (51 percent), and cadmium (68 percent) being from leachate from mine tailings in 2005 (Cope et al., 2008). Although mine tailings were being removed in the mining district and local roads were being paved in the early 2000s, many of the environmental problems remain in the mining district as of 2011.

Table 1.4 Concentrations of selected metals in a tailings sample from a tailings pile and two millpond fine tailings samples collected near Cardin, OK in 2004.

[Analyses by digestion and ICP-MS, U.S. Geological Research Laboratory, Denver,

Colorado]

Metal	Tailings pile sample		
	Unsieved Concentration, in mg/kg	Sieved Concentration (<2 mm), in mg/kg	Mean of Two Millpond Fine Tailings Samples Metal Concentration, in mg/kg (unsieved)
Aluminum	1,700	4,100	20,300
Cadmium	12.9	31.2	119
Iron	1,690	4,080	16,900
Lead	369	890	9,180
Manganese	13.8	33.2	158
Zinc	3,630	8,750	22,300

CHAPTER 2

Investigation of Historical Uptake of Lead and Zinc in the Tri-State Mining District through Laser-Ablation Inductively-Coupled Plasma Mass Spectroscopy Analyses of Tree Cores

Parts of this chapter are included in:

Andrews, W.J., Nairn, R.W., and Minarik, W.G., 2007, Preliminary assessment of time trends in bioavailable metals in the Tri-State lead/zinc mining district through analysis of tree cores, in 2007 National Meeting of the American Society of Mining and Reclamation, Gillette, WY, 30 Years of SMCRA and Beyond June 2-7, 2007. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502, p. 16-28.

Andrews, W.J., 2006, Investigation of time trends in bioavailable metals in the Tri-State mining district through analysis of metals concentrations in tree rings, in program of 135th SME annual meeting and exhibit and 7th ICARD, March 26-29, 2006, Saint Louis, MO, p. 62.

2.1 Abstract

Soils, vegetation, and water are contaminated by lead, zinc, and other metals in the abandoned Tri-State mining district. Natural attenuation and the long-term effects of reclamation projects may have decreased metals concentrations in the environment for most of the period after mining ceased ca. 1970. However, little environmental monitoring occurred during much of that period. To investigate trends in lead and zinc concentrations in the environment for periods when little environmental monitoring

occurred, 32 tree cores were sampled for lead and zinc content in the mining district and 6 reference tree cores were sampled for comparative purposes at a reference site in Norman, Oklahoma. Hypotheses of this work are that lead and zinc concentrations in tree growth rings gradually decreased after mining ceased ca. 1970, increased with rising water-table elevations and commencement of seepage of groundwater from the mine workings in starting in late 1979, again increased with short-term disturbance of tailings caused by reclamation activities in the late 1990s to the early 2000s, and that tree growth rings sampled in the reference areas would have different periods of significant changes in lead and zinc contents than trees sampled in the mining district. With the exceptions of lack of significant decreases of lead and zinc contents in tree growth rings from 1970 to about 1980 and lack of significant decreases in zinc concentrations in the 2000s, trends of contents of lead and zinc in tree growth rings from the early 1960s to the early 2000s corroborated those hypotheses.

2.2 Introduction

Very little environmental monitoring was done in the Tri-State mining district after the mines were abandoned ca. 1970. The few efforts at environmental monitoring (primarily water-quality sampling) that took place in the district were done after groundwater began seeping from the mine workings near Commerce, Oklahoma in November 1979, and during reclamation activities in the late 1990s to the early 2000s. The hypotheses of this chapter are that metals concentrations in tree rings decreased after cessation of mining ca. 1970, increased after water table elevations increased and groundwater started seeping from the mine workings in late 1979, subsequently decreased due to natural attenuation processes, and then increased from the late 1990s

to early 2000s due to short-term disturbance and dissemination of metals in mine tailings during a period of large-scale reclamation work (Figure 2.2). Because different metals-disseminating activities were likely to occur at different times in the mining district and the reference site, periods of significant trends in lead and zinc contents in tree growth rings at the reference site should not correspond to trends of those metals in growth rings of sampled mining district trees.

Metals in tree tissues primarily are taken up from soils, with tree roots commonly having the greatest metals concentrations of tree tissues (Hovmand et al., 1983; Baes and McLaughlin, 1984; Kabata-Pendias and Pendias, 1984; Watmough et al., 1999; Baltrėnaitė and Butkus, 2007; Mala et al., 2007). The degree to which an annual tree growth ring may incorporate metals depends on a variety of factors, such as the amount of bioavailable metals in the predominant root uptake zone (usually fine shallow roots less than 60 centimeters below the land surface (Sánchez-Pérez and others, 2007) or in deeper soils from which tap roots draw water and nutrients (particularly during drier periods), translocation of lead along phloem and xylem during tree growth, and the amount of metal dust in the air. Atmospheric deposition of metals, with subsequent sorption through leaves and twigs into growing bole wood, is considered to be a minor source of metals in tree tissues, particularly in areas where soils have substantial metals concentrations. (Baes, and McLaughlin 1984; Watmough et al., 1999).

Metals in tree growth rings have been analyzed for numerous papers as a means for determining historic trends of selected metals in the environment. From 2005-2007, I collected 32 tree cores in the mining district (Figure 2.1) as a means of examining

trends in quantities of lead and zinc in the terrestrial environment of the district for decades when little environmental monitoring was done. In addition to collection of tree cores throughout the mining district, I collected six tree cores at a reference site in Norman, Oklahoma for comparative purposes (at a rate of about 20 percent of the number of mining-district trees sampled). Norman is believed to be outside of the area where mine tailings have been used for construction buildings and roads and other purposes (verbal commun., Earl Hatley, L.E.A.D. Agency, 2006).

Many different species of trees have been sampled for metals. Most of the previous work in this field (Table 2.1) has focused on examination of patterns of concentrations of selected metals in bole wood (xylem ring or trunk) tissues in comparison to hypothesized local changes in local metals uses and emissions. The number of tree rings analyzed for time trends of lead and zinc in this dissertation (38) is more than has been found in any previous publication reviewed by this author (Table 2.1).

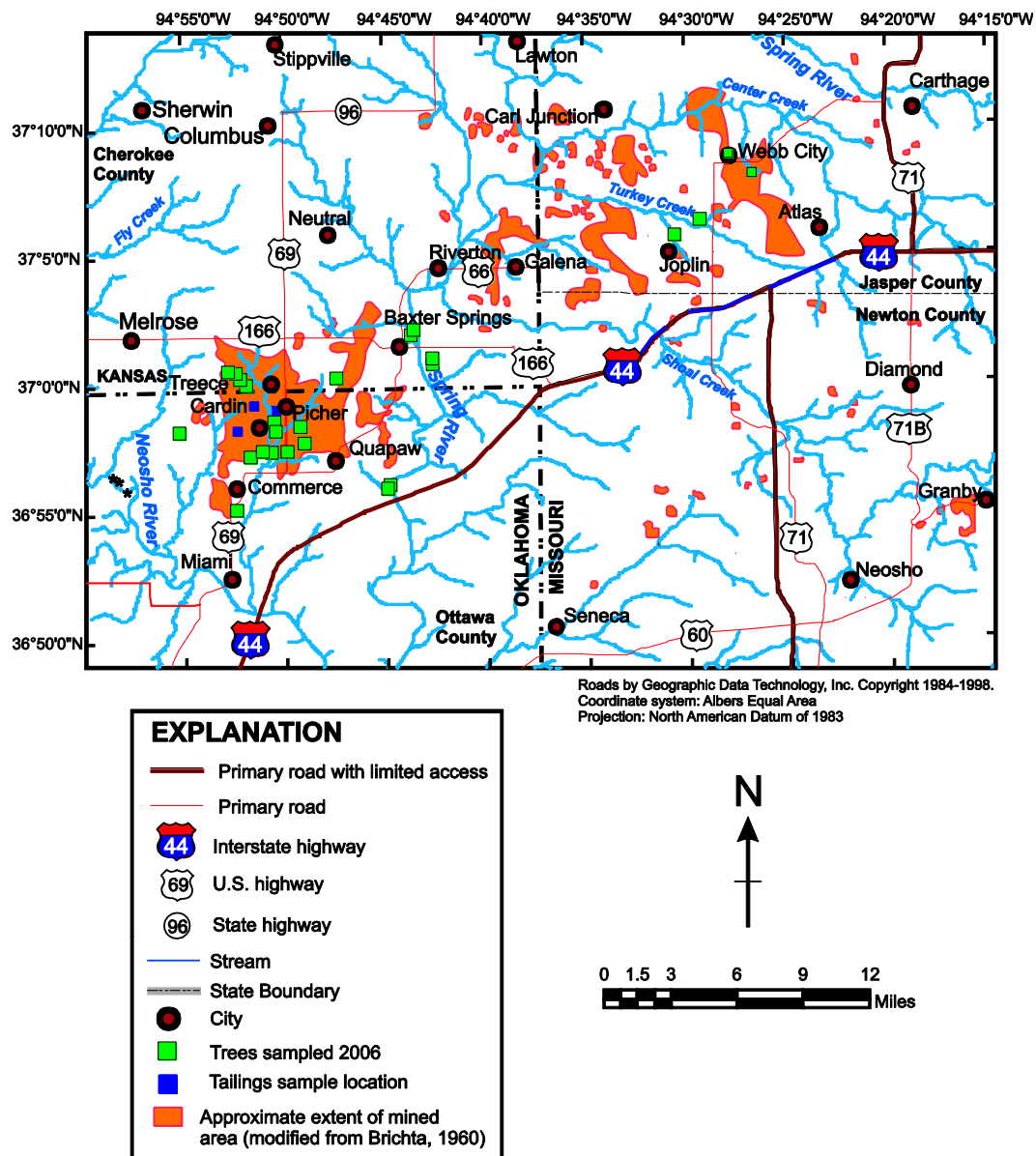


Figure 2.1 Locations of cored trees in the mining district.

Table 2.1 Species of trees previously analyzed for metals trends in tree rings.

[total number of all tree species sampled per paper are listed in red font]

Tree Species	Literature References
white oak (<i>Quercus alba</i>)	Baes and Ragsdale (1981) 33, Mallison et al., (2003) 13
red oak (<i>Quercus rubra</i>)	Brabander et al. (1999) 20
tulip poplar (<i>Liriodendron tulipifera</i>)	Baes and Ragsdale (1981) 33, Farrish et al. (2000) 14
hickory (<i>Carya</i> spp.)	Baes and Ragsdale (1981) 33
sycamore (<i>Acer pseudoplatanus</i> L.)	Watmaugh and Hutchinson (2003) 13
lime/lindon (<i>Tilia europaea</i> L.)	Watmaugh and Hutchinson (2003) 13
beech (<i>Fagus sylvatica</i> L.)	Watmaugh and Hutchinson (2003) 13
ash (<i>Fraxinus excelsior</i> L.)	Watmaugh and Hutchinson (2003) 13
eastern white pine (<i>Pinus strobus</i>)	Martin et al. (1997) 10
sugar maple (<i>Acer saccharum</i>)	Watmough et al. (1998) 3
black spruce (<i>Picea mariana</i>)	Begin et al. (2002) 18
Engelmann spruce (<i>Picea engelmannii</i>)	Witte et al. (2001) 20
Norway spruce (<i>Picea abies</i> (L.) Karst.)	Lindeberg (2004) 2
Scots pine (<i>Pinus sylvestris</i> L.)	Lindeberg (2004) 2
short-leaf pine (<i>Pinus echinata</i>)	Baes and McLaughlin (1984) 8
balsam fir (<i>Abies balsamea</i> L. Mill.)	Robitaille (1981) 2
eastern red cedar (<i>Juniperus virginiana</i>)	Guyette et al. (1991) 27
bald cypress (<i>Taxodium distichum</i>)	Devall et al., 2001 15

Hypothesized trends in metals recorded in annual tree growth rings

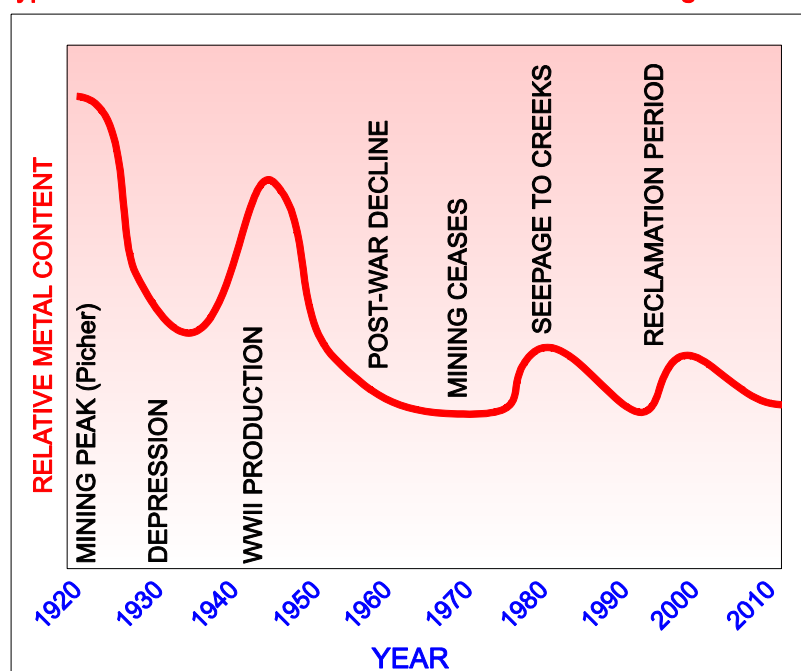


Figure 2.2 Hypothesized trends in lead and zinc content in annual tree growth rings in the Tri-State mining district.

2.3 Methods

Tree cores were collected from 32 trees in the mining district from 2005-2007. Prior to tree coring, tree species were identified, based on descriptions in Oklahoma Department of Agriculture (2000) and Wylie and Gass (1993). Because tailings from the mining district may have been used for roadways and other construction projects as far southwest as Oklahoma City (verbal commun., Earl Hatley, L.E.A.D. Agency, 2006), 6 reference trees on the campus of the University of Oklahoma in Norman, Oklahoma (25 miles beyond the nearest reported use of mine tailings) were sampled for comparative purposes at a rate of about 20 percent of the mining-district samples.

2.3.1 Tree Coring

I selected trees for coring to include a variety of tree species, tree sizes (Table 2.2), and surrounding previous and current land uses. A variety of sampled trees and sampling locations were chosen to represent the range of tree sizes and species growing in the mining district and to evaluate trends of lead and zinc with time across the extent of the mining district.

Tree diameters were measured at breast height (1.2 m), which is standard practice in this field, after which hand coring was done with Mora 20 x 0.64- or 30 x 0.64-cm stainless steel coring bits. After coring into the center of the tree (based on estimates of tree radius and corer-bit penetration) or to refusal (for 28 of the 38 trees), an extractor was inserted to remove each core from the hollow coring bit. To avoid damaging trees, only one core was collected from each tree, as was done for many of the studies listed in Table 2.1. Replication was achieved by collection of 500-2,000 closely spaced data points per core and by sampling adjacent pairs of trees (within 50 feet). After cores were extracted from the trees, notes were made regarding the conditions and continuities of the cores. Tree cores then were placed in plastic straws and straw ends then were sealed at both ends with duct tape. Straws were marked with a short identifying code for the tree and the ends corresponding to the oldest and youngest sections of the enclosed core were marked. Sealed cores were each placed in a ZiplocTM bag in a cooler containing dry ice, transported to the lab, and kept frozen prior to processing and analysis. Tree-ring thicknesses in the cores were measured to the nearest 0.1 millimeter using a binocular microscope and scale. Any losses of outer tree rings during coring were noted and tree growth rings were trimmed to the youngest complete ring.

Table 2.2 Characteristics and locations of trees sampled in the Tri-State mining district and a reference site.

Tree Identification Code ^a	Tree Species	Tree Diameter at Breast Height (cm)	Approximate Tree Height (m)	Length of Tree Core (cm)	Number of Rings in Tree Core	Location of Tree (Latitude and Longitude, in Decimal Minutes)
OO-1	plains cottonwood (<i>Populus deltoides</i> var. <i>monilifera</i>)	109	10.0	11.6	24	N36° 57.497 min W094° 50.351 min
OO-2	river birch (<i>Betula nigra</i>)	23.9	6.0	10.5	22	N36° 57.480 min W094° 50.701 min
OO-3	American elm (<i>Ulmus americana</i>)	37.6	9.0	13.8	25	N36° 58.348 min W094° 54.780 min
OO-4	sycamore (<i>Acer pseudoplatanus</i>)	67.5	14.0	12.5	27	N36° 55.995 min W094° 44.663 min
OO-5	American elm (<i>Ulmus americana</i>)	25.5	8.7	14.0	16	N36° 55.990 min W094° 44.670 min
OO-6	American elm (<i>Ulmus americana</i>)	26.1	11.8	11.5	21	N36° 57.850 min W094° 49.540 min
OO-7	plains cottonwood (<i>Populus deltoides</i> var. <i>monilifera</i>)	82.8	24.0	13.7	22	N36° 57.493 min W094° 49.687 min
OO-8	American elm (<i>Ulmus americana</i>)	69.4	18.8	12.0	21	N36° 58.457 min W094° 48.807 min
OO-9	green ash (<i>Fraxinus pennsylvanica</i>)	36.9	7.9	18.3	31	N36° 57.586 min W094° 50.407 min
OO-10	black oak (<i>Quercus velutina</i>)	39.8	12.8	12.0	12	N36° 57.706 min W094° 50.430 min

Table 2.2 Characteristics and locations of trees sampled in the Tri-State mining district and a reference site, continued.

Tree Identi- fication Code ^a	Tree Species	Tree Diameter at Breast Height (cm)	Approxi- mate Tree Height (m)	Length of Tree Core (cm)	Number of Rings in Tree Core	Location of Tree (Latitude and Longitude, in Decimal Minutes)
OO-11	black oak (<i>Quercus velutina</i>)	59.9	13.1	14.1	42	N36° 56.059 min W094° 44.710 min
OO-13	black oak (<i>Quercus velutina</i>)	12.4	9.2	6.5	15	N36° 57.381 min W094° 50.797 min
OO-14	black oak (<i>Quercus velutina</i>)	12.7	7.1	7.2	16	N36° 57.332 min W094° 50.799 min
OO-15	black oak (<i>Quercus velutina</i>)	23.6	7.5	8.6	19	N36° 57.310 min W094° 50.802 min
OO-17	eastern red cedar (<i>Juniperus virginiana</i>)	9.55	3.4	3.7	18	N36° 55.332 min W094° 52.334 min
OO-18	acacia (<i>Acacia sp.</i>)	27.4	5.0	3.3	9	N36° 55.300 min W094° 52.256 min
OO-19	black oak (<i>Quercus velutina</i>)	9.55	11.0	5.8	11	N36° 55.251 min W094° 52.194 min
OO-20	pin oak (<i>Quercus palustris</i>)	26.4	11.78	5.9	11	N36° 55.210 min W094° 52.195 min
JM-1	eastern red cedar (<i>Juniperus virginiana</i>)	19.1	4.5	9.6	19	N37° 03.090 min W094° 28.578 min
JM-2	plains cottonwood (<i>Populus deltoides</i> var. <i>monilifera</i>)	39.2	17.0	15.0	21	N37° 08.158 min W094° 27.970 min

Table 2.2 Characteristics and locations of trees sampled in the Tri-State mining district and a reference site, continued.

Tree Identi- fication Code ^a	Tree Species	Tree Diameter at Breast Height (cm)	Approxi- mate Tree Height (m)	Length of Tree Core (cm)	Number of Rings in Tree Core	Location of Tree (Latitude and Longitude, in Decimal Minutes)
JM-3	American elm (<i>Ulmus americana</i>)	49.4	7.3	7.6	18	N37° 08.160 min W094° 27.965 min
JM-4	plains cottonwood (<i>Populus deltoides</i> var. <i>monilifera</i>)	45.5	11.8	14.2	27	N37° 08.105 min W094° 26.322 min
JM-6	bur oak (<i>Quercus macrocarpa</i>)	54.1	13.4	22.1	22	N37° 07.946 min W094° 48.807 min
CK-1	plains cottonwood (<i>Populus deltoides</i> var. <i>monilifera</i>)	79.6	20.3	15.0	31	N37° 0.582 min W094° 52.318 min
CK-2	plains cottonwood (<i>Populus deltoides</i> var. <i>monilifera</i>)	40.4	13.7	16.7	31	N37° 0.375 min W094° 51.835 min
CK-3	plains cottonwood (<i>Populus deltoides</i> var. <i>monilifera</i>)	71.0	12.0	13.0	26	N37° 0.225 min W094° 51.773 min
CK-4	eastern red cedar (<i>Juniperus virginiana</i>)	15.9	3.5	7.2	25	N37° 0.113 min W094° 51.677 min
CK-5	northern red oak (<i>Quercus rubra</i>)	22.3	10.4	17.9	19	N37° 01.594 min W094° 43.477 min
CK-6	black oak (<i>Quercus velutina</i>)	59.9	14.3	22.7	43	N37° 01.583 min W094° 43.508 min

Table 2.2 Characteristics and locations of trees sampled in the Tri-State mining district and a reference site, continued.

Tree Identi- fication Code ^a	Tree Species	Tree Diameter at Breast Height (cm)	Approxi- mate Tree Height (m)	Length of Tree Core (cm)	Number of Rings in Tree Core	Location of Tree (Latitude and Longitude, in Decimal Minutes)
CK-7	black oak (<i>Quercus velutina</i>)	79.6	19.5	23.3	34	N37° 01.212 min W094° 43.209 min
CK-8	black oak (<i>Quercus velutina</i>)	38.8	13.4	19.8	23	N37° 01.223 min W094° 43.215 min
CK-9	Osage orange (<i>Maclura pomifera</i> (Raf.) Schneid)	37.3	8.0	9.6	43	N36° 59.945 min W094° 46.624 min
CO-1	black oak (<i>Quercus velutina</i>)	51.9	9.9	9.7	19	N35° 12.659 min W094° 26.704 min
CO-2	black oak (<i>Quercus velutina</i>)	9.55	5.0	6.1	17	N35° 12.738 min W094° 26.783 min
CO-3	pecan (<i>Carya illinoensis</i>)	34.7	11.1	6.2	31	N35° 12.724 min W094° 26.822 min
CO-4	black oak (<i>Quercus velutina</i>)	25.5	12.4	6.05	10	N35° 12.632 min W094° 26.548 min
CO-5	swamp white oak (<i>Quercus bicolor</i>)	14.3	14.7	7.1	10	N35° 12.632 min W094° 26.549 min
CO-6	pin oak (<i>Quercus palustris</i>)	25.5	12.1	7.2	10	N35° 12.640 min W094° 26.559 min

^a OO=Ottawa County, Oklahoma; JM=Jasper County, Missouri (one tree located just over the county line in Newton County, Missouri); CK=Cherokee County, Kansas; CO=Cleveland County, Oklahoma.

2.3.2 Analyses of Lead and Zinc Content of Tree Growth Rings

Lead and zinc concentrations of the tree cores were determined by Dr. William Minarik at the Department of Earth and Planetary Sciences at McGill University in Montreal, Quebec, Canada. At McGill University, core samples were ablated using a NewWave UP-213 ultraviolet laser system using helium as the carrier gas. The NewWave UP-213 is a frequency-quintupled Nd:YAG laser with an output wavelength of 213 nm. Spot size was controlled by an aperture, with apertures selectable in the range of 8 to 120 microns, with a 10 micron range being selected. The laser was pulsed at 5 to 10 hertz with an energy density of 5 to 12 joules per square centimeter. The pulse duration of this system was 5-7 nanoseconds, resulting in a fluence to the sample surface of more than a gigawatt per pulse. This power, combined with the ultraviolet wavelength, was sufficient to ablate material directly from the solid state into a gas plasma plume (avoiding the melting caused by infrared systems). Helium was used as a carrier gas due to its high thermal conductivity, which promotes rapid re-condensation of the plasma plume and the incorporated small particles.

The helium gas and ablation particles were combined with argon makeup gas before entering the injector of the Perkin Elmer Elan DRCplus inductively-coupled plasma-mass spectrometer (ICP-MS). Flow rates were optimized for maximum counts and minimum molecular isobaric interferences, and were 600-800 milliliters per minute (ml/min) for helium and 850-950 ml/min for argon.

Concentrations of lead and zinc were estimated from ICP-MS counts by subtracting background concentrations, dividing by carbon counts, and multiplying by correction factors based on known lead and zinc concentrations in a series of cellulose standards. The standards were prepared with solid metals-free cellulose powder and

known concentrations of the analyzed metals at McGill University.

Median concentrations of lead and zinc in each tree growth ring were converted to content (mass in milligrams per tree growth ring) of those metals using the following steps:

- a) each growth ring was assumed to be a symmetrical cylinder of even thickness (ring thickness as measured in the core),
- b) to determine the inside radius of each growth ring for cores that did not fully penetrate the center of each tree, the length (sum of ring thicknesses) of each core was subtracted from the measured trunk radius (one-half the measured diameter at breast height);
- c) the area of each growth ring was determined by computing the difference of the circular areas between the older and younger edges of each growth ring,
- d) a thickness of 1 centimeter was multiplied by the computed area of each growth ring to provide a ring volume,
- e) wood densities by species (The Engineering Toolbox, 2010) were multiplied by ring volumes to determine the wood mass of each ring, and
- f) the median concentrations of lead and zinc in each ring in mg/kg were multiplied by the computed mass of each ring in kg to determine contents of those metals in each ring, in mg.

Median annual lead and zinc contents (masses) per tree growth ring (year) for each sampled tree are shown as graphs in appendix I. Median annual lead and zinc contents

of the tree growth rings were grouped in boxplots (Figures 2.3-2.6) to graphically show general time trends of those metal contents. The Regional Kendall tau test (Helsel et al., 2006) was used to quantify trends of lead and zinc growth-ring contents over sliding 5-year periods for the trees sampled in the mining district and the reference site. Regional Kendall tau tests with p-values less than or equal to 0.05 were considered to indicate significant trends in lead and zinc contents of tree growth rings. An assumption of trend analysis is that regression residuals are independent. Time-series sets of hydrologic and other environmental data commonly exhibit serial correlation—dependence or correlation in time sequence between residuals, which violates the assumption of independence (Helsel and Hirsch, 1992). If sampling frequency is sufficiently high, serial correlation of residuals is certain to exist (Helsel and Hirsch, 1992). Given the probable gradual changes in lead and zinc concentrations in the terrestrial environment near the trees and the frequent nature of tree-core data-point sampling versus time, autocorrelation in tree-core metals content was probable. Correction for autocorrelation by grouping the data into time periods (in this case, sliding 5-year periods), was done to reduce the effects of dependence of residuals, as described in Helsel and Hirsch (1992).

2.4 Results and Discussion

Trends of lead and zinc contents (mass) in tree growth rings in the mining district, as shown graphically by the medians of annual boxplots in Figures 2.3-2.5, appeared to decrease during the early to mid-1960s, which was confirmed by Regional Kendall tau tests of those data (Table 2.3). Apparent increases in contents of those metals after mining ceased ca. 1970 (Figures 2.3-2.5) were not significant (Table 2.3). As shown on Figures 2.3-2.5 and Table 2.3, there were no significant changes in lead

and zinc contents of tree growth rings from the mid-1960s until after 1980, contradicting the hypothesis of gradual decline of lead and zinc concentrations in the environment in the years following cessation of mining. Significant increases in lead and zinc contents in the tree growth rings from about 1982 to the mid-1980s appear to correspond, albeit in a slightly lagged manner, to rising water-table elevations and the commencement of seepage of metals-rich groundwater from the mine workings in late 1979 (Figures 2.3-2.5 and Table 2.3), as was hypothesized. Subsequent significant decreases in lead and zinc contents in tree growth rings from the late 1980s and early 1990s probably indicated natural attenuation of those metals in the environment as the effects of seepage of groundwater from the mine workings tapered off. From the late-1990s to 2000, lead and zinc contents of tree growth rings significantly increased, corresponding to a disturbance of mine tailings and temporary increases in dissemination of metals during a period of numerous reclamation projects, as was hypothesized. Apparent decreases in lead contents from the early to mid-2000s were significant, but decreases in zinc contents in tree growth ring during that period were not significant (Figures 2.3-2.5 and Table 2.3). With the exception of a lack of significant decreases in lead and zinc content in tree growth rings after the closure of the mines ca. 1970 and in zinc since the early 1980s, the trends of lead and zinc contents in the sampled tree cores conformed to the hypotheses of metals trends with time in the mining district shown on Figure 2.2.

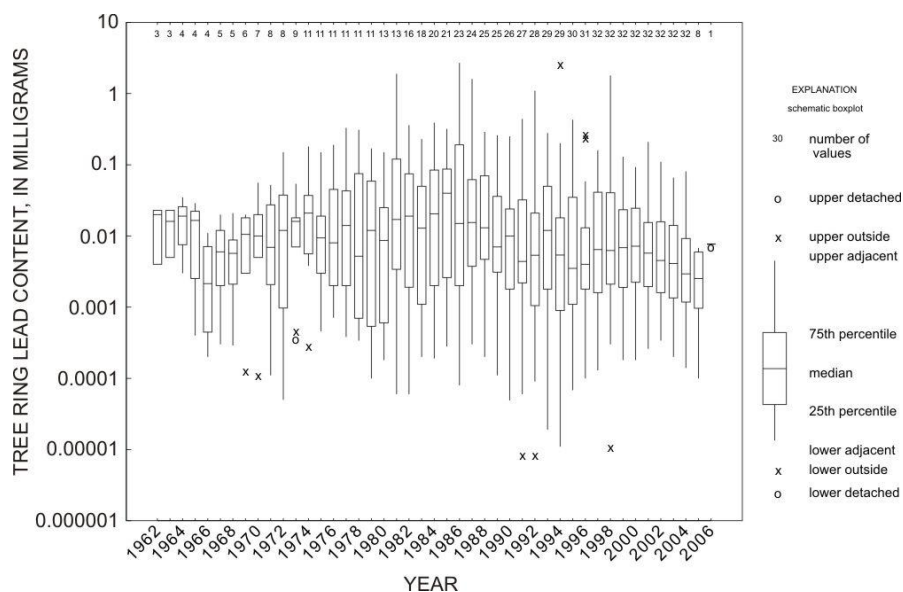


Figure 2.3 Boxplots of median annual lead content from 1962 through 2006 of tree growth rings sampled in the Tri-State mining district.

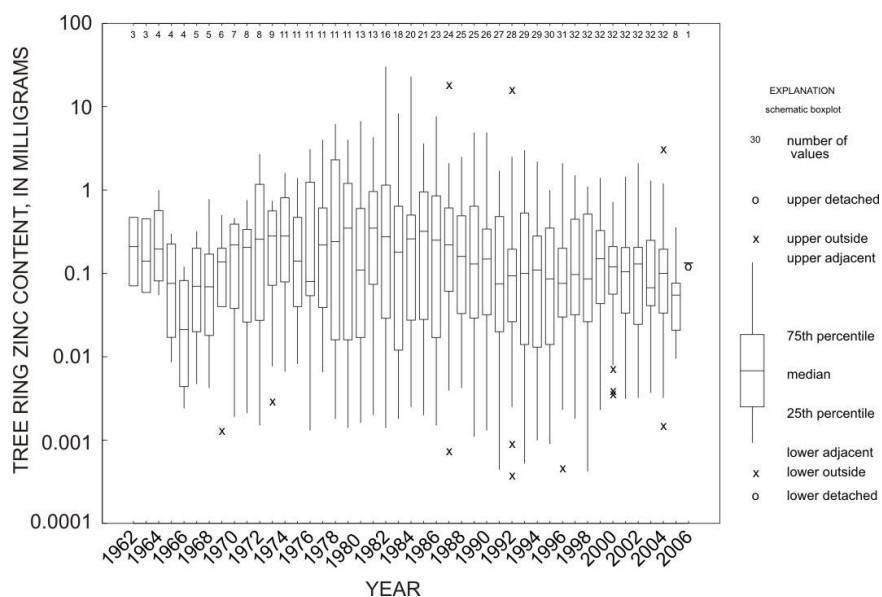


Figure 2.4 Boxplots of median annual zinc content of tree growth rings from 1962 through 2006 in the Tri-State mining district.

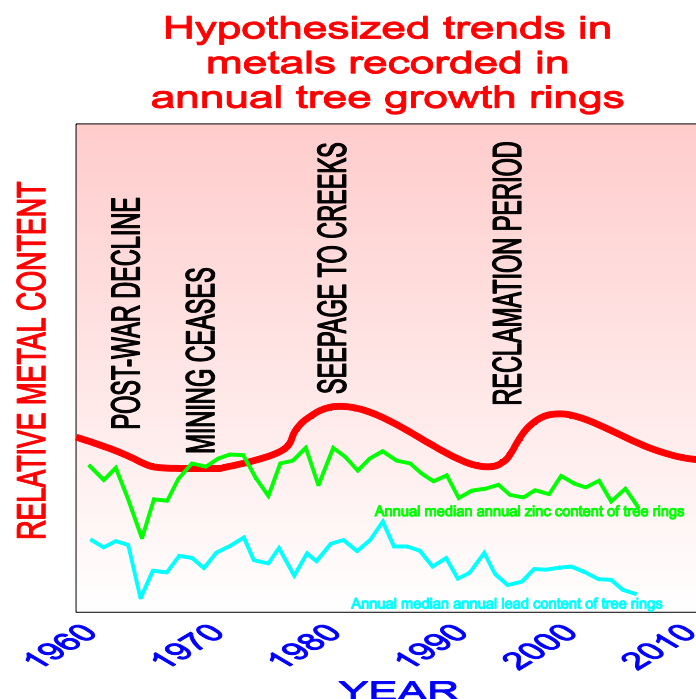


Figure 2.5 Schematic diagram of hypothesized trends in relative metals concentrations in tree rings (from Figure 2.2) compared to median annual lead and zinc contents of sampled tree cores (from Figures 2.3 and 2.4).

Lead and zinc content of tree growth rings collected from reference trees in Norman, Oklahoma had shorter cycles of increases and decreases than tree growth rings collected in the mining district (appendix I). In the tree growth rings collected at the reference site, there was a significant increase in zinc concentrations from 1982-86, significant decreases in both lead and zinc contents from 1990-94, significant increase in lead content from 1994-98, and significant decreases in lead content from 1996-2000 and 2001-2005 (appendix I, Figures 2.6 and 2.7, and Table 2.3). Periods of significant changes in lead and zinc content in tree growth rings at the reference site generally did not correspond with periods of similar changes in content of those metals in tree growth rings sampled in the mining district. Greater similarities of trends of lead and zinc

content in bole wood in the different species of reference trees (appendix I) indicates relatively consistent concentrations of lead and zinc in soils (Figure 2.8), air, and water at the reference site, compared to the mining district.

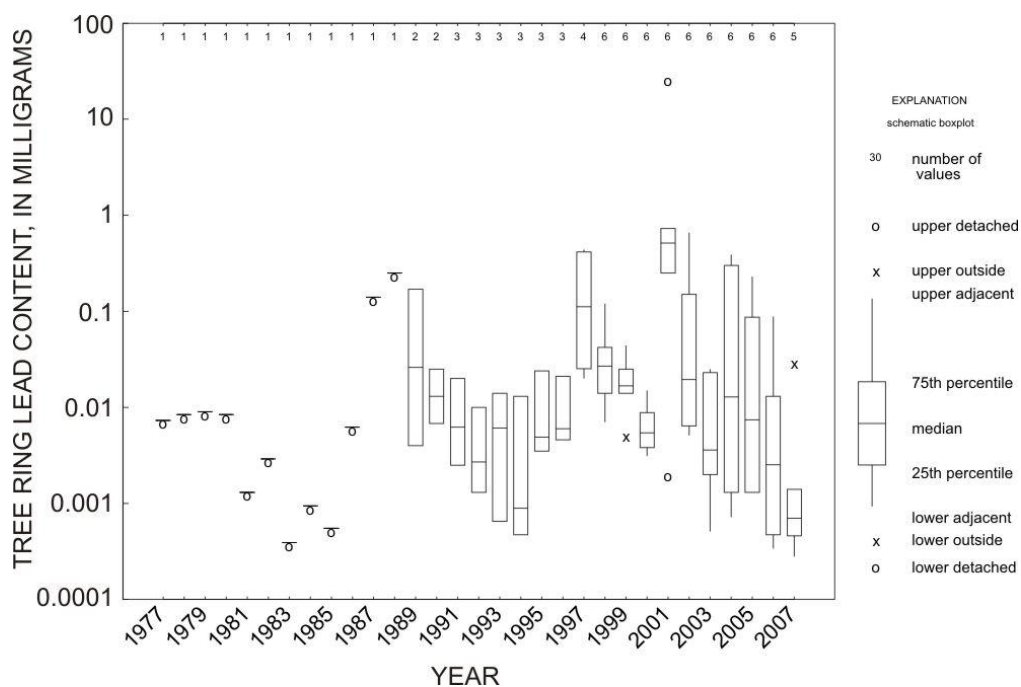


Figure 2.6 Boxplots of median annual lead content of tree growth rings from 1977 through 2007 at the reference site.

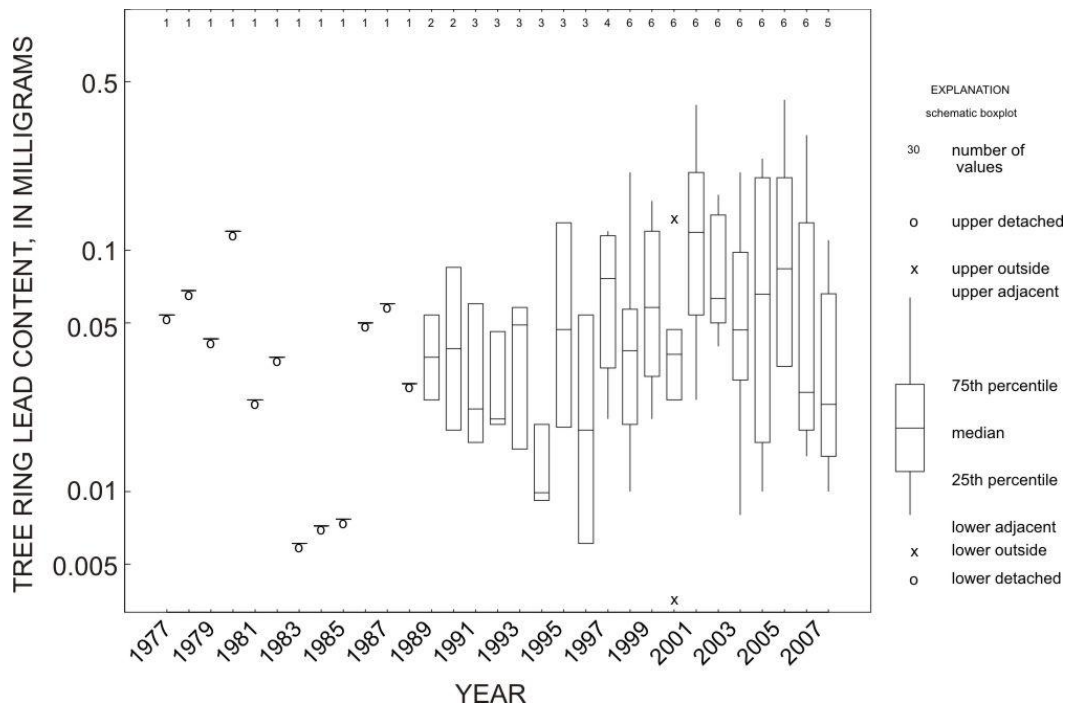


Figure 2.7 Boxplots of median annual zinc content of tree growth rings from 1977 through 2007 at the reference site.

Table 2.3 Regional Kendall tau values of median lead and zinc contents of tree rings sampled in the mining district and the reference site for 5-year periods.

[--, no data, p-value in parentheses, <, less than, p-values less than or equal to 0.05 in

bold red font]

Time Period	Mining District		Reference Site	
	Lead	Zinc	Lead	Zinc
1962-66	-0.545 (0.017)	-0.97 (<0.001)	--	--
1963-67	-0.500 (0.024)	-0.778 (<0.001)	--	--
1964-68	-0.488 (0.020)	-0.415 (0.052)	--	--
1965-69	-0.233 (0.28)	-0.070 (0.81)	--	--
1966-70	0.17 (0.42)	0.280 (0.15)	--	--
1967-71	-0.056 (0.83)	<0.001 (1.0)	--	--
1968-72	0.033 (0.92)	0.067 (0.76)	--	--
1969-73	0.043 (0.85)	0.014 (1.0)	--	--
1970-74	0.208 (0.18)	0.104 (0.53)	--	--
1971-75	0.176 (0.23)	-0.012 (1.0)	--	--
1972-76	0.065 (0.68)	-0.152 (0.29)	--	--
1973-77	-0.029 (0.88)	-0.039 (0.82)	--	--
1974-78	-0.200 (0.11)	-0.036 (0.82)	--	--
1975-79	-0.164 (0.20)	-0.045 (0.77)	--	--
1976-80	-0.209 (0.093)	-0.136 (0.30)	--	--
1977-81	-0.062 (0.65)	-0.170 (0.18)	-0.100 (1.0)	-0.200 (0.81)
1978-82	-0.017 (0.94)	-0.207 (0.94)	-0.500 (0.31)	-0.400 (0.46)
1979-83	-0.048 (0.72)	-0.024 (0.89)	-0.800 (0.086)	-0.600 (0.22)
1980-84	0.092 (0.42)	0.078 (0.51)	-0.600 (0.22)	-0.600 (0.22)
1981-85	0.083 (0.44)	0.064 (0.57)	-0.400 (0.46)	-0.200 (0.81)
1982-86	0.274 (0.0041)	0.123 (0.22)	0.200 (0.81)	0.400 (0.46)
1983-87	0.254 (0.0053)	0.086 (0.37)	0.800 (0.086)	1.00 (0.028)
1984-88	<0.001 (<0.001)	-0.042 (0.67)	0.800 (0.086)	0.600 (0.22)
1985-89	-0.097 (0.27)	-0.113 (0.21)	0.800 (0.086)	0.400 (0.46)
1986-90	-0.23 (0.0064)	-0.213 (0.012)	0.273 (0.63)	-0.182 (0.81)
1987-91	-0.24 (0.004)	-0.19 (0.023)	-0.385 (0.38)	-0.538 (0.18)
1988-92	-0.197 (0.016)	-0.063 (0.46)	-0.592 (0.12)	-0.294 (0.44)
1989-93	-0.031 (0.73)	0.077 (0.36)	-0.304 (0.32)	-0.043 (1.0)
1990-94	0.045 (0.60)	0.098 (0.23)	-0.615 (0.02)	-0.538 (0.045)
1991-95	0.074 (0.36)	0.059 (0.48)	0.000 (1.0)	-0.333 (0.20)
1992-96	-0.018 (0.85)	-0.074 (0.35)	0.200 (0.48)	-0.200 (0.48)
1993-97	-0.007 (0.96)	-0.037 (0.65)	0.467 (0.066)	-0.067 (0.89)
1994-98	0.153 (0.041)	0.070 (0.37)	0.613 (0.012)	0.097 (0.78)
1995-99	0.162 (0.028)	0.207 (0.0052)	0.143 (0.59)	-0.057 (0.89)
1996-2000	0.154 (0.036)	0.196 (0.0082)	-0.476 (0.019)	-0.024 (1.0)
1997-2001	-0.078 (0.30)	0.053 (0.49)	-0.231 (0.23)	0.115 (0.58)
1998-2002	-0.159 (0.030)	-0.003 (1.0)	0.000 (1.0)	0.317 (0.07)
1999-2003	-0.159 (0.029)	-0.034 (0.66)	-0.217 (0.23)	0.050 (0.84)
2000-2004	-0.197 (0.0065)	-0.034 (0.66)	-0.167 (0.37)	0.017 (1.0)
2001-2005	-0.085 (0.32)	-0.013 (0.91)	-0.450 (0.0090)	-0.033 (0.92)
2002-2006	-0.085 (0.44)	0.008 (1.0)	-0.317 (0.070)	-0.067 (0.76)
2003-2007	--	--	-0.339 (0.059)	0.000 (1.0)

2.5 Summary and Recommendations

To investigate trends in lead and zinc concentrations in the environment in the years after mines closed ca. 1970 and through periods of environmental change and reclamation work from the late 1970s to the early 2000s, cores collected from 32 trees in the Tri-State mining district were analyzed by laser-ablation inductively-coupled plasma mass spectrometry. Cores also were collected and analyzed from six trees in Norman, Oklahoma to compare trends of metals in the environment of the mining district to those in an area unaffected by mining and mine tailings use. Hypotheses about trends of lead and zinc content in tree growth rings were that content of those metals would have decreased after mining ceased (ca. 1970), that increases in contents of those metals would coincide with rising water tables and commencement of seepage of groundwater from the mine workings in late 1979 and with temporary disturbance and dissemination of metals caused by reclamation work done from the late 1990s through the early 2000s, and that periods of significant changes of lead and zinc content in tree growth rings would be different at the reference site than at the mining district.

Median lead and zinc contents in tree growth rings in the mining district significantly decreased during the 1960s as mining activities decreased. There were, however, no significant changes in lead and zinc contents in tree growth rings from the mid 1960s through 1982 after mining had ceased. Significant increases in lead and zinc contents in tree growth rings from 1982 to mid-1980s probably were due to rising groundwater levels and seepage of metals-contaminated groundwater from the abandoned mine workings, which started in late 1979. Subsequent significant decreases in lead and zinc contents of tree growth rings from the late 1980s to the early 1990s

may have been caused by natural attenuation processes. Significant increases in lead and zinc contents of tree growth rings from the mid 1990s through the early 2000s corresponded to a period of increased reclamation activities during which greater amounts of metals dust was likely to be disseminated for a short period in the local environment. With the exception of lack of significant decreases in lead and zinc content after the mines closed ca. 1970 to 1982 and lack of significant decreases in zinc content of tree growth rings in the 2000s, the trends of lead and zinc contents tree growth rings support the hypotheses of metals trends with time posited in this chapter.

Lead and zinc content of tree growth rings collected from reference trees in Norman, Oklahoma tended to have shorter cycles of increases and decreases than seen in cores of trees sampled in the mining district. In tree growth rings sampled from reference trees, zinc concentrations significantly increased from 1982-86, lead and zinc contents significantly decreased from 1990-94, lead content significantly increased from 1994-98, and lead content significantly decreased from 1996-2000 and 2001-2005. Trends of significant changes in lead and zinc content in tree growth rings sampled in the reference site generally did not correspond with time periods of significant trends in those metals in tree growth rings sampled in the mining district, supporting a hypothesis of this chapter. Greater similarities of trends of lead and zinc content in bole wood in the different species of reference trees indicates more consistent concentrations of lead and zinc in soils, air, and water at the reference site than at the mining district.

An additional source of data that could be collected to augment these tree-core analyses would be growth rings in mollusk shells collected from local streams. Limited

analyses of time trends in metals in growth rings of freshwater mussel shells were done, but are not described in this dissertation. Such data would provide more regionalized (or integrator) data of trends in metals draining from the mining district, rather than the localized (or indicator) data of the terrestrial environment provided by metals-content data from tree growth rings. Age-dated sampling of lead and zinc in sediment cores in Grand Lake, which receives water drainage from most of the district would be an additional line of evidence regarding trends in those metals with time in the environment of this abandoned mining district. Such information, which would provide insight about rates of natural attenuation and the effects of reclamation practices, would be transferable to many other large, metals-contaminated sites.

CHAPTER 3

Lead and Zinc Contents of Selected Tissues of Trees and Soils in Upland and Wetland Settings in the Tri-State Mining District and a Reference Site

3.1 Abstract

Tissues from 32 upland, 32 wetland, and 6 reference site trees were sampled to test the hypotheses that wetland tree tissues have greater lead and zinc concentrations than tissues in upland trees and that tissues of mining district trees have greater concentrations of those metals than tissues of trees growing in a reference site not affected by mining. Significantly greater concentrations of lead and zinc in leaves of wetland trees may preclude planting of trees in wetlands for phytoremediation in the mining district due to the bioavailable nature of metals in leaves for local wildlife. Similar lead concentrations in samples of bole wood from both mining district and reference site trees, despite much smaller lead concentrations in reference site soils, may indicate natural limits to lead uptake into woody tree tissues. Similar concentrations of lead and zinc in commercially-grown nuts and in nuts sampled in the mining district and from the reference site indicate that growing nut-bearing, high-value hardwood trees for commercial purposes may be feasible in the mining district.

3.2 Introduction

3.2.1 Potential for Use of Dendrochemistry to Design Phytoremediation in the Mining District

Water, soils, mine tailings, plants, wildlife, and humans are contaminated by lead and zinc in varying concentrations over the 3,100 km² extent of the abandoned Tri-State mining district (Parkhurst, 1987; Conder and Lanno, 1990; Carroll et al., 1998; O'Day, 1998; Datin and Cates, 2002; DeHay, 2003; Beyer et al., 2004; Oklahoma Department of Environmental Quality, 2003; DeHay et al., 2004; Angelo, 2005; White, 2005; Cope et al., 2008; Andrews et al., 2009). For a site as large as the Tri-State mining district, removal of millions of tons of metals-contaminated tailings, soils, and plants would be a daunting task.

Phytoremediation is potential method for remediating such a large metals-contaminated site. Phytoremediation is the use of plants to remove, breakdown, or sorb organic and inorganic chemicals in soils, groundwater, and surface water (U.S. Environmental Protection Agency, 1996; Raskin and Ensley, 2000; Pierzynski et al., 2002a and 2002b). Phytoremediation has the advantages of providing significant reduction in costs compared to traditional *in situ* and *ex situ* remediation methods, being easy to monitor, enabling reclaiming of metals in vegetation, and reducing leaching of contaminants to groundwater (U.S. Environmental Protection Agency, 1996; Lasat, 2000; Raskin and Ensley, 2000; Terry and Banuelos, 2000; Argonne National Laboratory, 2002; Gray, 2004a; LeDuc and Terry, 2005). Phytoremediation does, however, have limitations due to confinement of treatment to the area penetrated by plant roots, long treatment times, limited ability to prevent leaching of contaminants

into groundwater, failure of some plants to grow due to toxicity of contaminated soils, potential for ingestion of contaminated vegetation by animals, and failure of plants to take up less-bioavailable metals such as lead ((Pontes-Buarque et al., 2000; Prasad and Freitas, 2003; Gray, 2004a and 2004b).

There are two general types of phytoremediation--phytoextraction and phytostabilization. Phytoextraction relies on translocation of large quantities of metals from the rhizosphere (root zone) to harvestable plant shoots, which must be harvested and properly disposed. Phytostabilization is the use of plants to stabilize soils and immobilize metals in soils through conversion of metals to less leachable/soluble forms through chemical interactions of metals with plant roots and relatively small uptake of contaminants into above-ground plant tissues (Raskin and Ensley, 2000; Argonne National Laboratory, 2002; Halim et al., 2003; Gray, 2004a). Plants used for phytostabilization uptake metals from soils into their roots or precipitate minerals of metals around their roots, but do not translocate large quantities of metals to their shoots, limiting potential for consumption of metals in above-ground plant tissues by humans, livestock and wildlife (Prasad and Freitas, 2003). Phytostabilization also can provide dense vegetative ground covers that reduce soil erosion by wind and water, and limit migration of contaminants to groundwater due to evapotranspiration reducing recharge (Interstate Technology and Regulatory Cooperation Work Group, 1999; and Gray, 2004a). After mine tailings are removed from the mining district, vegetation from surrounding areas gradually will colonize the area. Additional trees, preferably high-value hardwood trees that would provide economic and ecological benefits, could be planted to accelerate revegetation and eventually improve the local economy. Prior to

mining, the district was a very productive area for growing hay. If mine tailings are removed from this site, the buried soils may have retained sufficient fertility to be a suitable substrate for growth of many types of plants. Knowledge of lead and zinc concentrations and content in tree tissues in the mining district provides information about uptake of those metals from local soils and air and whether growth of volunteer trees and planting of trees for phytoremediation and economic purposes will increase metals concentrations in tree tissues comprise parts of the food chain of wildlife, livestock, and humans.

The hypotheses of the research described in this chapter are that: (1) wetland trees have greater concentrations of lead and zinc due to greater concentrations of those metals in wetland soils, increased water availability in wetlands, and greater evapotranspiration than in uplands; (2) tissues of upland and wetland trees in the mining district contain greater lead and zinc concentrations than trees at a reference site not affected by mining, and (3) nut tissues of mining-district trees have significantly greater concentrations of lead and zinc than nuts growing at a reference site and nuts sold for human consumption due to greater metals concentrations in mining district soils than in typical commercial and agricultural areas. If these hypotheses are confirmed, then planting of trees for phytoremediation of this mining district would be contraindicated. If these hypotheses are rejected, then planting of trees for phytoremediation of this mining district would be supported.

3.3 Methods

3.3.1 Vegetation Sampling

To investigate lead and zinc concentrations in tree tissues, tissues (bole wood, leaves, twigs, nuts, and hulls) were sampled from 32 trees in upland areas of the mining district, 32 trees in wetland areas of the mining district, and 6 trees at a reference site (Table 3.1, Figure 3.1). Bole wood samples were collected by hand coring to the centers of the trees or to refusal using Mora 20 x 0.64- or 30 x 0.64-cm stainless steel corers (as described in chapter 2). Samples of approximately 25 grams of available leaves, twigs, seeds, and fruits were collected from trees in the mining district from June through December 2006 (Table 3.1).

Mine tailings from this district, locally known as “chat”, may have historically been used on roads and other construction projects at sites as distant as Oklahoma City, Saint Louis, and Chicago (verbal commun., Earl Hatley, L.E.A.D. Agency, 2006). Norman, Oklahoma, located 25 miles south of Oklahoma City, was chosen as a reference site for collection of tree tissues. From October 2006 to April 2007, tissues were sampled from six trees in Norman, Oklahoma (Table 3.3).

3.3.2 Soil Sampling

Soil samples were collected at the base of each sampled upland and reference tree or within each group of sampled trees using a stainless steel slotted tube sampler (0.28 m long by 0.037 m diameter). The top 15 cm of soil samples was homogenized and deposited in pre-cleaned glass jars. For the wetland study, conducted by other researchers of the Center for Restoration of Ecosystems and Wetlands at the University of Oklahoma, between 3 and 10 soil samples were collected at depths from 0-5 cm

below the land surface at arbitrarily selected locations at each of the six wetlands. All of the soil samples were frozen in the field with dry ice and kept frozen prior to sequential extractions and digestion and analyses.

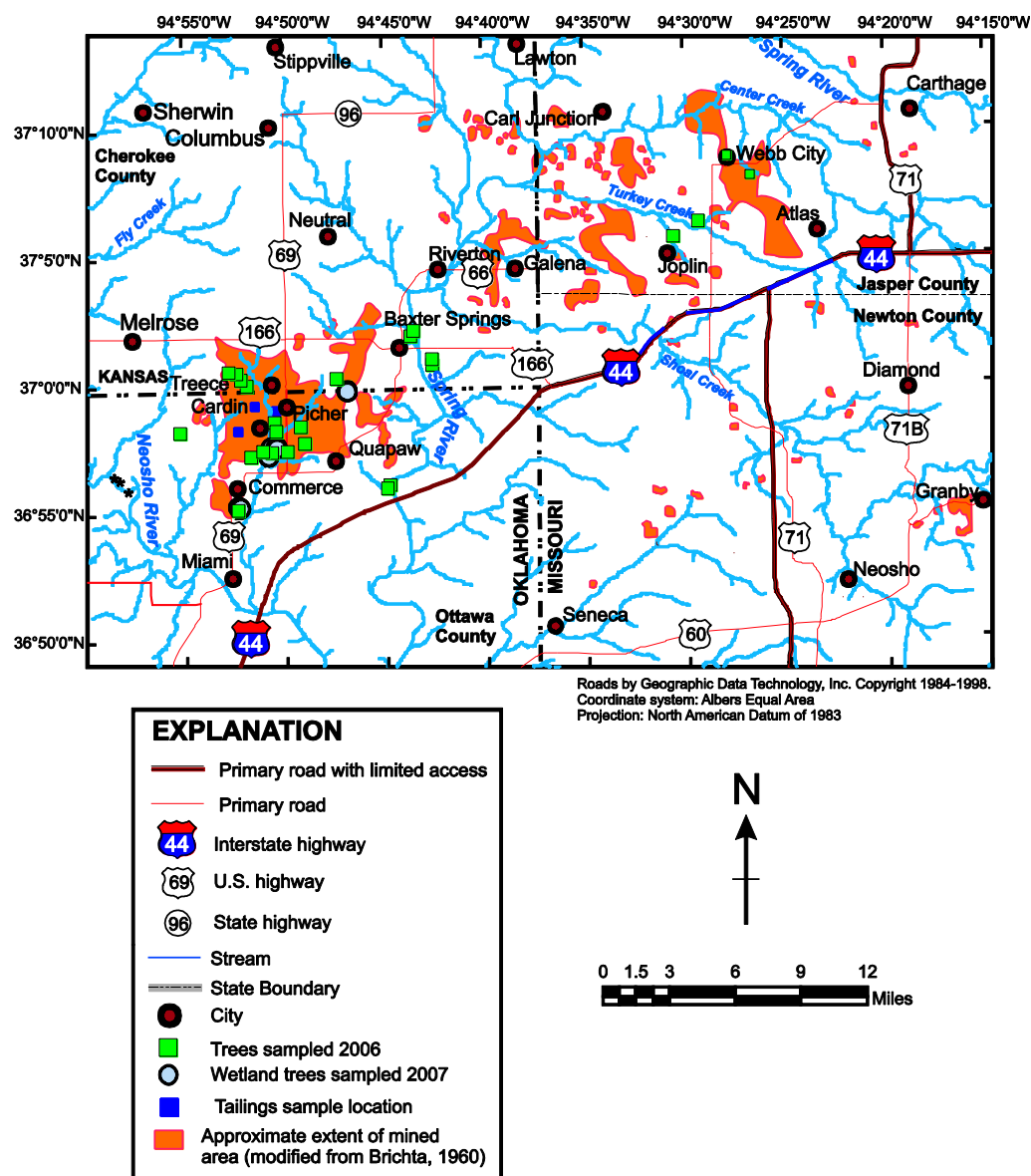


Figure 3.1 Locations of sampled wetland and upland trees in the Tri-State mining district.

Table 3.1 Upland trees sampled in the Tri-State mining district for lead and zinc content of bole wood, twigs, leaves, seeds, and nut hulls, June through December 2006.

County and State	Tree Number	Common Name	Species	Breast Height Diameter (cm)	Estimated Tree Height (m)	Bole Wood	Twigs	Leaves	Nuts/ Seeds and Nut Hulls
Ottawa, Oklahoma	OO-1	plains cottonwood	<i>Populus deltoides monilifera</i>	109	10			X	
	OO-3	American elm	<i>Ulmus americana</i>	37.6	9		X	X	
	OO-4	American sycamore	<i>Platanus occidentalis</i>	67.5	14	X	X	X	
	OO-5	American elm	<i>Ulmus americana</i>	25.5	8.7	X			
	OO-8			69.4	18.8	X			
	OO-10	black oak	<i>Quercus velutina</i>	39.8	12.8	X			X
	OO-11	black oak	<i>Quercus velutina</i>	59.9	13.1	X	X	X	
	OO-13	black oak	<i>Quercus velutina</i>	12.4	9.2	X			
	OO-14	black oak	<i>Quercus velutina</i>	12.7	7.1	X			
	OO-15	black oak	<i>Quercus velutina</i>	23.6	7.5		X	X	
	OO-16	black oak	<i>Quercus velutina</i>	21.0	11.4		X	X	
	OO-18	acacia	<i>Acacia sp.</i>	27.4	5.0	X	X	X	
	OO-19	black oak	<i>Quercus velutina</i>	9.55	11.0	X	X		
	OO-20	pin oak	<i>Quercus palustris</i>	26.4	11.8	X			
	OO-28 nr. OO-4	bur oak	<i>Quercus macrocarpa</i>	73.2	13.5		X	X	X
	OO-29 nr. OO-4	pin oak	<i>Quercus palustris</i>	30.2	10.9		X	X	
	OO-30 nr. OO-4	American sycamore	<i>Platanus occidentalis</i>	31.8	11.4		X	X	X
	OO-31 nr. OO-4	black hickory	<i>Carya texana</i>	28.7	14.0		X	X	

Table 3.1 Upland trees sampled in the Tri-State mining district for lead and zinc content of bole wood, twigs, leaves, seeds, and nut hulls, June through December 2006, continued.

Coun-ty and State	Tree Num-ber	Com-mon Name	Species	Breast Height Diame-ter (cm)	Estima-ted Tree Height (m)	Bole Wood	Twigs	Leaves	Nuts/ Seeds and Nut Hulls
Jasper, Missouri	JM-4	plains cotton-wood	<i>Populus deltoides monilifera</i>	45.5	11.8	X			X
	JM-5	post oak	<i>Quercus stellata</i>	93.9	13.4		X	X	X
	JM-6	bur oak	<i>Quercus macrocarpa</i>	54.1	13.4	X	X	X	X
	JM-7	post oak	<i>Quercus stellata</i>	60.8	12.5		X	X	X
	JM-8 nr JM-7	chest-nut oak	<i>Quercus prinus</i>	62.5	12.0		X	X	
Cherokee, Kansas	CK-1	plains cotton-wood	<i>Populus deltoides monilifera</i>	79.6	20.3	X			
	CK-2	plains cotton-wood	<i>Populus deltoides monilifera</i>	40.4	13.7	X			
	CK-3	plains cotton-wood	<i>Populus deltoides monilifera</i>	71.0	12.0	X			
	CK-4	eastern red cedar	<i>Juniperus virginiana</i>	15.9	3.5	X			
	CK-5	northern red oak	<i>Quercus rubra</i>	22.3	10.4	X	X	X	X
	CK-6	black oak	<i>Quercus velutina</i>	59.9	14.3	X	X	X	X
	CK-7	black oak	<i>Quercus velutina</i>	79.6	19.5	X	X	X	X
	CK-8	black oak	<i>Quercus velutina</i>	38.8	13.4	X	X	X	X
	CK-9	Osage orange	<i>Maclura pomifera</i>	37.3	8.8	X	X	X	

Table 3.2 Wetland trees sampled for lead and zinc content of bole wood, twigs, leaves, and seeds and/or fruits in Ottawa County, Oklahoma, April 2007.

Wetland Site Name	Tree Number	Common Name	Species Name	Breast Height Diameter (cm)	Bole Wood	Twigs	Leaves	Nuts/ Seeds and Nut Hulls
Mayer Ranch	OO-17	eastern red cedar	<i>Juniperus virginiana</i>	9.6	X	X	X	
	OO-24	black willow	<i>Salix nigra</i>	7.6	X	X	X	
	OO-44	eastern red cedar	<i>Juniperus virginiana</i>	6.7	X	X	X	
	OO-45	northern catalpa	<i>Catalpa speciosa</i>	7.0	X	X	X	X
	OO-46	choke-cherry	<i>Prunus virginiana</i>	6.7	X	X	X	
	OO-47	black willow	<i>Salix nigra</i>	21.3	X	X	X	
Adams A	OO-34	river birch	<i>Betula nigra</i>	5.4	X	X	X	
	OO-35	river birch	<i>Betula nigra</i>	20.1	X	X	X	
	OO-36	black oak	<i>Quercus velutina</i>	9.9	X	X	X	
	OO-37	river birch	<i>Betula nigra</i>	8.3	X	X	X	
	OO-38	river birch	<i>Betula nigra</i>	6.7	X	X	X	
Adams C	OO-39	green ash	<i>Fraxinus pennsylvanica</i>	18.5	X	X	X	
	OO-40	green ash	<i>Fraxinus pennsylvanica</i>	17.5	X	X	X	
	OO-41	choke-cherry	<i>Prunus virginiana</i>	8.6	X	X	X	
	OO-42	choke-cherry	<i>Prunus virginiana</i>	14.6	X	X	X	
	OO-43	green ash	<i>Fraxinus pennsylvanica</i>	7.6	X	X	X	
Rush West	OO-48	river birch	<i>Betula nigra</i>	8.6	X	X	X	
	OO-49	river birch	<i>Betula nigra</i>	7.3	X	X	X	
	OO-50	river birch	<i>Betula nigra</i>	10.2	X	X	X	
	OO-51	black willow	<i>Salix nigra</i>	13.4	X	X	X	
	OO-52	black willow	<i>Salix nigra</i>	14.3	X	X	X	

Table 3.2 Wetland trees sampled for lead and zinc content of bole wood, twigs, leaves, and seeds and/or fruits in Ottawa County, Oklahoma, April 2007, continued.

Wet- land Site Name	Tree Num- ber	Common Name	Species Name	Breast Height Diameter (cm)	Bole Wood	Twigs	Leaves	Nuts/ Seeds and Nut Hulls
Rush East	OO-53	green ash	<i>Fraxinus pennsylvanica</i>	6.4	X	X	X	
	OO-54	river birch	<i>Betula nigra</i>	5.4	X	X	X	
	OO-55	river birch	<i>Betula nigra</i>	5.4	X	X	X	
	OO-56	river birch	<i>Betula nigra</i>	5.4	X	X	X	
	OO-57	river birch	<i>Betula nigra</i>	5.4	X	X	X	
Hockerville	OO-58	green ash	<i>Fraxinus pennsylvanica</i>	13.4	X	X	X	
	OO-59	black willow	<i>Salix nigra</i>	5.1	X	X	X	
	OO-60	Northern catalpa	<i>Catalpa speciosa</i>	3.5	X	X	X	X
	OO-61	green ash	<i>Fraxinus pennsylvanica</i>	17.2	X	X	X	
	OO-62	black willow	<i>Salix nigra</i>	10.5	X	X	X	
	OO-63	northern catalpa	<i>Catalpa speciosa</i>	17.5	X	X	X	X

Table 3.3 Reference trees sampled for lead and zinc content of bole wood, twigs, leaves, seeds, and seed hulls in Norman, Oklahoma, October 2006 through April 2007.

County and State	Tree Number	Common Name	Species	Breast Circumference (cm)	Estimated Tree Height (m)	Bole Wood	Twigs	Leaves	Nuts/Seeds and Nut Hulls
Cleveland, Oklahoma	CO-1	black oak	<i>Quercus velutina</i>	51.9	9.9	X	X	X	X
	CO-2	Nuttall oak	<i>Quercus texana</i> Buckley	9.55	5.0	X	X	X	X
	CO-3	pecan	<i>Carya Illinois-ensis</i>	34.7	11.1	X	X	X	X
	CO-4	black oak	<i>Quercus velutina</i>	25.5	12.4	X	X	X	X
	CO-5	swamp white oak	<i>Quercus bicolor</i>	14.3	14.7	X	X	X	X
	CO-6	pin oak	<i>Quercus palustris</i>	25.5	12.1	X	X	X	X

3.3.3 Retail Nut Samples

To investigate whether seeds and nuts growing in the mining district contained significantly greater concentrations lead and zinc than commercially-grown nuts, nine nut samples, purchased in grocery stores between October 2006 and June 2009 (Table 3.4), were analyzed for concentrations of those metals. If nut samples collected from the mining district and nuts distributed for sale nationally were to have similar concentrations of lead and zinc, then nuts grown in the mining district should be suitable for commercial sale. The retail nut samples listed in Table 3.4 were likely to have been mixtures from large lots sourced from large numbers of farms in different areas of the U.S. Obtaining knowledge about specific geographic locations of where the nuts were grown, soil chemistry on those farms, and management practices were not

possible to obtain and such information was beyond the scope and intent of this data comparison.

Table 3.4 Retail nut samples analyzed for lead and zinc content, October 2006 through June 2009.

Sample Number	Common Name	Species	Brand	Identification Information
BW-1	black walnut	<i>Juglans nigra</i>	Fisher	Chef's naturals, 2-ounces, exp. 08/15/2007
BW-2				Chef's naturals, 2-ounces, exp. 02/17/2009
PC-1	pecan	<i>Carya spp.</i>	Fisher	Chef's Naturals, 2-ounces, exp. 10/04/2007
PC-2			Trader Joe's	16-ounces, exp. 10/29/2007
PC-3			Fisher	Chef's Naturals, 2-ounces, exp. 07/11/2009
EW-1	English walnut	<i>Juglans regia</i>	Diamond	4-ounces, Lot 0702954344S
EW-2			Fisher	Chef's naturals, 4-ounces, exp. 02/01/2008
EW-3			Market Pantry	2-ounces, exp. 03/26/2009
EW-4			Diamond	2-ounces, Lot 08035D332S

3.3.4 Sample Processing

All samples were kept frozen in sealed containers prior to processing and analyses. Samples were not washed prior to processing and analyses to better determine lead and zinc content that would be consumed by wildlife and livestock. I weighed tree-tissue and soil samples, and then dried the samples for 24 hours at 105 °C in a VWR Scientific Products 1350FM forced-air oven. I then ground the samples to less than 1 mm-size particles in a stainless steel Wiley mill prior to microwave-assisted nitric acid digestion (U.S. Environmental Protection Agency, 1994). Seeds, except for sycamore seed balls, were separated from shells, caps, and husks, and were processed and analyzed separately from those hull tissues. I processed Sycamore seed balls in their

entirety.

To investigate bioavailability of metals in soils, I extracted portions of the soil samples for 12-hours in deionized water, as described in O'Sullivan et al. (2005). I made subsequent stronger digestions using methods described in Tessier et al. (1979), using solutions of $MgCl_2$ (exchangeable fraction), sodium acetate and acetic acid (carbonate fraction), hydroxylamine hydrochloride and acetic acid (oxides fraction), hydrogen peroxide and nitric acid (organics fraction). I did final residual soil digestions using USEPA method 3051--microwave digestion with 70 percent nitric acid (U.S. Environmental Protection Agency, 2006). Only the water-soluble, exchangeable, and total (summation of sequential extractions) concentrations of lead and zinc for mining-district soils are described in this chapter. Total soil digestions were done for reference-tree soil samples using USEPA method 3051. Additional soil samples were not collected at upland trees OO-27 through OO-31 and tree JM-8, which were within 6 m of previously-sampled trees, as listed in Table 3.2.

To investigate phytoextraction of lead and zinc by trees in the Tri-State mining district and the reference site, regression estimates of the biomasses of sampled tree tissues, as computed from tree diameters and tree heights in East Texas by Xu and Li (2007), were multiplied by concentrations of lead and zinc in selected tree-tissue samples. Xu and Li (2007) did not separate the biomass of seeds and hulls, so because seeds comprise most of the weight of that biomass, concentrations of lead and zinc in seeds were multiplied by the seeds and hulls biomass based on regressions from that paper.

3.3.5 Sample Analyses for Lead and Zinc and Mineral Content

I analyzed all extracted and digested solutions of plant tissues and soils for lead and zinc content using a Varian VistaPRO Inductively-Coupled Plasma-Optical Emission Spectrometer (ICP-OES) using known standards and procedures described in Varian Corporation (2005) and EPA Method 200.7 (U.S. Environmental Protection Agency, 2001).

3.3.6 Data Analysis

To graphically portray differences in lead and zinc concentrations in tree tissues and soils, boxplots of lead and zinc concentrations in sample groups were made with TIBCO Spotfire S+ version 8.1 statistical and graphing software, (TIBCO, 2009). For preparation of those graphs, censored (non-detected) data values were estimated to be one-half of the method reporting level to avoid over- or under-weighting censored data values. Differences of locations of distributions of sample-group data were determined using the two-sample Wilcoxon rank-sum test (Wilcoxon, 1945) with approximate distribution and continuity correction, and a mean of zero under null hypothesis, using TIBCO Spotfire S+ version 8.1 statistical and graphing software. Two-sided p-values of 0.05 or less of the Wilcoxon rank-sum test support a 95 percent or greater confidence that the locations of distributions of two compared groups of numbers are different. Estimation of censored data values was not necessary for the Wilcoxon rank-sum test, which is a non-parametric test on ranked data.

3.4 Results and Discussion

3.4.1 Tree Tissues

Lead concentrations in leaf and twig samples were substantially greater in wetland trees than in upland trees sampled in the mining district (Figures 3.2 and 3.3), supporting the first hypothesis of this chapter. However, lead concentrations in bole wood samples of upland trees were about twice those of bole wood samples from wetland trees, partially refuting that hypothesis (Figures 3.2 and 3.3). Refuting another hypotheses, lead concentrations were not different or were greater in tissues of the reference trees in than in most tissues of upland trees sampled in the mining district (Figures 3.2-3.4). Refuting the last hypothesis of this chapter, commercial nut samples had similar lead concentrations as nuts sampled from reference trees and wetland and upland trees in the mining district (Figures 3.2-3.4).

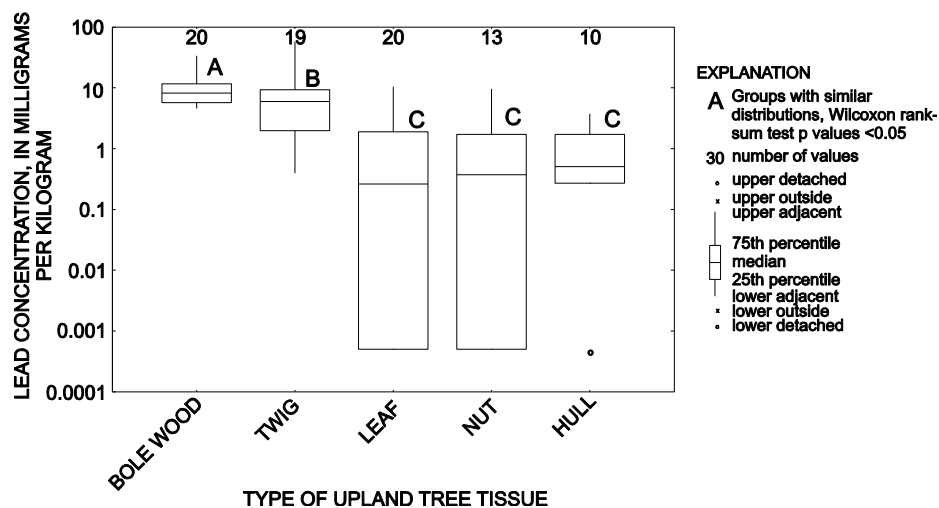


Figure 3.2 Boxplots of lead concentrations in upland tree-tissue samples collected in the Tri-State mining district in January through November 2006.

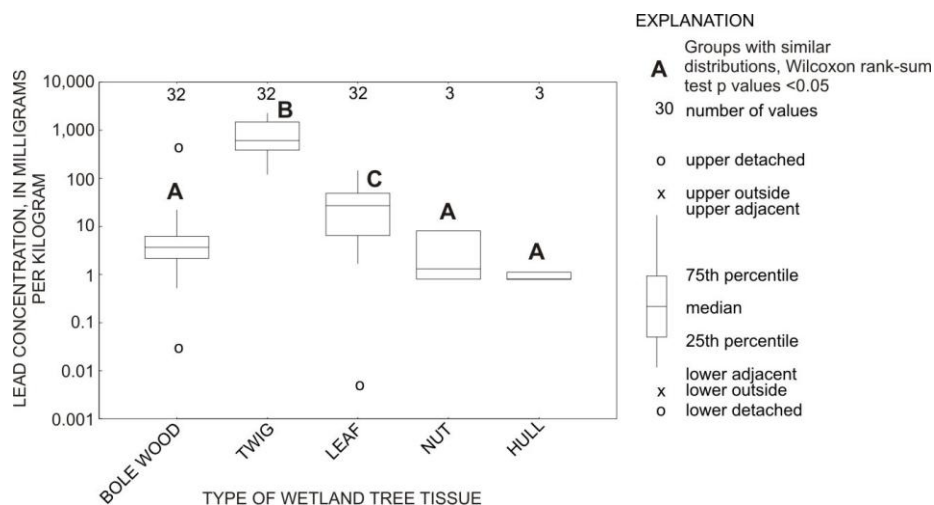


Figure 3.3 Boxplots of lead concentrations in wetland tree-tissue samples collected in the Tri-State mining district in April 2007.

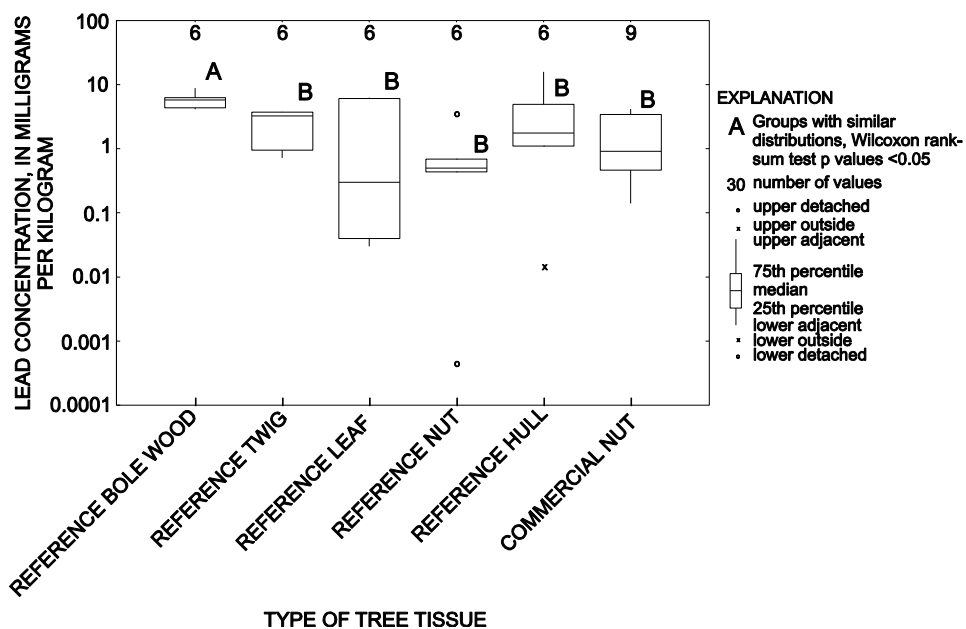


Figure 3.4 Boxplots of lead concentrations in reference-tree samples collected in Norman, Oklahoma, October 2006 through April 2007, and retail nut samples purchased from October 2006 through June 2009.

Concentrations of zinc in bole wood, twigs, and leaves of wetland trees were 5-10 times greater than in upland trees in the mining district (Figures 3.5 and 3.6), supporting the hypothesis of greater zinc concentrations in wetland trees. However, zinc concentrations in nut and hull tissues were similar in upland and wetland trees (Figures 3.5 and 3.6), partially refuting that hypothesis. Zinc concentrations in reference tree bole wood were similar to those in upland trees, but zinc concentrations of other reference tree tissues ranged from one-tenth to about half of those in upland tree tissues (Figures 3.5 and 3.6). Zinc concentrations of commercial nut samples were not different than those in the nut tissues sampled in the mining district or the reference site (Figures 3.5-3.7).

Because of concerns about toxicity of metals in wood products, the British Standards Institution set limits, known as PAS 100:2005, of 200 mg/kg for lead and 400 mg/kg for zinc (British Standards Institution, 2005). Most upland and wetland tree tissues sampled from mining district did not exceed the PAS100:2005 standard for lead content, but some upland tree tissues and most wetland twig samples exceeded the PAS100:2005 standard for zinc content (Figures 3.5-3.7), which may be problematic for production of compost and other wood byproducts from trees harvested in the mining district. Because metals concentrations can increase as organic matter is oxidized during composting, testing of compost made from local tree tissues would be advisable prior to marketing such compost.

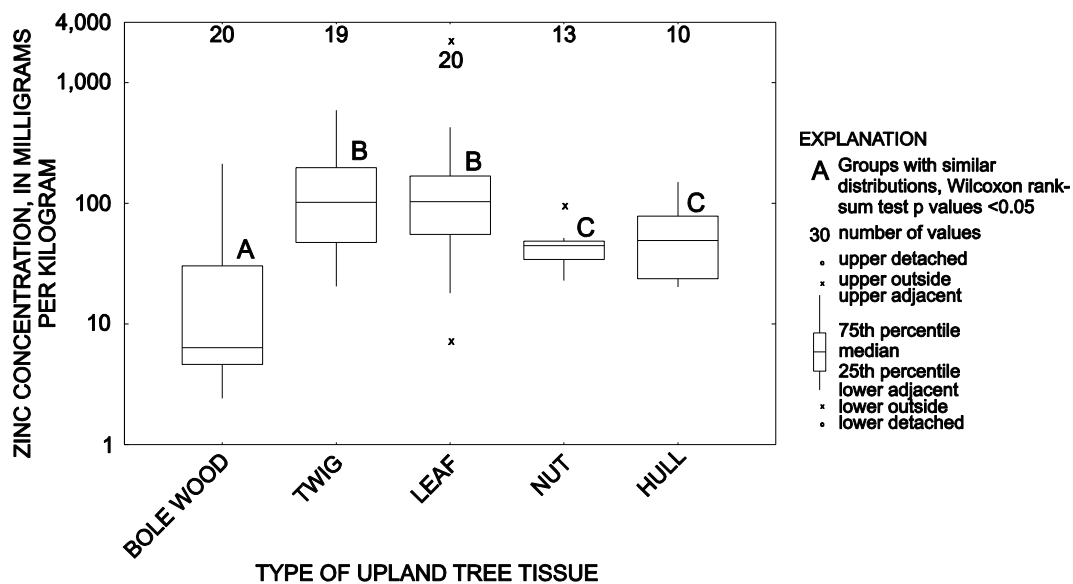


Figure 3.5 Boxplots of zinc concentrations in upland tree-tissue samples collected in the Tri-State mining district in January through November 2006.

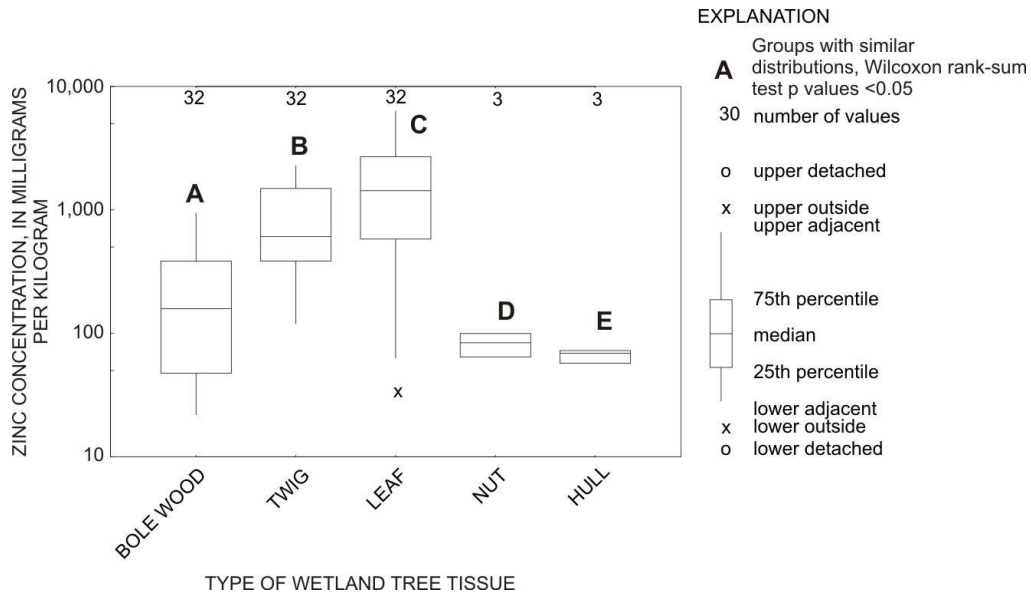


Figure 3.6 Boxplots of zinc concentrations in wetland tree-tissue samples collected in the Tri-State mining district in April 2007.

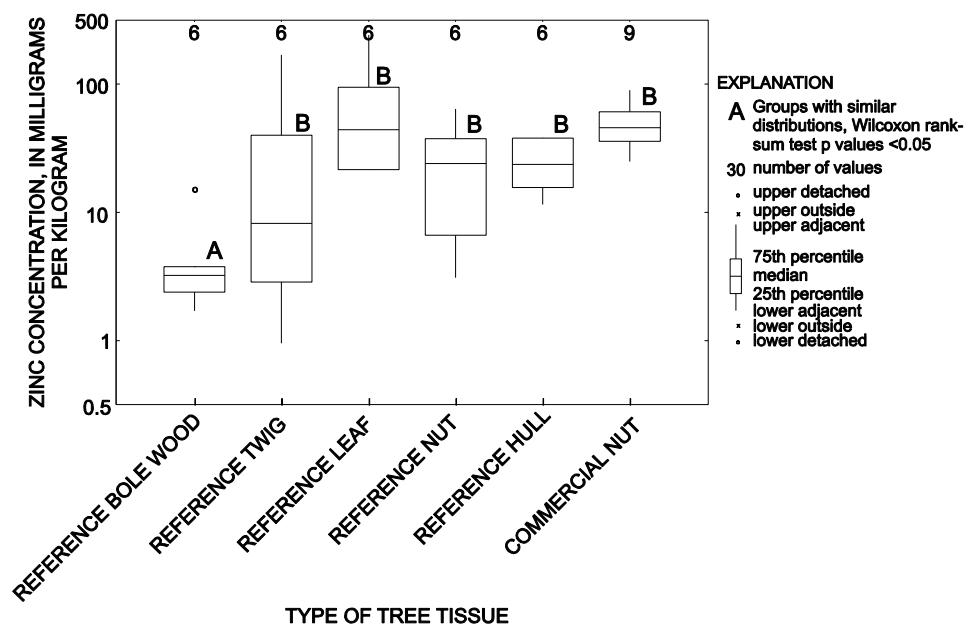


Figure 3.7 Boxplots of zinc concentrations in reference-tree samples collected in Norman, Oklahoma, October 2006 through April 2007, and retail nut samples purchased from October 2006 through June 2009.

Lead and zinc concentrations in tree tissues collected for this chapter generally were less than those reported near active sites of mining and smelting and less than those reported in urban areas in previously published papers (Table 3.5, Figures 3.2-3.7).

3.4.2 Soil Samples

Soil samples were sequentially extracted to compare amounts of lead and zinc likely to be bioavailable (water soluble plus exchangeable fractions) to total concentrations of those metals. Total lead and zinc concentrations in soils were about an order of magnitude greater than exchangeable concentrations of those metals, due to lead and zinc being bound to organic-compound and residual fractions such as sulfide

minerals. Concentrations of water-soluble lead in upland soils that were significantly less than in wetland soils may be an artifact of greater leaching of lead in upland than wetland soils.

Table 3.5 Synopses of lead and zinc concentrations reported in tree tissues in other papers.

[--, not specified in paper; <, less than]

Paper Citation	Location	Land Use	Distance From Possible Source(s)	Sampled Media	Metal Statistic	Numeric Value(s) (in mg/kg)
Connor et al. (1972)	Centreville, Missouri	Ore-hauling road	<30 m	Eastern red cedar branch tips (converted from ashed concentrations)	Geometric mean lead	1,200
			>30 m		Geometric mean lead	42.0
			<30 m		Geometric mean zinc	64.8
			>30 m		Geometric mean zinc	23.4
Van Hook et al. (1977)	Eastern Tennessee	Deciduous forest	--	black oak leaves	Mean lead	5.2
					Mean zinc	28
				black oak branches	Mean lead	3.5
					Mean zinc	9.7
				black oak bole wood	Mean lead	2.2
					Mean zinc	5.3
Parker et al. (1978)	Northwest Indiana	black oak forests (urban)	--	black oak leaves	Mean lead	12.8
		black oak forests (rural)				<1.0
		black oak forests (urban)			Mean zinc	63.0
		black oak forests (rural)				30.5

Table 3.5 Synopses of lead and zinc concentrations reported in tree tissues in other papers, continued

[--, not specified in paper; <, less than]

Paper Cita- tion	Location	Land Use	Distance From Possible Source(s)	Sampled Media	Metal Statis- tic	Numeric Value(s) (in mg/kg)
Palmer and Kucera (1980)	Eastern Missouri	forests near lead and zinc mining	0-8 km	washed sycamore leaves	Range of lead	1.3-1,120
				washed sycamore twigs	Range of lead	1.8-320
Hutton (1984)	Southwest England	oak forests near zinc smelter	<3 km	oak leaves	Mean lead	61.0
					Mean zinc	149
Beyer et al. (1985)	Palmerton, Pennsyl- vania	forests near zinc smelters	<1 km	tree leaves	Mean lead	21
Rags- dale and Berish (1988)	Atlanta, Georgia	urban road	<10 m	hickory tree bole wood	Range of lead	4.8-17
			>10 m			1.0-5.5
Pier- zynski et al., 2002	Dearing, Kansas	forest near zinc smelter	<1 km	poplar leaves	Max- imum lead Max- imum zinc	33.0 3,610
Rad- ema- cher (2003)	European Union Nations	forests	--	leaves and needles	Median lead	2.1
					Median zinc	33

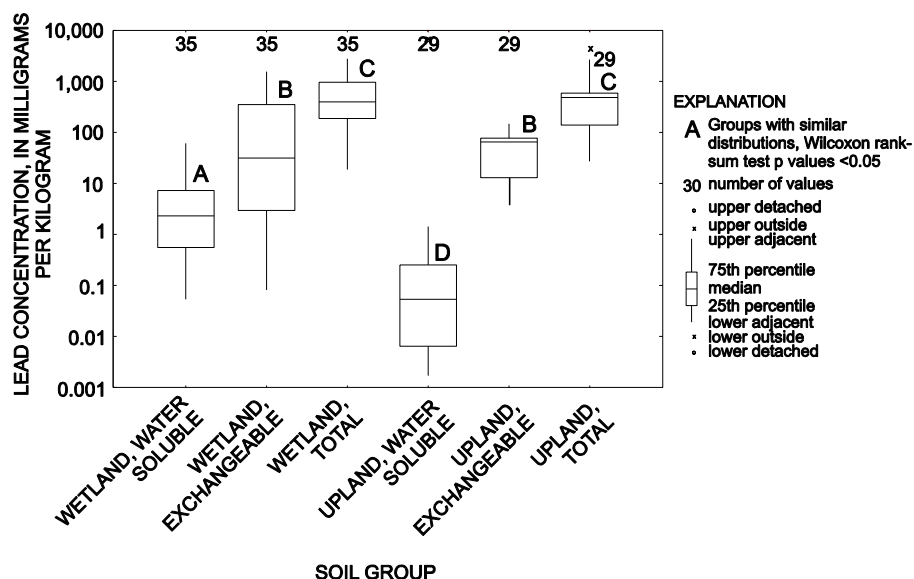


Figure 3.8 Boxplots of water-soluble, exchangeable, and total lead concentrations in soil samples collected in wetlands in April 2007, and in uplands from January-November 2006.

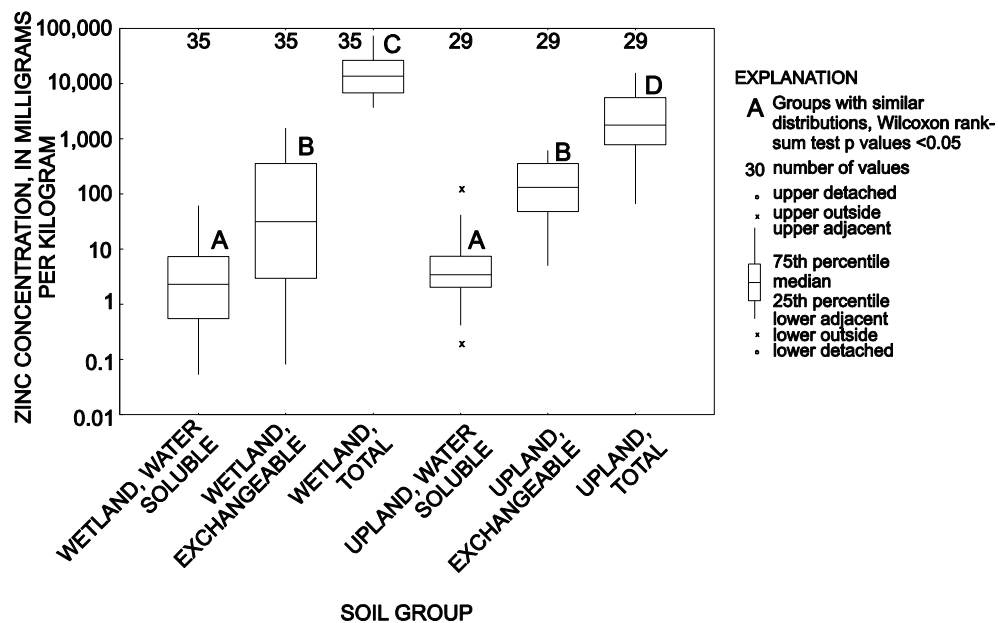


Figure 3.9 Boxplots of water-soluble, exchangeable, and total zinc concentrations in soil samples collected in wetlands in April 2007, and in uplands in January-November 2006.

Soil samples collected in the mining district had significantly less total lead than zinc concentrations (Figure 3.10). Reference soil samples had total lead and zinc concentrations an order of magnitude or less than those in upland mining district soil samples. Unlike mining district soils, lead and zinc concentrations were similar in the reference soil samples (Figures 3.10). Much less lead concentrations in soils in the reference site, but similar lead contents in tissues of those trees as in the upland trees in the mining district, may indicate natural limits to lead uptake in bolewood. About half of the wetland and upland soil samples collected in the mining district had total lead concentrations exceeding a 500 mg/kg Residential Clean-up Standard (U.S. Environmental Protection Agency, 2007b). None of the reference soil samples had total lead concentrations exceeding that standard (Figure 3.10). Fine tailings particles, which have the greatest metals concentrations of tailings, contained 2-5 times the lead and zinc concentrations of local soils. Previously published papers have reported total lead and zinc concentrations in mining, smelting, and urban areas were similar to or greater than total concentrations of those metals in soil samples described in this chapter (Table 3.6, Figure 3.10).

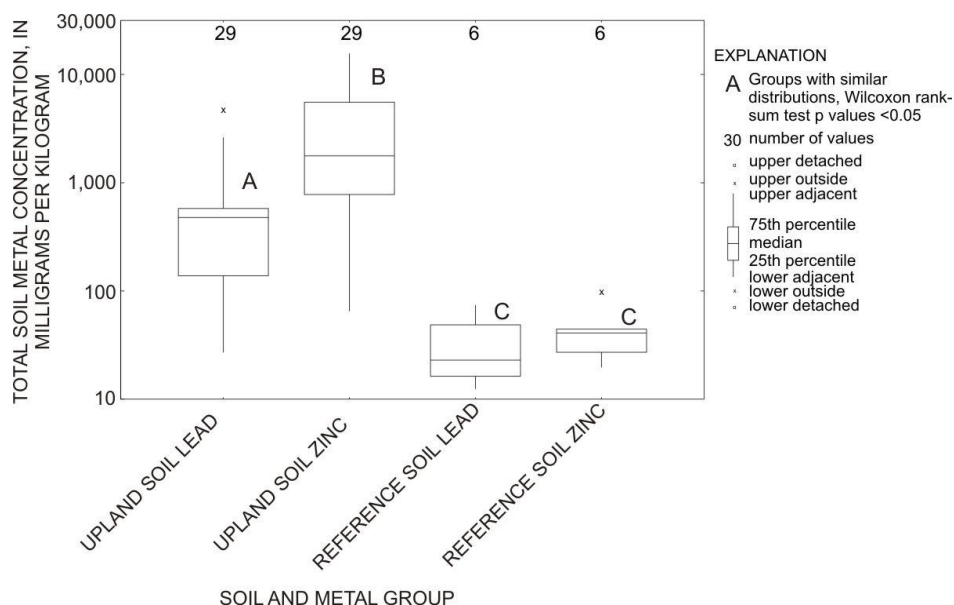


Figure 3.10 Boxplots of total lead and zinc concentrations in soil samples collected in uplands in the Tri-State mining district in January-November 2006 and October 2006-April 2007 in Norman, Oklahoma.

Table 3.6 Synopses of lead and zinc concentrations reported in soils in other papers.

[--, not specified in paper; <, less than]

Paper Citation	Location	Land Use	Distance from Possible Source(s)	Sampled Media	Metal Statistic	Numeric Value(s) (in Milligrams per Kilogram)
Connor et al. (1972)	Centreville, Missouri	Ore-hauling road	<30 m	subsurface soil, 5-10 cm depth	Geometric mean lead	500
			>30 m		Geometric mean zinc	<10
			<30 m		Geometric mean lead	195
			>30 m		Geometric mean zinc	52
Buchauer (1973)	Palmerton, Pennsylvania	Forests near zinc smelter	<1 km	A1-horizon	Range lead	200-1,100
					Range zinc	50,000-80,000
Chaney et al. (1978)	Northwest Indiana	black oak forests (urban)	--	0.0-2.5 cm depth	Mean zinc	2,000
		black oak forests (rural)				62

Table 3.6 Synopses of lead and zinc concentrations reported in soils in other papers, continued.

[--, not specified in paper; <, less than]

Paper Citation	Location	Land Use	Distance from Possible Source(s)	Sampled Media	Metal Statistic	Numeric Value(s) (in Milligrams per Kilogram)
Parker et al. (1978)	North-west Indiana	black oak forests (urban)	--	dune soils, 0-0.25 centimeter depth	Mean lead	463
		black oak forests (rural)				20.5
		black oak forests (urban)			Mean zinc	122
		black oak forests (rural)				41.6
		black oak forests (rural)				
Roberts and Johnson (1978)	North Wales	abandoned lead/zinc mine	<6 km	0-5 cm depth	Range lead	95-5,000
Johnson et al. (1982)	North Wales	abandoned lead/zinc mine	--	0-5 cm, >50% unvegetated	Geometric mean lead	1,660
				0-5 cm depth, <50% unvegetated		1,000
				0-5 cm depth, 100% vegetated		323
				0-5 cm depth, >50% unvegetated	Geometric mean zinc	4,320
				0-5 cm depth, <50% unvegetated		3,190
				0-5 cm depth, 100% vegetated		676
Hutton (1984)	South-west England	oak forests near zinc smelter	<3 km	A-horizon soil	Mean lead	1,430.0
					Mean zinc	1,010
Pierzynski and Schwab (1993)	Tri-State mining district, Kansas	farm field	125 m from Spring River	0.0-15 cm depth	Mean lead	110
					Mean zinc	1,165

Table 3.6 Synopses of lead and zinc concentrations reported in soils in other papers, continued.

[--, not specified in paper; <, less than]

Paper Citation	Location	Land Use	Distance from Possible Source(s)	Sampled Media	Metal Statistic	Numeric Value(s) (in Milligrams per Kilogram)
Storm et al. (1994)	Palmer-ton, Pennsylv-ania	forests near zinc smelters	3-30 km	A1-horizon soil	Maximum lead	196
					Maximum zinc	4,160
Pierzynski et al., 2002a	Dearing, Kansas	forest near zinc smelter	<1 km	0-15 cm depth	Mean lead	14,100
					Mean zinc	47,200
Pierzynski and Schwab (1993)	Tri-State mining district, Kansas	farm field	125 m from Spring River	0.0-15 cm depth	Mean lead	110
					Mean zinc	1,165

3.4.3 Estimated Tree-Tissue Lead and Zinc Contents

Lead and zinc contents of selected trees were estimated to determine if trees growing in the mining district would be useful for phytoextracting substantial quantities of metals from soils into above-ground tissues or if trees were likely to be more useful for phytostabilizing metals in mining-district soils. Estimated lead and zinc contents of tissues of selected trees in the mining district (a few grams to tens of grams) were relatively small, compared to total soil concentrations of those metals in mining district soils (grams to tens of grams per kilogram) (Table 3.7, Figure 3.12). Relatively small quantities of lead and zinc taken up in tree tissues compared to lead concentrations in local soils indicate that the trees sampled in the mining district appear to be more useful for phytostabilization (stabilizing soils and taking up small quantities of metals) than phytoextraction (taking up large quantities of lead and zinc from soils).

Table 3.7 Estimated lead and zinc contents of selected upland trees sampled in the mining district and trees sampled in the reference site.

[--, not estimated]

Tree	Estimated Foliage Biomass (kg)	Estimated Foliage Lead Content (g)	Estimated Foliage Zinc Content (g)	Estimated Woody Biomass (kg)	Estimated Woody Lead Content (g)	Estimated Woody Zinc Content (g)	Estimated Nut and Hull Biomass (kg)	Estimated Nut and Hull Lead Content (g)	Estimated Nut and Hull Zinc Content (g)
Upland Mining District Trees									
OO-4	17.1	<0.001	0.13	605	3.55	1.46	11.4	<0.001	0.360
OO-11	40.2	<0.001	5.65	1560	10.1	8.04	3.97	<0.001	0.187
OO-18	3	0.004	0.62	352	3.1	1.64	--	--	--
JM-6	33.7	<0.001	1.52	1680	9.53	6.33	4.56	<0.001	0.234
CK-5	4.05	<0.001	0.22	207	1.87	1.19	0.414	--	--
CK-6	43.8	<0.001	6.73	1570	11.9	13.7	3.97	0.002	0.200
CK-7	104	0.046	6.48	2840	29.0	22.0	6.91	0.066	0.299
CK-8	17.5	0.004	1.01	6.25	3.61	3.44	3.97	<0.001	0.192
CK-9	8.74	0.014	1.19	168	0.77	0.59	18.2	--	--
Reference Trees									
CO-1	23	<0.001	0.49	1150	10.2	3.91	2.87	0.002	0.071
CO-2	0.656	<0.001	0.01	32	0.14	0.12	0.311	<0.001	0.007
CO-3	10.9	<0.001	2.64	7.45	4.66	11.9	8.60	0.033	0.550
CO-4	4.5	0.01	0.11	2.57	1.57	0.78	0.587	<0.001	0.004
CO-5	0.8	0.005	0.08	76	0.42	0.18	0.484	<0.001	0.002
CO-6	29	0.175	2.27	2.57	1.06	0.44	0.646	<0.001	0.024

3.5 Summary and Recommendations

Lead concentrations in leaf and twig samples were substantially greater in wetland trees than in upland trees sampled in the mining district, supporting the hypothesis of greater lead concentrations in wetland tree tissues. However, lead concentrations in bole wood samples of upland trees were about twice those of bole wood samples from wetland trees, partially refuting that hypothesis. Contrary to the hypothesis of mining-district trees having greater lead concentrations than reference trees, lead concentrations were not different or were greater in tissues of the reference

trees in than in most tissues of upland trees in the mining district. Commercial nut samples had similar lead concentrations as nuts sampled from reference trees and wetland and upland trees in the mining district, refuting the hypothesis that nut tissues of trees in the mining district would have greater lead concentrations.

Concentrations of zinc in bole wood, twigs, and leaves of wetland trees were 5-10 times greater than in upland trees in the mining district, supporting the hypothesis of greater zinc concentrations in wetland trees. However, zinc concentrations in nut and hull tissues were similar in upland and wetland trees, partially refuting that hypothesis. Zinc concentrations in reference tree bole wood samples were similar to those in samples from upland trees, but zinc concentrations of other reference tree tissues ranged from one-tenth about half of those in upland tree tissues. Zinc concentrations of commercial nut samples were not different than those of nut samples collected in the mining district or the reference site.

Comparison to lead and zinc contents in tree tissues in other areas of metal mining and smelting and large urban areas indicated that tree tissues in this mining district are not severely contaminated by those metals. Most upland and wetland tree tissue tissues in the Tri-State mining district did not exceed the PAS100:2005 compost standard for lead content, but some upland tree tissues and most wetland twig samples exceeded the PAS100:2005 standard for zinc content. Exceedance of that zinc standard may preclude use of some of the tissue groups of mining district trees. Testing of composts made with local tree tissues would be needed prior to distribution and sale of such composts, as metals concentrations probably would increase as organic matter is oxidized during composting.

Soils comprise the largest source of metals that may be taken up by trees. The sum of water-soluble and exchangeable fractions is assumed to represent the bioavailable lead and zinc content of soils. Total soil contents of those metals typically were an order of magnitude greater than exchangeable-fraction concentrations of those metals, due to substantial portions of lead and zinc being in soils bound to organic compound and residual fractions such as sulfide minerals. Soil samples collected in the Tri-State mining district had significantly less total lead concentrations than zinc concentrations. Reference soil samples supported the hypothesis of having less total lead and zinc concentrations than mining district soils. Unlike soils in the mining district, lead and zinc concentrations in the reference soils were not substantially different. Nearly half of the soil samples collected in the mining district had lead concentrations exceeding a residential clean-up standard of 500 mg/kg. None of the reference soil samples had lead concentrations exceeding that standard.

Other reports of total lead and zinc concentrations in mining and smelting and urban areas were similar to or greater than total concentrations of those metals in soil samples described in this chapter. Similar lead contents in mining district trees and reference site trees, despite much greater lead concentrations in mining district soils, may indicate natural limits to lead uptake in trees and partially refutes the hypothesis of lead contents being greater in all tissues of mining-district trees than in reference-site trees. Estimates of lead and zinc content in biomass of selected trees in the mining district and control site indicate that trees can serve a greater role for phytostabilization than phytoextraction of those metals, refuting the hypothesis that very large lead and zinc contents of trees in the mining district would preclude planting of trees for

phytoremediation.

Despite decades of work by numerous researchers in this mining district, numerous data gaps remain. More knowledge of atmospheric transport and deposition of fine metals would be useful for better understanding sources and cycling of metals in the environment of sites like this mining district. Sampling tissues of terrestrial wildlife and livestock would be an additional means of determining the extent of metals contamination of the mining district and whether meat and other tissues of terrestrial mammals in the district should be sold for human consumption.

CHAPTER 4

Changes in Selected Metals Concentrations from the mid-1980s to the mid-2000s in a Stream Draining the Oklahoma Part of the Tri-State Mining District

This chapter has been accepted for publication in the Open Environmental and Biological Monitoring Journal (<http://www.bentham.org/open/toebmj/>).

4.1 Abstract

Total concentrations of iron, manganese, and zinc decreased significantly at similar flow conditions from the mid-1980s to the mid-2000s in Tar Creek, which receives drainage from most of the Oklahoma part of the abandoned Tri-State mining district. Total concentrations of aluminum, much of which probably are derived from erosion of local soils and shales, did not decrease between the two sampling periods. Increase of the reporting level of total lead concentrations by a factor of 100 from the mid-1980s to the mid-2000s obscured changes in lead concentrations between the two sampling periods. Natural attenuation processes and the long-term effects of reclamation activities probably contributed to the improvement of the aquatic environment in Tar Creek over that 20-year period.

4.2 Introduction

In addition to changes in metals concentrations in terrestrial media with time described in chapter 2 of this dissertation, changes in water quality with time also can provide evidence of changes in environmental quality of a metals-contaminated area.

Activities causing such changes in the abandoned Tri-State mining district include the long-term (rather than short-term dissemination) effects of reclamation activities involving removal of tens of millions of tons of metals-rich mine tailings, and natural attenuation processes, such as local streams draining many tons of particulate and dissolved metals downstream from the mining district (Andrews et al., 2009). An additional natural attenuation process is the sequestering of relatively mobile dissolved metals in local soils and streambed sediments in less-mobile forms such as oxide, hydroxide, oxyhydroxide, and carbonate minerals (Wilkin, 2008; O'Day et al., 1998; Carroll et al., 1998). Conversely, short-term disturbance and transport of relatively stable piles of mine tailings and subsequent oxidation of relatively immobile metallic sulfide minerals from some reclamation activities may have temporarily increased mobility of metals in the Tri-State mining district during parts of the past several decades (Schaider et al., 2007).

Several reclamation projects have been done in the Picher mining district in the decades since its closure ca. 1970. Tens of millions of tons of mine tailings have been removed for commercial uses (State of Oklahoma, 2000a and b; Datin and Cates, 2002). Dikes and diversion structures were installed in the headwaters of Tar Creek near Douthat, Oklahoma in the late 1980s, with goals of reducing the volume of surface water flowing into the mine workings through open mineshafts, and reducing discharges of metals-rich water from the mines to local streams (U.S. Environmental Protection Agency, 2008).

Natural processes in the mining district also may have increased metals in streams in this abandoned mining district. After the underground mine workings filled

with groundwater, metals-rich water started to seep to local streams in November, 1979. Quantities of water discharging from mine seeps in the Oklahoma part of the mining district, however, generally decreased in the 1990s and 2000s (oral commun., Robert W. Nairn, University of Oklahoma, September 11, 2008). The reasons for decreases in those discharges may be complex, including changes in recharge, collapses and eventual plugging of seep conduits, reclamation activities such as diverting local streams from flowing into mineshafts, and plugging of abandoned mineshafts and prospect borings. Planned burial of metals-rich fine tailings in the flooded underground mine workings may reduce future runoff of metals from the land surface in the mining district, but has an uncertain potential for contributing metals to groundwater-flow systems underlying the mining district (U.S. Environmental Protection Agency, 2007a).

The hypothesis of this chapter is that significant decreases in concentrations of selected metals in surface water occurred between two sampling periods in the mid-1980s and the mid-2000s in the abandoned Oklahoma part of the Tri-State mining district. Such changes probably were due to the combined effects of natural attenuation processes and the long-term (rather than short-term metals-dissemination effects) of reclamation activities.

Streamflow and water-quality data described in this chapter were collected at the U.S. Geological Survey's (USGS) Tar Creek at 22nd Street streamflow-gaging station near Miami, Oklahoma during two sampling periods: from February 1984 through February 1986 (mid-1980s) and from June 2004 through April 2006 (mid-2000s) by the USGS and the Oklahoma Department of Environmental Quality (ODEQ). Evaluating trends in data gathered from regular periodic sampling at the

station over several decades, similar to data collected from tree rings in Chapter 2 of this dissertation, would have been more useful for trend analyses. However, such data were not available, so changes in stream-water quality in the Oklahoma part of the mining district only could be compared between the mid-1980s and mid-2000s time periods.

The streamflow-gaging station where sampling was done is on the main drainage of the Oklahoma part of the abandoned Tri-State mining district, downstream from most of the known historical mining activities. Water quality at this streamflow-gaging station integrates the effects of mining, reclamation, and other land uses occurring in mined and other upstream parts of this basin. This streamflow-gaging station also has the most streamflow and water-quality data of all sampled sites near the mining district during these and other time periods. Analysis of these data will indicate whether there have been long-term decreases in concentrations of metals discharging from a stream draining a large abandoned mining district on a time scale of two decades.

4.3 Methods

4.3.1 Water-quality Sampling

In the mid-1980s, the USGS collected 25 water samples for analysis of metals concentrations at the streamflow-gaging station (Parkhurst, 1987). In the mid-2000s, the USGS, in cooperation with the ODEQ and the U.S. Environmental Protection Agency (USEPA), collected 22 water-quality samples at this streamflow-gaging station.

Streamflow and selected water-quality parameters were measured in the field using USGS protocols published at the times of sampling (Brown et al., 1970; Rantz et al., 1982; Wilde et al., 1998; Wilde et al., 1999). Streamflow at very low baseflows were estimated at 0.1 cubic feet per second during the sampling events.

Chemical analyses of unfiltered water samples by flame atomic absorption spectrometry were done in the mid-1980s at the USGS National Water-Quality Laboratory in Lakewood, Colorado, using methods described in Brown et al. (1970) and Skougstad et al. (1979). Unfiltered, acid-preserved surface-water samples collected by USGS and ODEQ staff in the mid-2000s were digested and analyzed by inductively-coupled plasma-atomic emission spectrometry with Thermo Jerrell Ash Trace ICP Analyzer at the U.S. Environmental Protection Agency-certified ODEQ Laboratory in Oklahoma City, Oklahoma, using USEPA Method 200.7 (Martin et al., 1994). Streamflow and water-quality data described in this chapter are available in the USGS National Water Information System, accessible, as of 2011, on the internet at <http://waterdata.usgs.gov/nwis>.

4.3.2 Data Analysis

Streamflow and water-quality data were analyzed through graphical comparison of streamflow versus metals concentrations and use of the non-parametric Wilcoxon rank-sum test (Wilcoxon, 1945) of significance of difference of locations of distributions of total (unfiltered) metals-concentration data collected during the two time periods. Graphing of metals concentrations versus streamflow and Wilcoxon rank-sum tests were done with the S+ 7.0 statistical and graphing package (Insightful

Corporation, 2005). For graphing of censored data values (less than the level of quantification, also known as the reporting level) censored values were estimated to be one-half of the laboratory reporting level (to avoid over- or under-estimating censored data values). Censored values (reporting levels) were retained in the data sets for analysis by the Wilcoxon rank-sum test, rather than adjusted, because that test is non-parametric (relies on ranking of data, rather than absolute data values). For the Wilcoxon rank-sum test, two-sided p-values of 0.05 or less support a 95 percent or greater confidence that the locations of distributions of two groups of data are different and a value of 0.10 or less for two-sided p-values supports a 90 percent or greater confidence that the locations of distributions of two groups of data are different. Because metals concentrations tend to increase or decrease with streamflow in the mining district (Andrews et al., 2009), streamflows during the sampling periods and at times of sample collection were compared.

Another measure of changes in quantities of lead and zinc draining from the Oklahoma part of this mining district can be made through estimation of loads (masses of the metals per unit time flowing past a stream cross section) of those metals in the mid-1980s versus the mid-2000s. Mean daily streamflow data for the sampling periods were retrieved from the USGS NWIS data base (accessible on the internet as of January 2011 at <http://waterdata.usgs.gov>), as were the water-quality data described in this chapter. Daily estimated loads at the Tar Creek near Miami, Oklahoma streamflow-gaging station were computed by: linear regression of measured lead and zinc concentrations versus streamflow at times of sampling for the two sampling periods (Table 4.1), estimation of daily loads by substituting mean daily streamflow recorded at

the streamflow-gaging station in the regression equations, and computation of medians of the daily loads for the two sampling periods.

4.3.3 Quality Assurance/Quality Control

In the mid-1980s, several water samples were collected at the streamflow-gaging station at intervals of an hour or more between samples, but no field quality-control samples such as split samples, duplicate samples collected within short time intervals, or field or equipment blanks were collected. Lack of collection of such quality-control samples was typical of many water-quality sampling projects conducted during that period (oral commun. David Parkhurst, U.S. Geological Survey, 2008).

In the mid-2000s, several types of quality-control samples were collected at the streamflow-gaging station. Equipment blanks for major ions and metals were collected using metals-grade blank water prior to data collection. Analyzed metals were not detected in those equipment blanks. One field blank and two field duplicate samples were collected at the station (at frequencies of about 5 and 10 percent of field samples, respectively). No metals were detected in the field blank. Relative percent differences between all metals concentrations in the two field duplicate samples ranged from 0 to 10.5 percent.

4.4 Results and Discussion

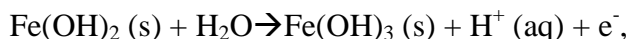
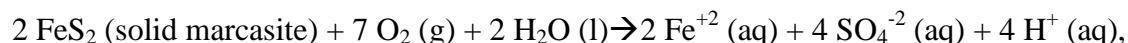
4.4.1 Streamflow

Mean daily streamflow at the station was significantly greater during the mid-1980s sampling period than in the mid-2000s sampling period (Figures 4.1 and 4.2, Wilcoxon rank sum test $Z=10.3$, $p=0.01$). However, streamflows at the times of

collection of water-quality samples were not significantly different at an alpha value less than or equal to 0.10 between the two sampling periods (Figure 4.3, Wilcoxon rank sum test $Z=1.39$, $p=0.0829$). Because of the similarity in streamflows at times of sampling between the two periods, metals concentrations were not adjusted for differences in flow conditions at the times of sampling.

4.4.2 pH

As with all Mississippi Valley-type mining districts, this district is underlain by carbonate host rocks (McKnight and Fisher, 1970; Paradis et al., 2007). Dissolution of carbonate rocks tends to buffer acids formed during the dissolution of metallic sulfide and disulfide minerals and subsequent oxidation of metals. Buffering occurs during dissolution of marcasite and oxidation of ferrous iron to form minerals such as ferric hydroxide and goethite, as expressed by the following reaction equations (Hem, 1992; Pontes-Buarque et al., 2000; Lemos et al., 2007):



and by dissolution of limestone from acids produced by iron oxidation—



With time, fresh, reactive surfaces of metallic sulfide and disulfide mineral crystals undergo reactions such as those shown in the previous equations, forming hydroxides, oxyhydroxides, and hydroxysulfate minerals, with other dissolved metals commonly sorbing onto surfaces of those minerals (Wilkin, 2008; Nordstrom, et al., 1982). Such reactions, along with carbonate buffering and formation of metallic

carbonate minerals, tend to neutralize acidity, increasing the stability of metallic hydroxide precipitates (Elder, 1988).

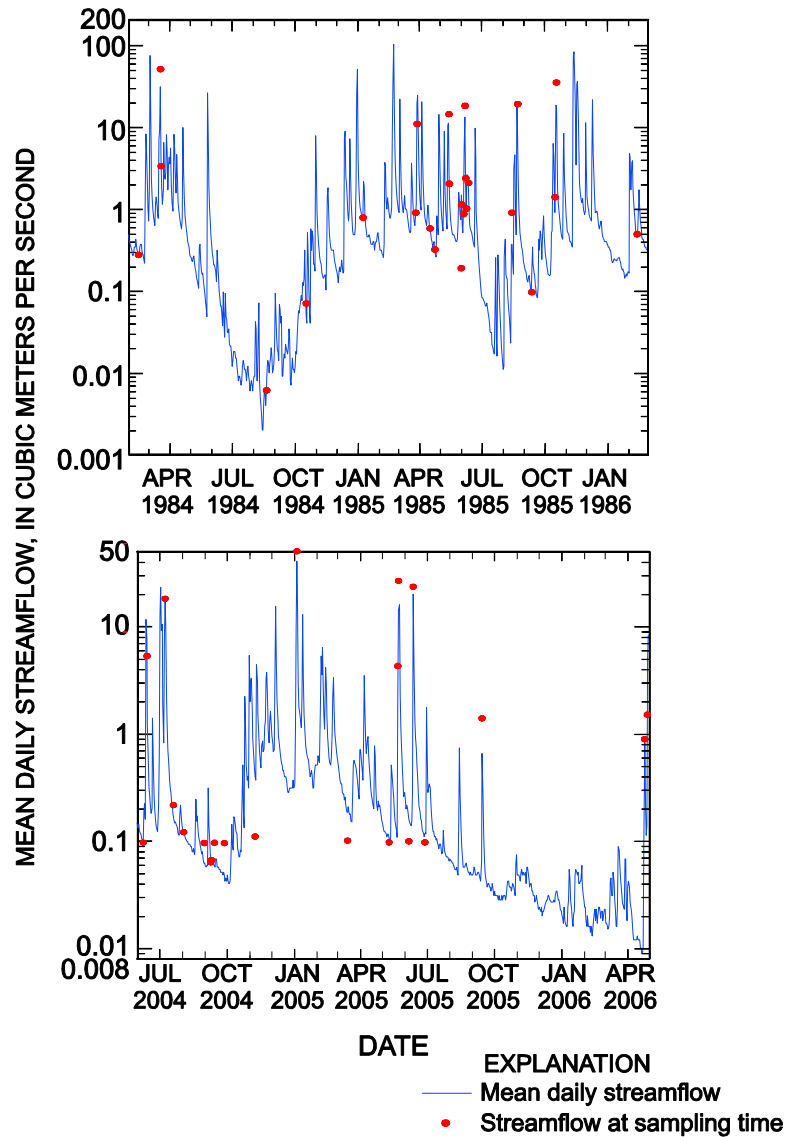


Figure 4.1 Hydrographs of daily mean streamflow from February 1984 through February 1986 and from June 2004 through April 2006, at the Tar Creek at 22nd Street Bridge at Miami, Oklahoma streamflow-gaging station.

Figure 4.2 Boxplots of daily mean streamflow, February 1984 through February 1986 and from June 2004 through April 2006, at the Tar Creek at 22nd Street Bridge at Miami, Oklahoma streamflow-gaging station.

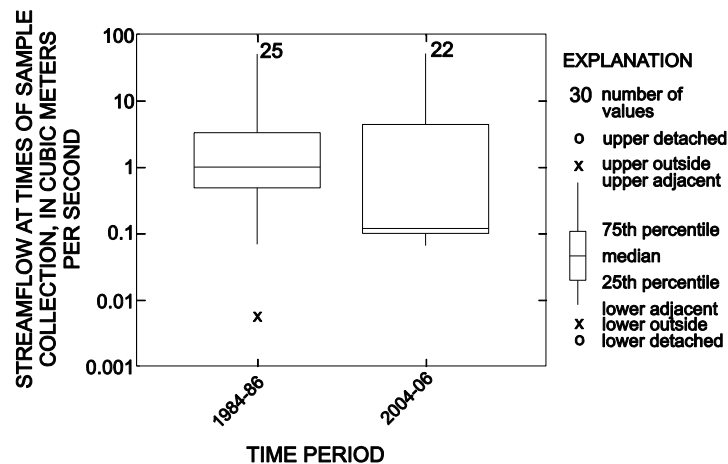


Figure 4.3 Boxplots of streamflow at times of sampling, February 1984 through February 1986 and from June 2004 through April 2006, at the Tar Creek at 22nd Street Bridge at Miami, Oklahoma streamflow-gaging station.

Values of pH significantly increased between the two sampling periods (Wilcoxon rank sum test $Z=4.29$, p = less than 0.001, Figure 4.4). The general increase in pH in water at this station probably was caused by the geochemical processes previously described in this chapter. Slight increases of pH with streamflow at this station may be the result of buffering caused by runoff of calcareous minerals from tailings and the land surface.

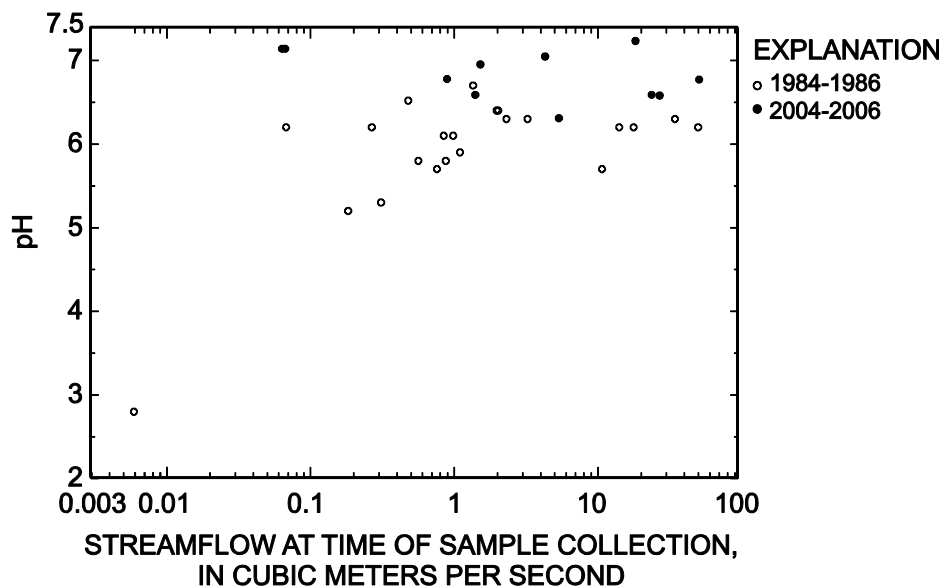


Figure 4.4 Graph of pH versus streamflow, February 1984 through February 1986 and June 2004 through April 2006, at the Tar Creek at 22nd Street Bridge at Miami, Oklahoma streamflow-gaging station.

4.4.3 Metals Concentrations

4.4.3.1 Aluminum

Aluminum most commonly occurs in clay minerals in sedimentary rocks and soils. In water, aluminum is typically associated with suspended particles of

aluminosilicate or hydroxide minerals, rather than being dissolved as a metallic ion (Hem, 1992, p. 73-75). Although there are tens of thousands of mg/kg of aluminum in local fine tailings (Table 1.4), aluminum in Tar Creek also may be derived from erosion of clay minerals from shales of the Mississippian-age Krebs formation, which underlies the most of the Tar Creek Basin (McKnight and Fischer, 1970; Table 1.2 of this dissertation). Re-suspension of clays in streambed sediments also may be an important mechanism causing exponential increases in total aluminum concentrations with increasing streamflow in Tar Creek (Figure 4.5; Andrews et al., 2009). Aluminum concentrations were not significantly different between the two sampling periods (Wilcoxon rank sum test score $Z=0.680$, $p=0.248$), indicating relatively constant sources of aluminum in this basin with time.

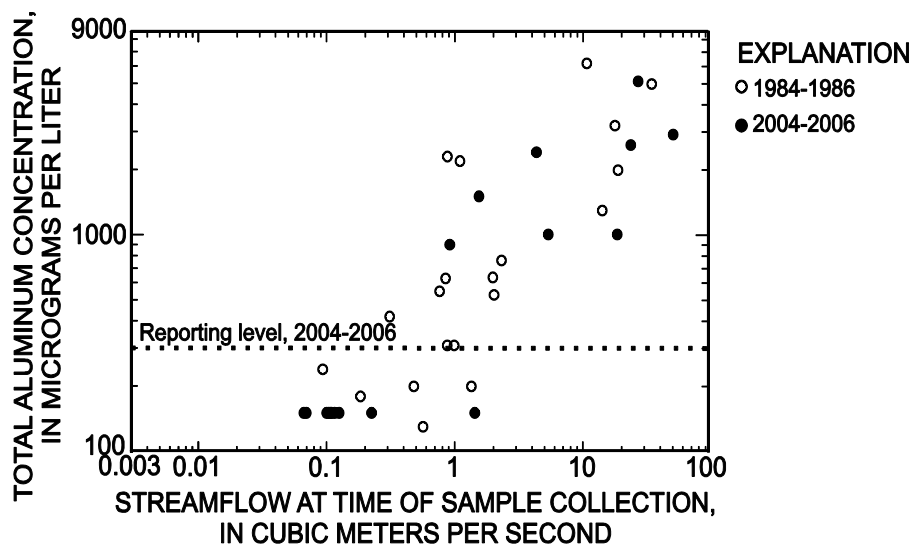


Figure 4.5 Total aluminum concentrations versus streamflow, February 1984 through February 1986 and June 2004 through April 2006, at the Tar Creek at 22nd Street Bridge at Miami, Oklahoma streamflow-gaging station.

4.4.3.2 Iron

Iron typically occurs in oxidized, circum-neutral (pH~7) surface water as particles of iron oxides and oxyhydroxides, whereas in reducing conditions that are more common in groundwater, iron is more likely to be present in the dissolved phase as the ferrous (Fe^{+2}) ion or precipitated as sulfide and disulfide minerals such as ferrous sulfide, marcasite, and pyrite (Hem, 1992) or as the carbonate mineral siderite (FeCO_3). The iron disulfide minerals marcasite and pyrite were ubiquitous in now-flooded underground mine workings and tailings piles on the land surface in the Picher mining district (McKnight and Fisher, 1970). As those minerals gradually dissolve, substantial concentrations of ferrous iron are dissolved in water seeping from the mine workings and tailings to local streams (Cope et al., 2008; DeHay, 2003; DeHay et al., 2004).

Oxidizing conditions in those streams caused precipitation of more than 0.5 m of goethite-rich sediments on the beds of many streams draining the district (Figure 4.6). Similar to aluminum, fine mine tailings in the district contain thousands to tens of thousands of mg/kg of iron (Table 1.4), which can be flushed into local streams by runoff, but nearly all of the metal load in upstream parts of the creek near Douthat, Oklahoma in 2005 were from seepage of iron-rich groundwater from the flooded underground mines (Cope et al., 2008).

Iron concentrations at this streamflow-gaging station significantly decreased by a factor of about 5 from the mid-1980s to the mid-2000s (Figure 4.7, Wilcoxon rank-sum test statistic $Z=5.30$, $p=\text{less than } 0.001$). Reasons for the decreases in iron concentrations in Tar Creek may include:

- (1) anoxic conditions in the mine workings not being as conducive to oxidation

and dissolution of remaining iron-sulfide minerals (Nordstrom et al., 1982; Elder, 1988),

- (2) the most accessible of those minerals on surfaces of the underground workings being either dissolved and flushed from the system over that period and/or having been stabilized by coatings of iron oxide, hydroxide, and carbonate minerals, and,
- (3) small particles of iron having been: a) eroded downstream during that period, b) stabilized as concretions of ferric minerals, and c) becoming less easily eroded from the land surface due to stabilization by colonizing by volunteer plants, an important natural-attenuation process (Figure 4.8).



Figure 4.6 Iron oxide and hydroxide deposits at a roadside ditch and on the bed of Tar Creek at Douthat, Oklahoma, 2003-2006 (W.J. Andrews photos).

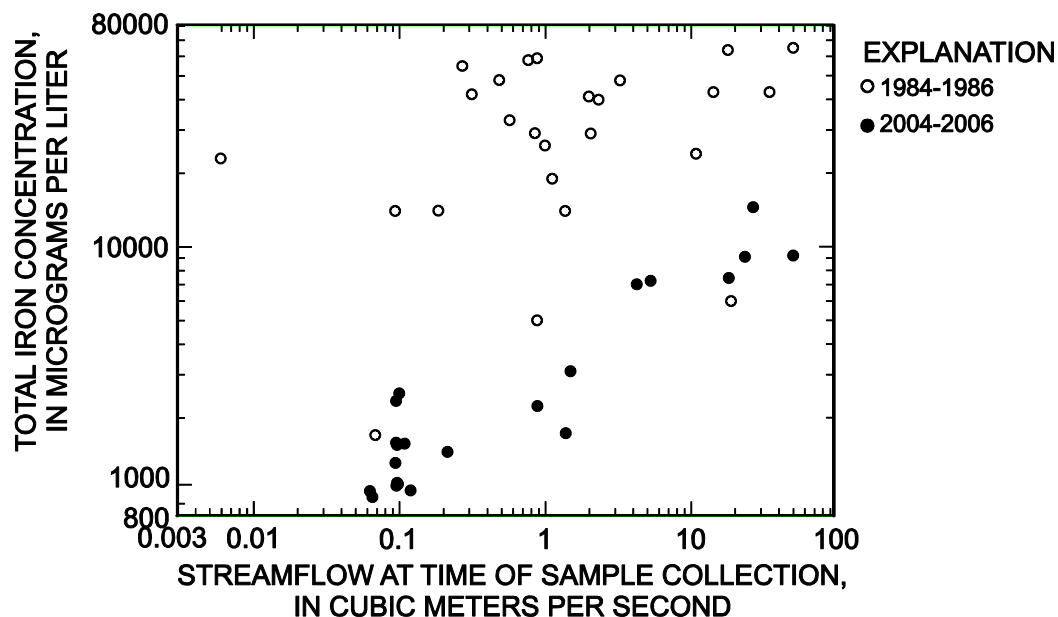


Figure 4.7 Total iron concentrations versus streamflow, February 1984 through February 1986 and June 2004 through April 2006, at the Tar Creek at 22nd Street Bridge at Miami, Oklahoma streamflow-gaging station.

The trend of increasing iron concentrations with streamflow, particularly for water-quality samples collected in the mid-2000s (Figure 4.7), indicates that runoff of iron-bearing particles from the land surface and/or re-suspension of iron-rich streambed sediments are the primary transport agents of iron to the water column at this streamflow-gaging station. Another source of increased iron concentration with increasing streamflow, however, may be increased discharge from flooded mine workings during wetter periods, which comprised as much as 99 percent of iron in upstream segments of Tar and Lytle Creeks in 2005 (Cope et al., 2008).



Figure 4.8 Grasses invading previously bare mine tailings in the mining district at a tailings pile at Douthat, Oklahoma in August 2004 and a tailings pile near Picher, Oklahoma in July 2003 (W.J. Andrews photos).

4.4.3.3 Manganese

Hydrous oxides of iron and manganese are potential substrates for sorption of other metals in aquatic environments. However, because the reduced manganous (Mn^{+2}) ion is more stable than the ferrous (Fe^{+2}) ion in aerated water, manganese tends to precipitate more slowly in surface water than iron (Elder, 1988).

Similar to iron, total manganese concentrations decreased significantly from the mid-1980s to the mid-2000s (Figure 4.9, Wilcoxon rank-sum test statistic $Z=4.65$, p =less than 0.001), by a factor of about 4. Decreases of total manganese concentrations with increasing streamflow (Figure 4.9), indicate that relatively little manganese is precipitating in streambed sediments and that manganese seeping from anaerobic groundwater in the underground mine workings and elsewhere is diluted during higher streamflows/runoff events.

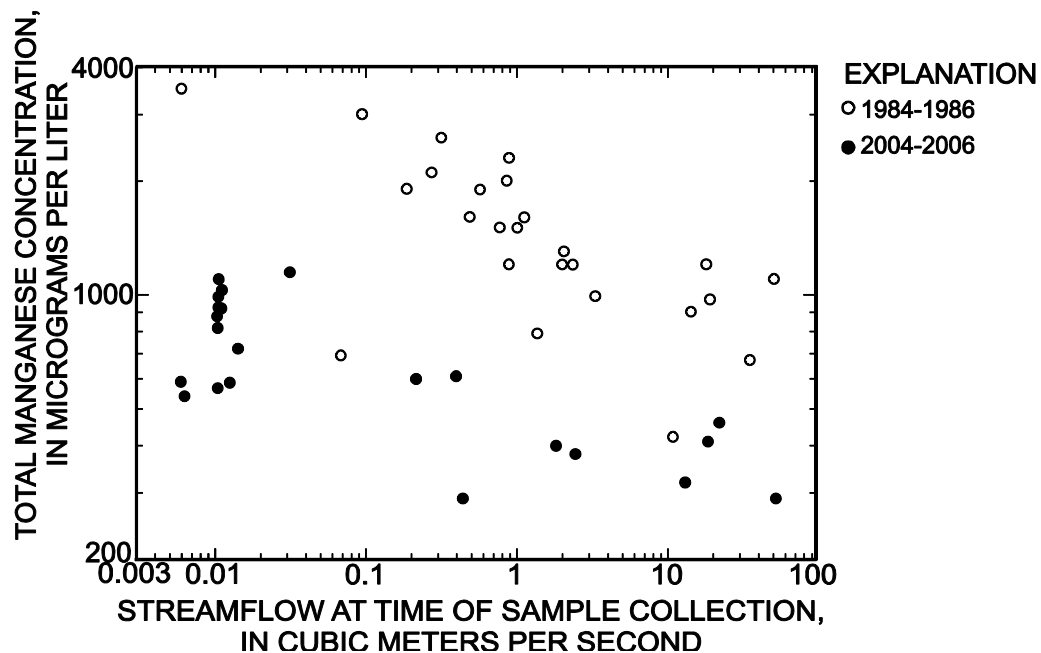


Figure 4.9 Total manganese concentrations versus streamflow, February 1984 through February 1986 and June 2004 through April 2006, at the Tar Creek at 22nd Street Bridge at Miami, Oklahoma streamflow-gaging station.

4.4.3.4 Lead

Lead generally is less mobile in water than other metals due to its propensity to precipitate as sulfide, carbonate, hydroxycarbonate, and phosphate minerals; to adsorb to organic and inorganic sediment surfaces; and to co-precipitate with iron and manganese oxides (Hem, 1992, p. 143). Changes in lead concentrations between the two sampling periods are obscured by a much higher reporting level (10 µg/L) for samples collected during the mid-2000s compared to the 0.1 µg/L reporting level for samples collected during the mid-1980s (Figure 4.10). Although lead concentrations appear to be greater in the mid-2000s sampling period on Figure 4.10, that difference is an artefact of the 100x greater reporting limit for the samples collected in the later period, with censored values being shown on Figure 4.10 at the relatively large concentration of 5 µg/L, as described in the methods section of this chapter. The Wilcoxon rank-sum test statistic ($Z=-1.60$, $p=0.945$) indicated no significant difference in lead concentrations between the sampling periods. Occurrence of greater concentrations of lead at greater streamflows indicates that runoff of lead particles on the land surface or re-suspension of lead-bearing streambed sediments during higher streamflows are the principal transport agents of lead to the water column of this stream, similar to results described in the upstream part of this basin in 2005 (Cope et al., 2008).

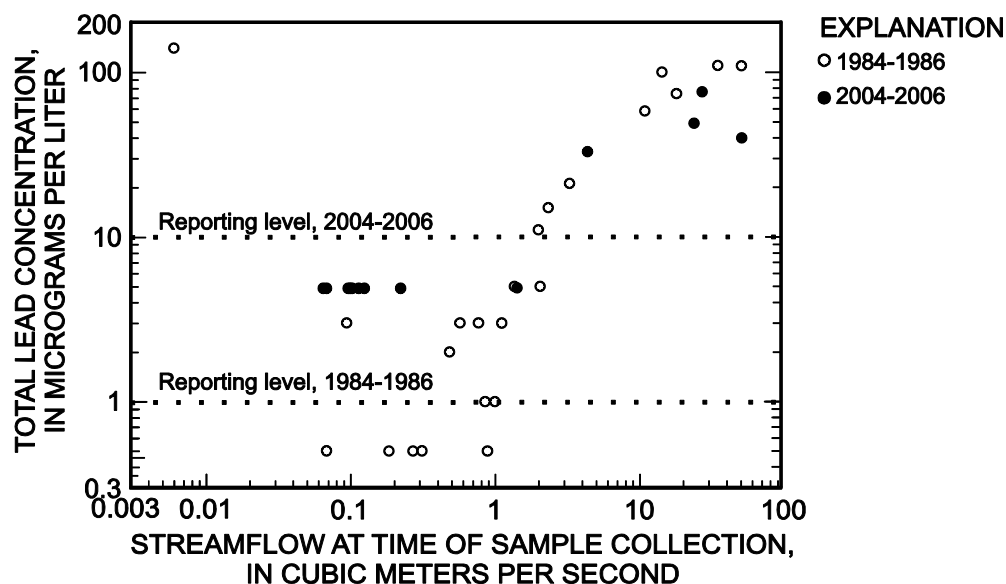


Figure 4.10 Total lead concentrations versus streamflow, February 1984 through February 1986, and June 2004 through April 2006, at the Tar Creek at 22nd Street Bridge at Miami, Oklahoma streamflow-gaging station.

4.4.3.5 Zinc

Zinc was the primary metal mined from this abandoned mining district and remains in concentrations of tens of thousands of mg/kg (parts per million) in fine mine-tailing particles (Datin and Cates, 2002; Table 1.4). Zinc concentrations in water typically were greater than aluminum, lead, and manganese concentrations (Figures 4.5, 4.9-4.11). Zinc also was present in significantly greater concentrations in the mid-1980s (Wilcoxon rank sum test statistic $Z=5.45$, $p=\text{less than } 0.001$) than in the mid-2000s at this streamflow-gaging station (Figure 4.11). Zinc concentrations at similar streamflows decreased by about a factor of 10 between the two sampling periods (Figure 4.11), similar to decreases in zinc content in some of the tree cores sampled in the mining district (appendix I).

As the sulphide oxidizes in sphalerite (ZnS), zinc is dissolved as the Zn^{+2} ion, which can subsequently form relatively insoluble zinc oxides (such as zincite ZnO), hydroxides (such as $\text{Zn}(\text{OH})_2$), zinc hydroxycarbonate minerals (such as hydrozincite, $\text{Zn}(\text{OH})_6(\text{CO}_3)_2$), and complexes with iron hydroxide minerals. Such mineral formation is particularly common in well-buffered carbonate systems common in this and other Mississippi River Valley-type deposits (oral commun., Paul L. Younger, Newcastle University (U.K.), 3/2006; O'Day et al., 1998; Carroll et al., 1998; Paradis et al., 2007, American Water Works Association Research Foundation, 1996; Hem, 1992; Morel and Hering, 1993, p. 359).

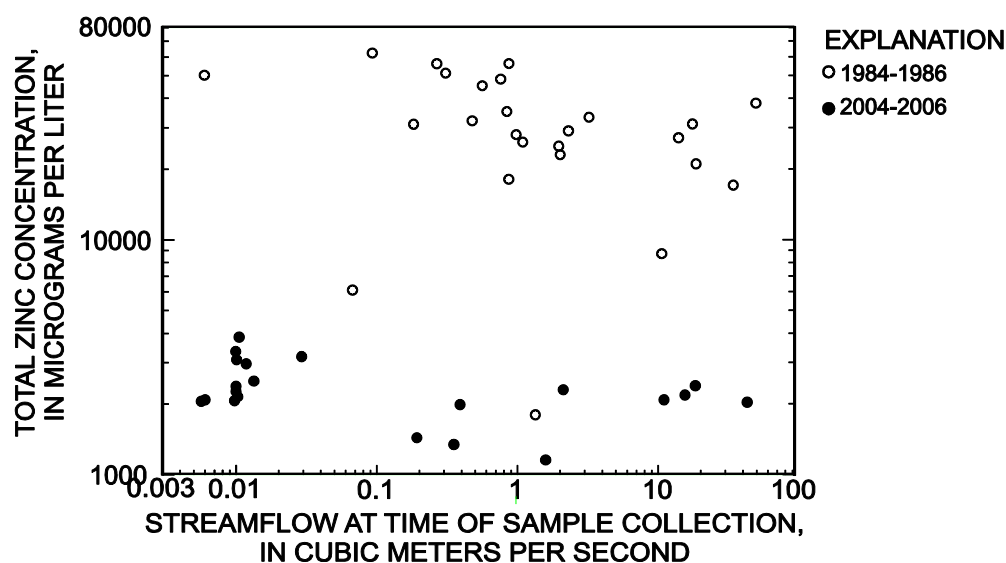


Figure 4.11 Total zinc concentrations versus streamflow, February 1984 through February 1986 and June 2004 through April 2006, at the Tar Creek at 22nd Street Bridge at Miami, Oklahoma streamflow-gaging station.

Lesser zinc concentrations at greater streamflows for both sampling periods (Figure 4.11) indicate that, like manganese, the primary source of total zinc in water at the station is seepage of zinc-rich water from flooded underground mine workings and other groundwater (Cope et al., 2008), rather than runoff from the land surface or re-suspension of bed sediments.

4.4.4 Estimated Annual Lead and Zinc Loads

As with concentrations of zinc in samples collected during the mid-1980s and the mid-2000s, median daily loads of lead and zinc decreased substantially in the latter period. However, because the earlier period had greater streamflows (Figure 4.2), loads, which are a product of streamflow and concentration, were likely to be greater in the earlier period. Because lead concentrations increase exponentially with streamflow, the load of lead, in particular, was likely to be greater in the earlier period, as shown by the ratio of those median daily loads in Table 4.1.

Table 4.1 Linear regressions of lead and zinc concentrations and estimates of median daily loads for periods corresponding to two sampling periods at the Tar Creek at 22nd Street Bridge at Miami, Oklahoma in the mid-1980s and the mid-2000s.

[q, mean daily streamflow, in cubic feet per second]

Sampling Periods	Linear Regression Equations	Median Daily Load, in Kg/d	Ratio of Median Daily Load of Lead Versus Zinc
2/1/1984-1/31/1985	Pb=0.0706(q)+13.3 (r ² =0.487) Zn=-6.20(q)+33,400 (r ² =0.029)	Pb=0.42 Zn=977	0.043
6/1/2004-4/30/2006	Pb=0.0332(q)+7.82 (r ² =0.613) Zn=-0.232(q)+2,370	Pb=0.08 Zn=22.6	0.0035

4.5 Summary and Recommendations

From the mid-1980s to the mid-2000s, no significant changes occurred in concentrations of aluminum and lead in Tar Creek downstream of the abandoned mining district, whereas there were significant decreases in total concentrations of iron, manganese, and zinc in water samples collected from the creek. Changes in lead concentrations may have been masked by a much greater reporting limit during the second sampling period in the mid-2000s. Iron, manganese, and zinc are relatively mobile metals which commonly occur in groundwater from dissolution of metallic sulfide and disulfide minerals known to be abundant in flooded underground mine workings. These metals also can reach local streams through runoff from mine tailings and contaminated soils at the land surface. Significant decreases in the concentrations of those metals in Tar Creek between the two sampling periods indicate that environmental conditions in the Picher mining district are gradually improving, probably due to a combination of natural attenuation and the long-term beneficial effects (rather than short-term effect of increasing metals dissemination) of reclamation activities. Median estimated daily loads of lead and zinc in the two sampling periods indicated that the quantities of those metals flowing down the primary drainage of the Oklahoma part of the mining district were much greater in the mid-1980s than the mid-2000s. Part of that difference, however, can be attributed to significantly greater streamflows during the earlier sampling period. Decreases in metals in Tar Creek and gradual decreases in lead and zinc contents in many of the tree cores sampled in the mining district (chapter 2 and appendix I) corroborate gradual decreases in concentrations of these metals in local terrestrial and aquatic environments from the

mid-1980s to the mid-2000s.

Water-quality improvements in this abandoned mining district from the mid-1980s to the mid-2000s are likely to be due to a combination of natural attenuation processes and the long-term beneficial effects of reclamation activities, including: natural runoff and geochemical stabilization of iron, manganese, and zinc in oxidizing conditions at the land surface and anaerobic conditions in the flooded underground mine workings; colonization of mined areas by volunteer plants which stabilize tailings and metals-contaminated soils, and reduce runoff and seepage of metals to local streams; and reclamation activities, such as removal of tens of millions of tons of mine tailings, and alteration of stream courses and seeps to intended to reduce recharge of flooded underground mine workings.

Long-term periodic sampling of water quality in Tar Creek and other streams draining the mining district is needed to provide more reliable estimates of long-term water-quality changes in the mining district as part of better monitoring the roles of natural attenuation and reclamation activities in improving environmental quality of aquatic and terrestrial ecosystems.

CHAPTER 5

Summary of Results and Recommendations

Thirty-two tree cores collected in the Tri-State mining district and six reference trees in Norman, Oklahoma were analyzed by laser-ablation inductively-coupled plasma mass spectrometry to investigate trends of lead and zinc in the environment in the years after mines closed ca. 1970 through periods of reclamation projects from the late 1990s to the early 2000s. Contrary to a hypothesis of this research, lead and zinc contents of tree growth rings did not significantly decreased after mining ceased ca. 1970. Increase in lead and zinc contents of tree growth rings followed a period of increasing water-table elevations and the start of seepage of metals-contaminated water from the mine workings in late 1979, supporting a hypothesis of this research. Disturbance of mine tailings by reclamation activity in the late 1990s and early 2000s coincided with temporary increases of content of those metals in tree growth rings, supporting another hypothesis of this research. Although lead content of tree growth rings significantly decreased after those reclamation activities into the mid-2000s, zinc contents of tree growth rings did not have a similar significant decrease during that period. Periods of significant changes in lead and zinc contents of tree growth rings at a reference site did not correspond to such periods in the mining district, supporting another hypothesis of this research. Inter-tree similarity of trends and content of lead and zinc in bole wood in the reference trees indicated relatively homogenous concentrations of lead and zinc in soils, air, and water at the reference site.

Tree tissues from 32 upland and 32 wetland trees in the mining district and 6

reference trees in Norman, Oklahoma were analyzed for lead and zinc concentrations to determine the suitability of tree planting as a means of phytoremediation of the abandoned Tri-State mining district. Lead concentrations in leaf and twig samples were substantially greater in wetland trees than in upland trees sampled in the mining district, supporting a hypothesis of greater lead concentrations in wetland tree tissues. However, lead concentrations in bole wood samples of upland trees were about twice those of bole wood samples from wetland trees, partially refuting that hypothesis. Contrary to a hypothesis of mining-district trees having greater lead concentrations than reference trees, lead concentrations were not different or were greater in tissues of the reference trees than in most tissues of upland trees in the mining district. Commercial nut samples had similar lead concentrations as nuts sampled from reference trees and wetland and upland trees in the mining district, refuting a hypothesis that nut tissues of trees in the mining district would have greater lead concentrations. Concentrations of zinc in bole wood, twigs, and leaves of wetland trees were 5-10 times greater than in upland trees in the mining district, supporting a hypothesis of greater zinc concentrations in wetland trees. However, zinc concentrations in nut and hull tissues were similar in upland and wetland trees, partially refuting that hypothesis. Zinc concentrations in reference tree bole wood samples were similar to those in samples from upland trees, but zinc concentrations of other reference tree tissues ranged from one-tenth to one-half of those in upland tree tissues, partially supporting a hypothesis of this research. Zinc concentrations of commercial nut samples were not different than those in nuts sampled from trees in the mining district or the reference site, refuting a hypothesis of this research. Test planting of black walnut and pecan trees and analyses

of metals content of nuts from those would be advisable, however, prior to widespread planting of such trees in the district for production of nuts and other tree byproducts.

Despite much greater total lead concentrations in mining district soils than at the reference site, similar lead concentrations in bole wood in mining district and reference site trees may indicate natural limits to uptake of lead into woody tree tissues.

Relatively small estimated contents of lead and zinc in selected trees growing in the mining district and the reference site indicate compared to contents of those metals in soils indicate that trees probably are more effective at phytostabilization of metals in soils rather than phytoextraction of those metals..

Water-quality data collected in the mid-1980s and the mid-2000s at a streamflow-gaging station receiving drainage from most of the Oklahoma part of the mining district were compared to see if natural attenuation and the long-term effects of reclamation activities had improved water-quality over those two decades. Significant decreases in iron, manganese, and zinc concentrations between the two sampling periods indicate that environmental conditions in the Oklahoma part of the mining district are gradually improving, probably due to a combination of natural attenuation and human reclamation activities. Gradual decreases in lead and zinc content of many of the tree cores sampled in the mining district with time corroborate probable gradual decreases of some metals in the terrestrial and aquatic environments in this abandoned mining district.

Additional research might be conducted in the future to provide additional lines of evidence for sources, cycling, and trends of metals in the environment of this abandoned mining district. Limited analysis of freshwater mussel shells collected in the

Spring and Neosho Rivers, not presented in this dissertation, could be expanded to more definitively investigate time trends of metals in the aquatic environment of the mining district. Age-dated sediment coring of Grand Lake, which receives drainage from most of the mining district, also would provide data that would corroborate general time trends of metals in the environment of the mining district. Such data would also provide regionalized integrator data that would be more representative of trends in the mining district as a whole than tree core data, which are indicative of time trends of metals in very localized areas of the terrestrial environment of the mining district. Long-term, consistent water-quality sampling of streams draining the mining district would provide data useful for estimating long-term trends in water quality in this mining district and the effects of natural attenuation and reclamation projects in reducing metals concentrations in the environment. More knowledge of atmospheric transport and deposition of fine metals would be useful for better understanding sources and cycling of metals in the environment of sites like this mining district. Sampling tissues of terrestrial wildlife and livestock would be an additional means of determining the extent of metals contamination of the mining district and whether meat and other tissues of terrestrial mammals in the district should be sold for human consumption. Such additional research would provide better understanding of fate and transport of metals in the environment and the short- and long-term effects of natural attenuation and reclamation activities on the presence of metals in aquatic and terrestrial environments.

BIBLIOGRAPHY

- American Water Works Association Research Foundation. 1996. Internal corrosion of water distribution systems. American Water Works Association Research Foundation, 586 p.
- Andrews, W.J., Becker, M.F., Mashburn, S.L., and Smith, S.J. 2009. Selected metals in sediments and streams in the Oklahoma part of the Tri-State mining district, 2000-2006. U.S. Geological Survey Scientific Investigations Report 2009-5032, 36 p.
- Angelo, R.T. 2005. Residual effect of lead and zinc mining on freshwater mussels in the Spring River. Kansas Department of Health and Environment. Accessed on June 14, 2007 at URL: http://www.dce.siu.edu/pdfs/tristatepdf/angelo-mussel_contaminant_study.pdf
- Argonne National Laboratory. 2002. Peconic River remedial alternatives—phytostabilization: Brookhaven National Laboratory, 4 p.
- Associated Press. 2008. Pollution brings end to Oklahoma mining town: Associated Press, May 12, 2008. Accessed on June 15, 2008 at URL: http://www.msnbc.msn.com/id/24555711/ns/us_news-environment/page/1/
- Baes, C. F., III, and Ragsdale, H. L. 1981. Age-specific lead distribution in xylem rings of three tree genera in Atlanta, Georgia. *Environmental Pollution Series B* (2): 21-35.
- Baes, C.F., III, and McLaughlin, S.F. 1984. Trace elements in tree rings: evidence of recent and historical air pollution. *Science* (224): 494-497.
- Baltrėnaitė, Edita, and Butkus, Donatas. 2007. Modelling of Cu, Ni, Zn, Mn and Pb transport from soil to seedlings of coniferous and leafy trees. *Journal of Environmental Engineering and Landscape Management* (XV): 200-207.
- Begin, C., Savard, M.M., Parent, M., Marion, J., and Smirnov, A. 2002. A dendrochronological and dendrogeochemical investigation on impacts of smelter emissions in the Rouyn-Noranda region: Geological Association of Canada, conference proceedings, Saskatoon 2002 Technical Program, SY: Distribution of metals in the environment around smelters. Accessed on January 20, 2004 at URL: http://gac.esd.mun.ca/gac_2002/search_abs/sub_program.asp?sess=98&form=10&abs_no=288
- Beyer, W.N., Patee, O.H., Sileo, L., Hoffman, D.J., and Mulhern, B.M. 1985. Metal contamination in wildlife living near two zinc smelters. *Environmental Pollution Series A* (38): 63-86.

- Beyer, W.N., Dalgarn, J., Dudding, S., French, J.B., Mateo, R., Miesner, J., Sileo, L., and Spann, J. 2004. Zinc and lead poisoning in wild birds in the Tri-State mining district (Oklahoma, Kansas, and Missouri). *Archives of Environmental Contamination and Toxicology* (48): 108-117.
- Brabander, D.J., Keon, N., Stanley, R.H.R., and Hemond, H.F. 1999. Intra-ring variability of Cr, As, Cd, and Pb in red oak revealed by secondary ion mass spectrometry: implications for environmental biomonitoring. *Proceedings of the National Academy of Sciences of the United States of America* (96): 14,635-14,640.
- Brichta, L. C. 1960. Catalog of recorded exploration drilling and mine workings, Tri-State zinc-lead district, Missouri, Kansas, and Oklahoma. U. S. Bureau of Mines Information Circular IC7993, 13p.
- British Standards Institution. 2005. PAS 100:2005--Specification for composted materials. British Standards Institution, 47 p.
- Brown, E., Skougstad, M.W., and Fishman, F.J. 1970. Methods for collection and analysis of water samples for dissolved minerals and gases. U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 160 p.
- Buchauer, M.J. 1973. Contamination of soil and vegetation near a zinc smelter by zinc, cadmium, copper, and lead. *Environmental Science and Technology* (7): 131-135.
- Carroll, S.A., O'Day, P.A., and Piechowski M. 1998. Rock-water interactions controlling Zn, Cd, and Pb concentrations in surface waters and sediments, U. S. Tri-State mining district. 2. Geochemical interpretation. *Environmental Science and Technology* (32): 956-965.
- Chaney, W.R., Kelly, J.M., and Strickland, R.C. 1978. Influence of cadmium and zinc on carbon dioxide evolution from litter and soil from a black oak forest. *Journal of Environmental Quality* (7): 115-119.
- Christenson, S.C., 1995, Contamination of wells completed in the Roubidoux aquifer by abandoned zinc and lead mines, Ottawa County, Oklahoma. U.S. Geological Survey Water-Resources Investigations Report 95-4150, 114 p.
- Coder, K.D., 1998, Tree root growth control series: Root growth requirements and limitations. University of Georgia Cooperative Extension Service, Forest Resources Publication FOR98-9, 7 p.
- Conder, J.M., and Lanno, R.P. 1990. Heavy metal concentrations in mandibles of white-tailed deer living in the Picher mining district. *Bulletin of Environmental Contamination and Toxicology* (63): 80-86.

- Connor, J.J., Shacklette, H.T., and Erdman, J.A. 1972. Extraordinary trace-element accumulations in roadside cedars near Centerville, Missouri, in Geological Research 1971. U.S. Geological Survey Professional Paper 750-B, p. B151-B156.
- Cope, C.C., Becker, M.F., Andrews, W.J., and DeHay K. 2008. Streamflow, water quality and metal loads from chat leachate and mine outflow into Tar Creek, Ottawa County, Oklahoma, 2005. U.S. Geological Survey, Scientific Investigations Report 2007-5115, 24 p.
- Datin, D.L., and Cates, D.A., 2002, Sampling and analysis of chat piles in the Tar Creek Superfund Site. Oklahoma Department of Environmental Quality, 69 p.
- DeHay, K.L. 2003. Assessment and comparison of 1976-77 and 2002 water quality in mineshafts in the Picher mining district, northeastern Oklahoma and southeastern Kansas. U.S. Geological Survey Water-Resources Investigations Report 03-4248, 65 p.
- DeHay, K.L., Andrews, W.J., and Sughru, M.P. 2004. Hydrology and ground-water quality in the mine workings within the Picher mining district, northeastern Oklahoma, 2002-03. U.S. Geological Survey Scientific Investigations Report 2004-5043, 71 p.
- Devall, M.S., Latimer, S.D., Thien, L.B., Ellgaard, E.G., Thomas, C.E., and Kumar, S.D. 2001. Metal deposition in bald cypress tree rings: Tree rings and people, An international conference on the future of dendrochronology, September 22-26, 2001, Davos, Switzerland. Accessed on November 19, 2004 at URL: <http://www.wsl.ch/forest/dendro2001/abstracts/abs117.ehtml>
- Durbin, J., and Watson, G.S. 1951. Testing for serial correlation in least squares regression, II. *Biometrika* (38): 159-179.
- Elder, J.F., 1988. Metal biogeochemistry in surface-water systems—a review of principles and concepts. U.S. Geological Survey Circular 1013, 43 p.
- Everett, D. 2004. Tri-State lead and zinc district. Oklahoma Historical Society. Accessed on May 2, 2004 at URL: <http://www.ok-history.mus.ok.us/enc/tri-statemines.htm>
- Farrish, K., LaChastity, Filliand, E., Trotman, E., and Watts, K. 2000. Lead concentrations of tulip poplar rings in the Great Smoky Mountain National Park: Western Carolina University. Accessed on January 19, 2005 at URL: www.wcu.edu/ubms/pdf%6C200@5Clead.pdf
- Ferderer, D.A. 1996. National overview of abandoned mine land stations utilizing the Minerals Availability System (MAS) and geographic information system (FIS) technology. U.S. Geological Survey Open-File Report 96-549, 42 p.

- Gibson, A.M. 1972. Wilderness bonanza, the Tri-State district of Missouri, Kansas, and Oklahoma. University of Oklahoma Press, Norman, Oklahoma, 362 p.
- Goodrum, P.D., Reid, V.H., and Boyd, C.E. 1971. Acorn yields, characteristics, and management criteria of oaks for wildlife. *Journal of Wildlife Management* (35): 520-532.
- Gray, K.A., 2004a. Section 3: General phytoremediation. Northwestern University, 3 p. Accessed on September 11, 2004 at URL: http://www.civil.nwu.edu/ehe/HTML_Kag/Kimweb/MEOP/section3.htm
- Gray, K.A., 2004b. Section 2: Phytoremediation of lead. Northwestern University, 4 p. Accessed on September 11, 2004 at URL: http://www.civil.nwu.edu/ehe/HTML_Kag/Kimweb/MEOP/section4.htm
- Guyette, R.P., Cutter B., and Henderson, G.S. 1991. Long-term correlations between mining activity and levels of lead and cadmium and tree-rings of red cedar. *Journal of Environmental Quality* (20): 146-150.
- Halim, M., Conte, P., and Piccolo, A. 2003. Potential availability of heavy metals to phytoextraction from contaminated soils induced by exogenous humic substances. *Chemosphere* (52): 265-275.
- Helsel, D.R., and Hirsch, R.M. 1992. Statistical methods in water resources. Elsevier, Amsterdam, Netherlands, 529 p.
- Helsel, D.R., Mueller, D.K., and Slack, J.R. 2006. Computer program for the Kendall family of trend tests. U.S. Geological Survey Scientific Investigations Report 2005-5275, 4 p.
- Hem J.D. 1992. Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water-Supply Paper 2254, 3rd ed., 4th printing, 263 p.
- Hovmand, M.F., Tjell, J.C., and Mosbaek, H. 1983. Plant uptake of airborne cadmium. *Environmental Pollution (Series A)* (30): 27-38.
- Hughes, R.J., Watmough, S.A., and Hutchinson, T.C., 1999. $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in tree rings as monitors of environmental change. *Environmental Science and Technology* (33): 670-673.
- Hutton, M. 1984. Case 7.6, Impact of airborne metal contamination on a deciduous woodland system *in Effects of pollutants at the ecosystem level*, eds. Sheehan, P.J., Miller, D.R., Butler, G.C., and Bourdeau, P. John Wiley and Sons, Ltd., New York, New York, p. 365-375.
- Insightful Corporation. 2005. S-plus 7 for Windows users guide. Insightful Corporation, Seattle, Washington, 664 p.

- Interstate Technology and Regulatory Cooperation Work Group. 1999. Phytoremediation decision tree: Interstate Technology and Regulatory Cooperation Work Group, Phytoremediation Work Team, 36 p. Accessed on September 12, 2004 at URL: <http://www.clu-in.org/download/partner/phytotree.pdf>
- Johnson, A.H., Siccama, T.G., and Friedland, A.J. 1982. Spatial and temporal patterns of lead accumulation in the forest floor in the northeastern United States. *Journal of Environmental Quality* (11): 577-580.
- Kabata-Pendias, A., and Pendias, H. 1984. Trace elements in soils and plants. CRC Press, Inc., Boca Raton, Florida, 315 p.
- Kansas Geological Survey. 2003. Lead and zinc mining: Kansas Geological Survey. Accessed on May 3, 2004 at URL: <http://www.kgs.ku.edu/Extension/ozark/mining.html>
- Kehely, E., Warner, W., and Wood, F. 2003. Historical survey of Indian-owned mill tailing piles in the Picher mining field, Ottawa County, Oklahoma. OA Systems Corporation, Amarillo, TX, 116 p.
- Lasat, M.M., 2000. Phytoextraction of metals from contaminated soil: a review of plant/soil/metal interaction and assessment of pertinent agronomic issues. *Journal of Hazardous Substance Research* (2): 5-1—5-25.
- LeDuc, D.L., and Terry, Norman. 2005. Phytoremediation of toxic trace elements in soil and water. *Journal of Industrial Microbiology and Biotechnology* (32): 514-520.
- Lemos, V.P., da Costa, M.L., Lemos, R.L., and de Faria, M.S.G. 2007. Vivianite and siderite in lateritic iron crust: an example of bioreduction. *Quimica Nova* (30): 36-40.
- Lin, Z-Q., Barthakur, N.N., Schuepp, P.H., and Kennedy, G.G. 1995. Uptake and translocation of ⁵⁴Mn and ⁶⁵Zn applied on foliage and bark surfaces of balsam fir (*Abies balsamea* (L.) MILL.] seedlings. *Environmental and Experimental Botany* (4): 475-483.
- Lindeberg, J. 2004. X-ray based tree ring analyses, Doctoral Dissertation, Swedish University of Agricultural Sciences, Acta Universitatis Agriculturae Sueciae. *Silvestria* vol. 299, 25 p. Accessed on January 20, 2005 at URL: <http://diss-epsilon.slu.se/archive/00000462/>
- Luza, K.V. 1986. Stability problems associated with abandoned underground mines in the Picher field, northeastern Oklahoma: Oklahoma Geological Survey. Circular 88, 113 p.

- Mala, J., Machova, P., Cvrckova, H., and Vanek, T., 2007. Heavy metals uptake by the hybrid aspen and rowan-tree clones. *Journal of Forest Science* (53): 491-497.
- Mallison, S., Miller, J., Lechler, P. 2003. Assessment of variations in heavy metal accumulation by *Quercus alba*: a dendrochemical-lead isotopic approach: Ecological Society of America 2003 Annual Meeting, Poster Session no. 14, Forest Ecology. Accessed on January 20, 2005 at URL: <http://abstracts.co.allenpress.com/pweb/esa2003/document/?ID=26156>
- Marcher, M.V., and Bingham, R.H. 1971. Reconnaissance of the water resources of the Tulsa Quadrangle, northeastern Oklahoma. Oklahoma Geological Survey, Hydrologic Atlas 2, 4 plates.
- Martin, R.R., Zanin, J.P., Bensette, M.J., Lee, M., and Furimsky, E. 1997. Metals in the annual rings of eastern white pine (*Pinus strobus*) in southwestern Ontario by secondary ion mass spectroscopy (SIMS). *Canadian Journal of Forestry Research/Review of Canadian Research in Forestry* (27): 76-79.
- Martin, T.D., Brockhoff, C.A., Creed, J.T., and EMMC Methods Work Group. 1994. Method 200.7: Determination of metals and trace elements in water and wastes by inductively-coupled plasma-atomic emission spectrometry. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, 58 p. Accessed on June 30, 2008 at URL: http://www.epa.gov/waterscience/methods/method/files/200_7.pdf
- McKnight, E.T., and Fischer, R.P. 1970. Geology and ore deposits of the Picher field, Oklahoma and Kansas. U.S. Geological Survey Professional Paper 588, 165 p.
- Morel, F.M.M., and Hering, J.G. 1993. Principles and applications of aquatic chemistry. John Wiley and Sons, Ltd., New York, New York, 588 p.
- Nordstrom, D.K. 1982. In: Kittrick, J.A., Famming, D.S., and Hossner, L.R. (eds.), Aqueous pyrite oxidation and consequent formation of secondary iron minerals in The environmental geochemistry of mineral deposits, 6A. Society of Economic Geologists. Littleton Press, Littleton, Colorado, p. 37-56.
- O'Day, P.A., Carroll, S.A., and Waychunas, G.A. 1998. Rock-water interactions controlling Zn, Cd, and Pb concentrations in surface waters and sediments, U. S. Tri-State mining district. 1. Molecular identification using X-ray absorption spectroscopy. *Environmental Science and Technology* (32): 943-955.
- Oklahoma Climatological Survey, 2010, The climate of Ottawa County. Oklahoma Climatological Survey. Accessed on October 14, 2010 at URL: http://climate.mesonet.org/county_climate/Products/County_Climatologies/county_climate_ottawa.pdf

- Oklahoma Department of Agriculture. 2000. Forest trees of Oklahoma. Oklahoma Department of Agriculture, Forestry Services, 205 p.
- Oklahoma Department of Environmental Quality. 2003. Fish tissue metals analysis in the Tri-State mining area. Oklahoma Department of Environmental Quality, Report # I-006400-01, 33 p.
- O'Sullivan, A.D., Conlon, R., Moran, B.M., and Otte, M. 2005. Characterization of constructed wetland substrates by chemical sequential extraction and X-Ray Diffraction analyses. *Biology and Environment* (105B): 87-94.
- Palmer, K.T., and Kucera, C.L. 1980. Lead contamination of Sycamore and soil from lead mining and smelting operations in eastern Missouri. *Journal of Environmental Quality* (9): 106-110.
- Paradis, S., Hannigan, P., and Dewing, K. 2007. *In: Goodfellow, WD, Ed., Mississippi Valley-type lead-zinc deposits. Mineral deposits of Canada: A synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods. Geological Association of Canada, Mineral Deposits Division, Special Publication No. 5, 19 p.*
- Parker, G.R., McFee, W.W., and Kelly, J.M. 1978. Metal distribution in forested ecosystems in urban and rural northwestern Indiana. *Journal of Environmental Quality* (7): 337-342.
- Parkhurst, D.L. 1987. Chemical analyses of water samples from the Picher Mining Area, Northeast Oklahoma and Southeast Kansas. U.S. Geological Survey Open-File Report 87-453, 13 p.
- Pierzynski, G.M., and Schwab, A.P. 1993. Bioavailability of zinc, cadmium, and lead in a metal-contaminated alluvial soil. *Journal of Environmental Quality* (22): 247-254.
- Pierzynski, G.M., Schnoor, J.L., Youngman, A., Licht, L., and Erickson, L.E.. 2002a. Poplar trees for phytostabilization of abandoned zinc-lead smelter. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management* (6): 177-183.
- Pierzynski, G.M., Lambert, M., Hetrick, B.A.D., Sweeney, D.W., and Erickson, L.E., 2002b, Phytostabilization of metal mine tailings using Tall fescue: *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management* (6): 212-217.
- Pontes-Buarque, M., Tessis, A.C., Bonapace, J.A.P., Monte, M.B.M., de Souza-Barros, F., and Vieyra, A. 2000. Surface charges and interfaces: implications for mineral roles in prebiotic chemistry. *Anais da Academia Brasileira de Ciencias* (22): 317-322.

- Prasad, M.N.V., and Freitas, H.M.O. 2003. Metal hyperaccumulation in plants—biodiversity prospecting for phytoremediation technology. *Electronic Journal of Biotechnology* (6) no. 3, 37 p.
- Rademacher, P. 2003. Atmospheric heavy metals and forest ecosystems. Institute for World Forestry Work Report 2003/12, 19 p.
- Rantz, S.E., et al. 1982. Measurement and computation of streamflow: Volume 1, Measurement of stage and outflow. U.S. Geological Survey Water-Supply Paper 2175, 284 p.
- Raskin, Ilya, and Ensley, B.D. 2000. Phytoremediation of toxic metals: using plants to clean up the environment. John Wiley and Sons, Ltd., New York, New York, 285 p.
- Roberts, R.D., and Johnson, M.S. 1978. Dispersal of heavy metals from abandoned mine workings and their transference through terrestrial food chains. *Environmental Pollution* (15): 293-310.
- Robertson D. 2006, Hard as the rock itself, place and identity in the American mining town. University Press of Colorado, Boulder, Colorado, 216 p.
- Roubitaille, G. 1981. Heavy-metal accumulation in the annual rings of balsam fir *Abies balsamea* (L.) Mill. *Environmental Pollution, Series B* (2): 193-202.
- Sánchez-Pérez, J.M., Lucot, Eric, Bariac, Thierry, and Trémolières, Michèle, 2008. Water uptake by trees in a riparian hardwood forest (Rhine floodplain, France: *Hydrological Processes* (22): 366-375.
- Schaidter L.A., Senn, D.B., Brabander, D.J., McCarthy, K.D., and Shine, J.P. 2007. Characterization of zinc, lead and cadmium in mine waste: Implications for transport, exposure and bioavailability. *Environmental Science and Technology* (41): 4164-4171.
- Schmitt, C.J., and Brumbaugh, W.G. 1990. National Contaminant Biomonitoring Program: concentrations of arsenic, cadmium, copper, lead, mercury, selenium, and zinc in fresh water fishes of the United States, 1976-1984. *Archives of Environmental Contamination and Toxicology* (19): 731-747.
- Skougstad, M.W., Fishman, M.J., Friedman, L.C., Erdmann, D.E., and Duncan, S.S. 1979. Methods for determination of inorganic substances in water and fluvial sediment. U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 1,159 p.
- State of Oklahoma. 2000a. Governor Frank Keating's Tar Creek Superfund Task Force, Final Report. Office of Secretary of Environment, October 1, 2000, 27 p.

- State of Oklahoma. 2000b. Final report of the Chat Use Subcommittee of Governor Frank Keating's Tar Creek Superfund Task Force. Office of Secretary of Environment, 29 p.
- Stewart D.R. 1986. A brief description of the historical, ore production, mine pumping, and prospecting aspects of the Tri-State zinc-lead district of Missouri, Kansas, and Oklahoma. Guidebook to the geology and environmental concerns in the Tri-State lead-zinc district, Missouri, Kansas, and Oklahoma. Association of Missouri Geologists, 33rd annual field trip, September 26-27, 1986, p. 16-29.
- Storm, G.L., Fosmire, G.J., and Bellis, E.D. 1994. Persistence of metals in soil and selected vertebrates in the vicinity of the Palmerton Zinc Smelters. *Journal of Environmental Quality* (23): 508-514.
- Strojan, C.J. 1978, Forest leaf litter decomposition in the vicinity of a zinc smelter. *Oecologia* (32): 203-212
- Subsidence Evaluation Team. 2006. Picher mining field, northeast Oklahoma, subsidence evaluation report. U.S. Army Corps of Engineers, Tulsa District, 149 p.
- Terry, Norman, and Banuelos, Gary. 2000. Phytoremediation of contaminated soil and water. Lewis Publishers, Boca Raton, Florida, 376 p.
- Tessier, A., Campbell, P.G.C., and Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* (51): 844-851.
- The Engineering Toolbox. 2010. Wood densities, Accessed on November 18, 2010 at URL: http://www.engineeringtoolbox.com/wood-density-d_40.html
- TIBCO. 2009. TIBCO Spotfire S+. Accessed on November 30, 2009 at URL: <http://www.spotfire.tibco.com/Products/SPLUS-Client.aspx>
- Tri-State Ore Producers' Association. 1954. Tri-State district lead and zinc mines report. Tri-State Ore Producers' Association, Picher, Oklahoma, variously paged.
- U.S. Environmental Protection Agency. 1994. Method 3051, Microwave assisted acid digestion of sediments, sludges, soils, and oils. Accessed on May 1, 2007 at URL: <http://www.epa.gov/sw-846/pdfs/3051.pdf>, 14 p.
- U.S. Environmental Protection Agency. 1996. A Citizen's Guide to Phytoremediation. Accessed on October 5, 2005 at URL: <http://clu-in.com/citguide/phyto.htm>

- U.S. Environmental Protection Agency, 2001, Method 200.7, Trace elements in water, solids, and biosolids by inductively coupled plasma-atomic emission spectrometry. U.S. Environmental Protection Agency. EPA-821-R-01-010, 68 p.
- U.S. Environmental Protection Agency. 2006. Technical factsheet on: lead. U.S. Environmental Protection Agency. Accessed on May 10, 2007 at URL: <http://www.epa.gov/OGWDW?dwh/t-ioc/lead.html>
- U.S. Environmental Protection Agency. 2007a. Criteria for the safe and environmentally protective use of granular mine tailings known as “chat”, U.S. Environmental Protection Agency. Final Rule—July 18, 2007. Accessed on July 2, 2008 at URL: <http://www.epa.gov/epaoswer/other/mining/chat/>
- U.S. Environmental Protection Agency. 2007b. Superfund explanation of significant difference for the Record of Decision. Tar Creek Superfund Site-Operable Unit 2, Ottawa County, Oklahoma, Accessed on October 14, 2010 at URL: <http://www.epa.gov/superfund/sites/rods/fulltext/e2007060002082.pdf>
- U.S. Environmental Protection Agency. 2008. Five year review of the Tar Creek Superfund site, Ottawa County, Oklahoma. U.S. Environmental Agency, Region VI, Dallas, Texas, 50 p. Accessed on August 20, 2008 at URL: <http://epa.gov/earth1r6/6sf/pdf/files/5yeartarcreek.pdf>
- Van Hook,,R.I., Harris, W.F., Henderson, G.S.. 1977. Cadmium, lead, and zinc distributions and cycling in a mixed deciduous forest. *Ambio* (6): 281-286.
- Varian Corporation. 2005. Vista-PRO and Vista-MPX ICP-OES Spectrometers operation manual. Varian Corporation, doc. #8510165900, variously paged
- Vos, G., Hovens, J.P., and Delft, W.V. 1987. Arsenic, cadmium, lead and mercury in meat, livers and kidneys of cattle slaughtered in The Netherlands during 1980-1985. *Food Additives and Contaminants*, (4): 73-88.
- Watmough, S.A., Hughes, R.J., and Hutchinson, T.C.. 1999. $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in tree rings as monitors of environmental change. *Environmental Science and Technology* (33):670–673.
- Watmough, S.A., Hutchinson, T.C., and Sager, E.P.S. 1998. Changes in tree ring chemistry in sugar maple (*Acer saccharum*) along an urban-rural gradient in southern Ontario. *Environmental Pollution* (101): 381-390.
- Watmough, S.A., and Hutchinson, T.C. 2003. A comparison of temporal patterns of trace metal concentration in tree rings in four common European tree species adjacent to a CU-CD refinery. *Water, Air, and Soil Pollution* (146): 225-241.

- White, R.L. 2006. Revegetation of abandoned Pb-Zn tailings impoundments with native tall grass prairie vegetation. Master's thesis. University of Oklahoma, 229 p.
- Wilcoxon, F. 1945. Individual comparisons by ranking methods. *Biometrics Bulletin* (1): 80–83.
- Wilde, F.D., Radtke, D.B., Gibs, J., and Iwatsubo, R.T. (Eds.). 1998. National field manual for the collection of water-quality data — Cleaning of equipment for water-quality samples. U.S. Geological Survey, *Techniques of Water-Resources Investigations*, book 9, chap. A3.
- Wilde, F.D., Radtke, D.B., Gibs, J., and Iwatsubo, R.T. (Eds.). 1999. National field manual for the collection of water-quality data — Collection of water-quality samples. U.S. Geological Survey *Techniques of Water-Resources Investigations*, book 9, chap. A4.
- Wilkin R.T. 2008. Metal attenuation processes at mining sites: U.S. Environmental Protection Agency, Ground Water Issue, 13 p. Accessed on September 15, 2008 at URL: <http://www.epa.gov/ada/download/issue/600R07092.pdf>
- Witte, K., Wanty, R., Ridley, W.I., and Harrison, W.J. 2001. Use of tree ring chemistry to evaluate natural baselines and historic metal loads from a base-metal mine and mill, Colorado, USA. Geological Society of America 2001 Annual Meeting, Session no. 55, Paper no. 55-0. Accessed on November 19, 2004 at URL: http://gsa.confex.com/gsa/2001AM/finalprogram/abstract_22469.htm
- Wylie, J.E., and Gass, R. 1993. Missouri trees. Missouri Department of Conservation, 52 p.
- Yelpatyevshy, P.V., Arghanova, V.S., Lutsenko, T.N. 1995. Heavy metals in polluted ecosystem of an oak forest. *Science of the Total Environment* (162): 13-18.

APPENDIX I

Diagrams of Annual Median Tree-Ring Lead and Zinc Content for Trees Cored in the Tri-State Mining District, 2005-2007

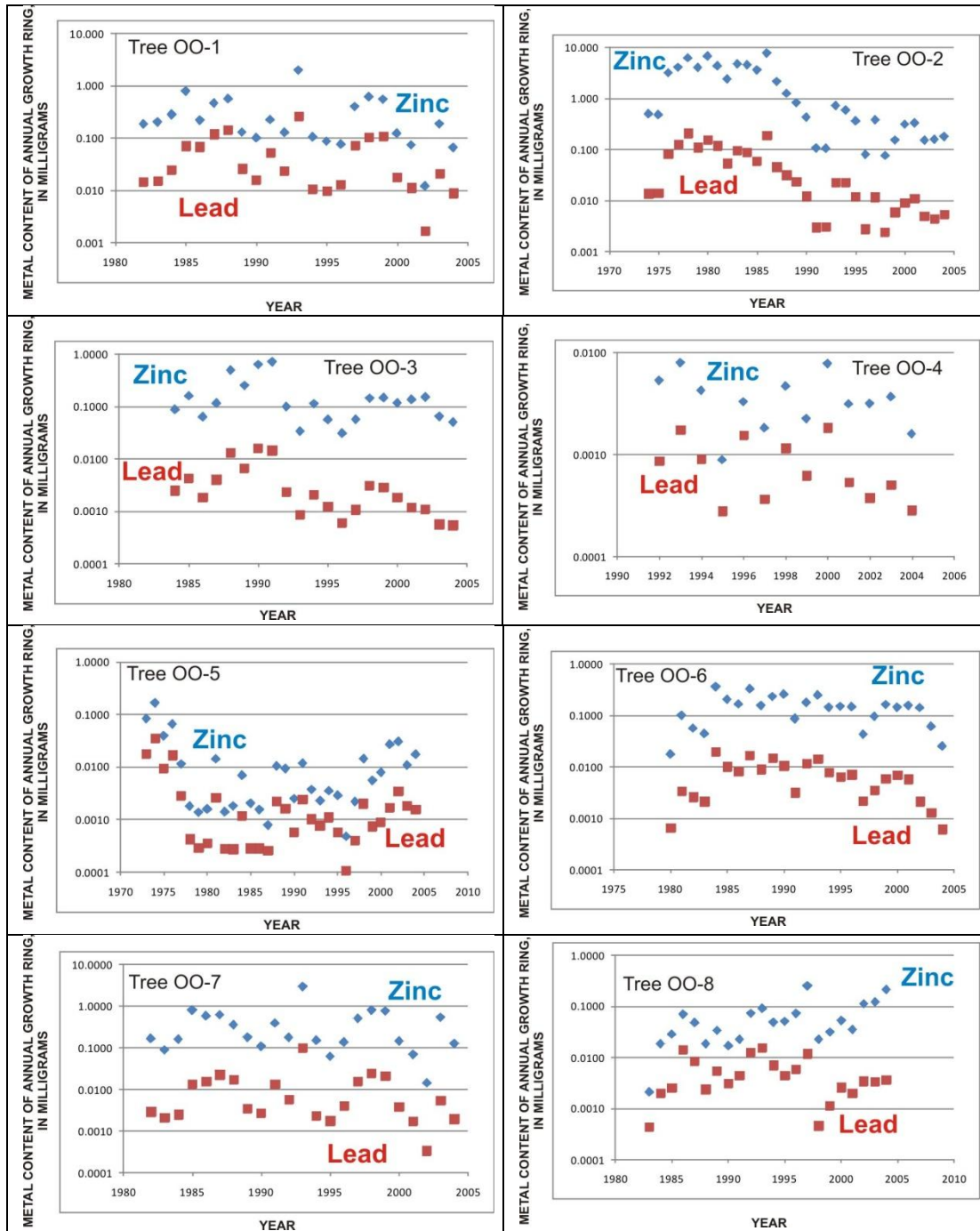


Figure I.1 Graphs showing estimated annual \log_{10} mean trimmed lead and zinc concentrations in tree cores collected in the Tri-State mining district and Cleveland County, Oklahoma, 2005-2007.

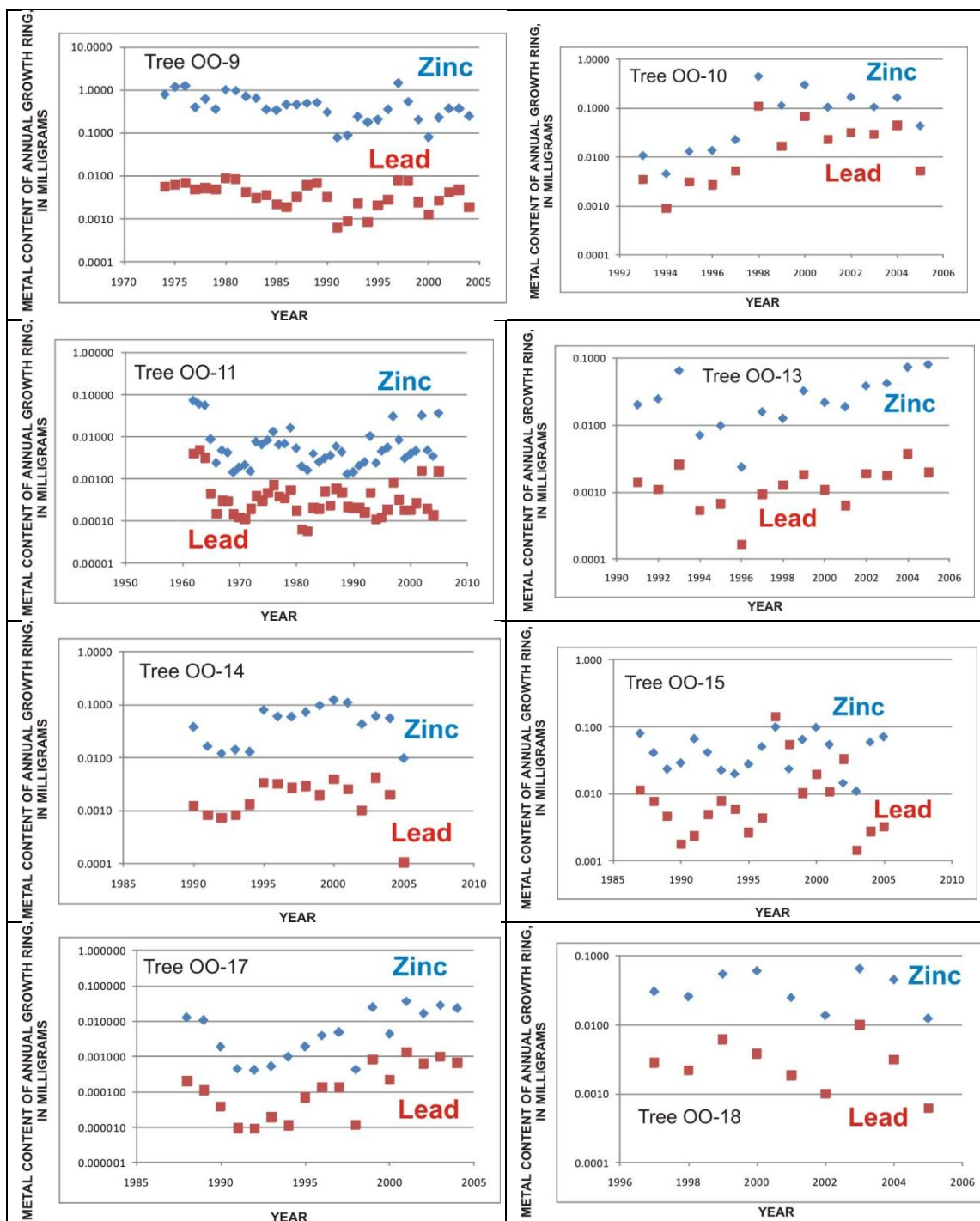


Figure I.1 Graphs showing estimated annual \log_{10} mean trimmed lead and zinc concentrations in tree cores collected in the Tri-State mining district and Cleveland County, Oklahoma, 2005-2007, continued.

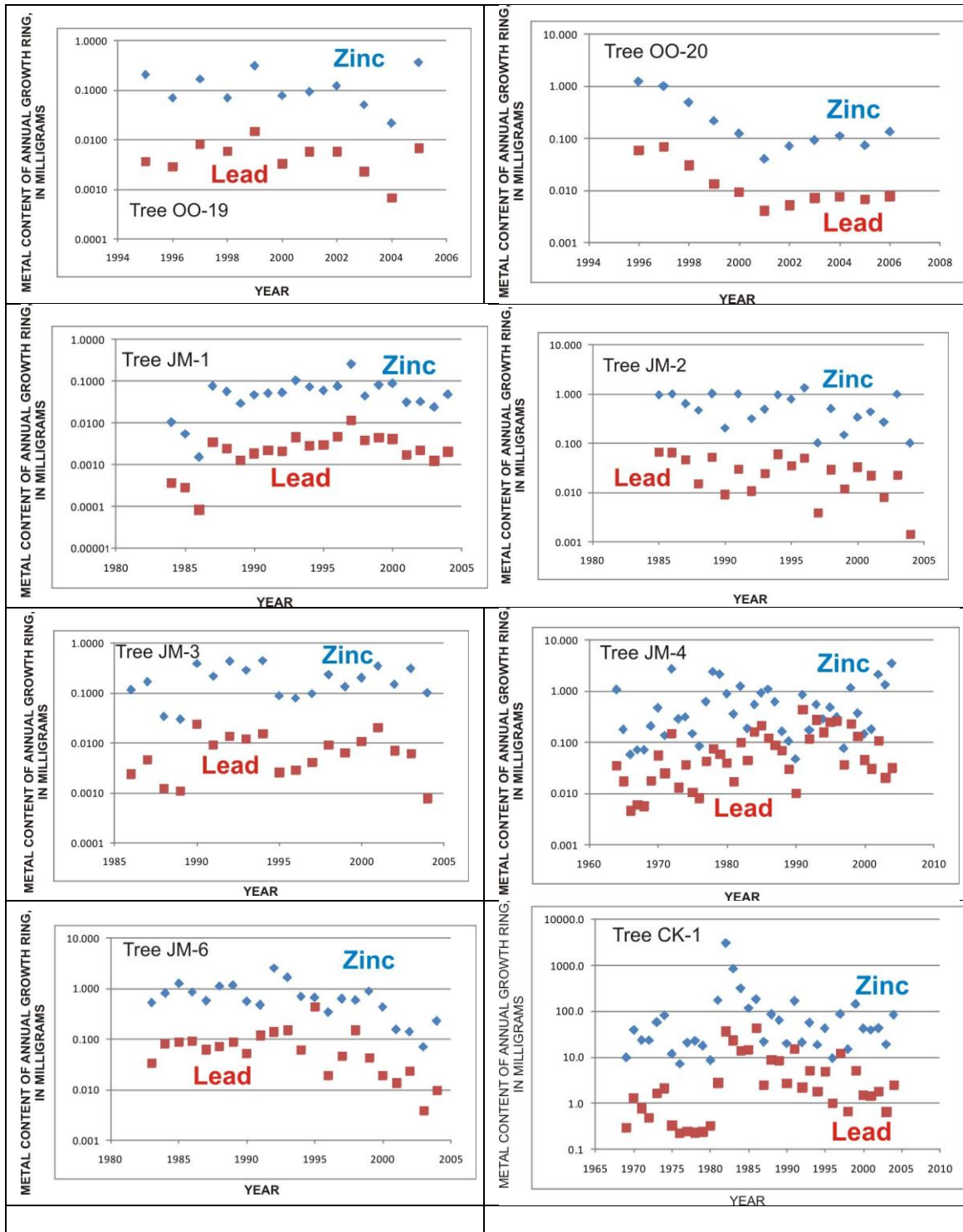


Figure I.1 Graphs showing estimated annual \log_{10} mean trimmed lead and zinc concentrations in tree cores collected in the Tri-State mining district and Cleveland County, Oklahoma, 2005-2007, continued.

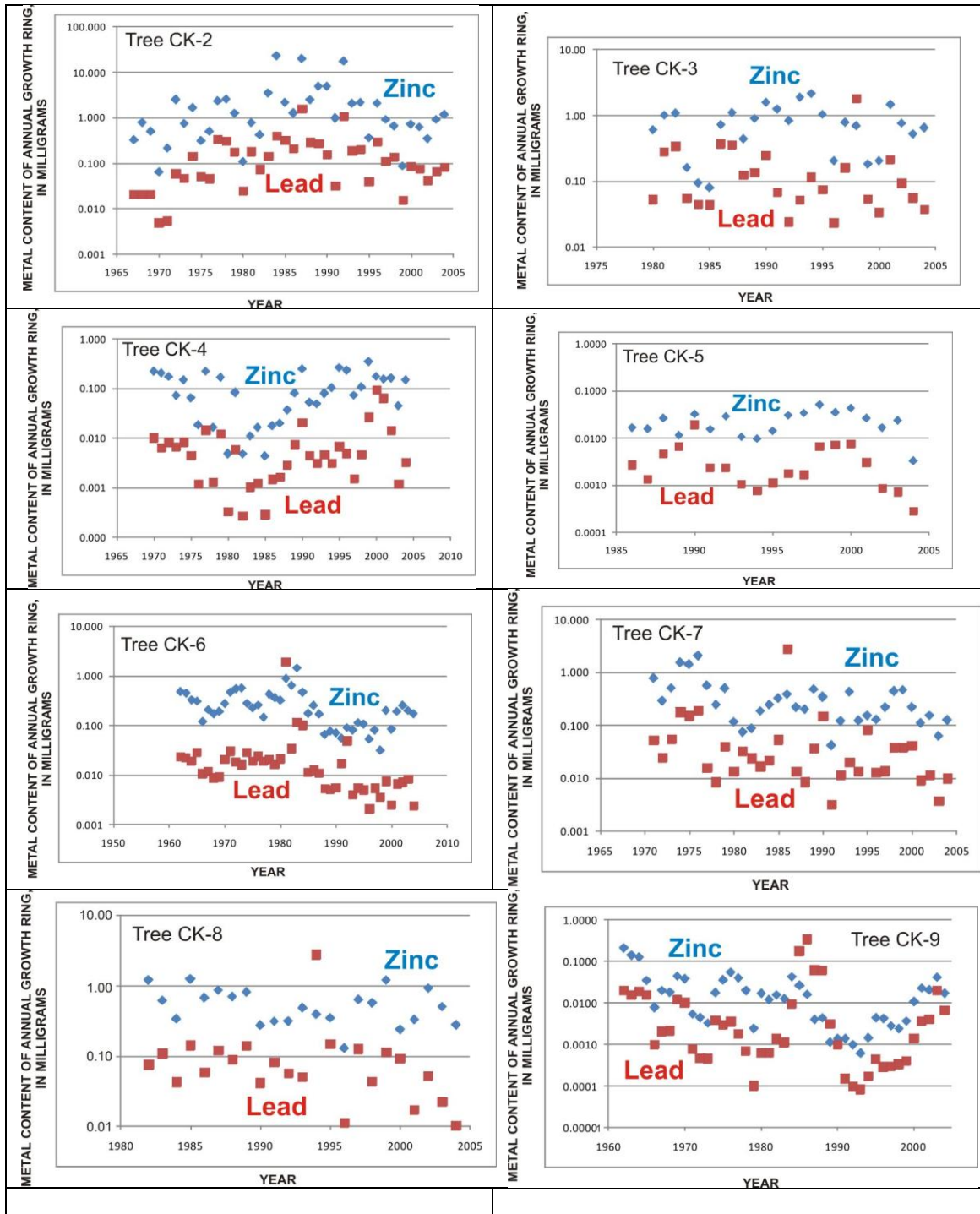


Figure I.1 Graphs showing estimated annual \log_{10} mean trimmed lead and zinc concentrations in tree cores collected in the Tri-State mining district and Cleveland County, Oklahoma, 2005-2007, continued.

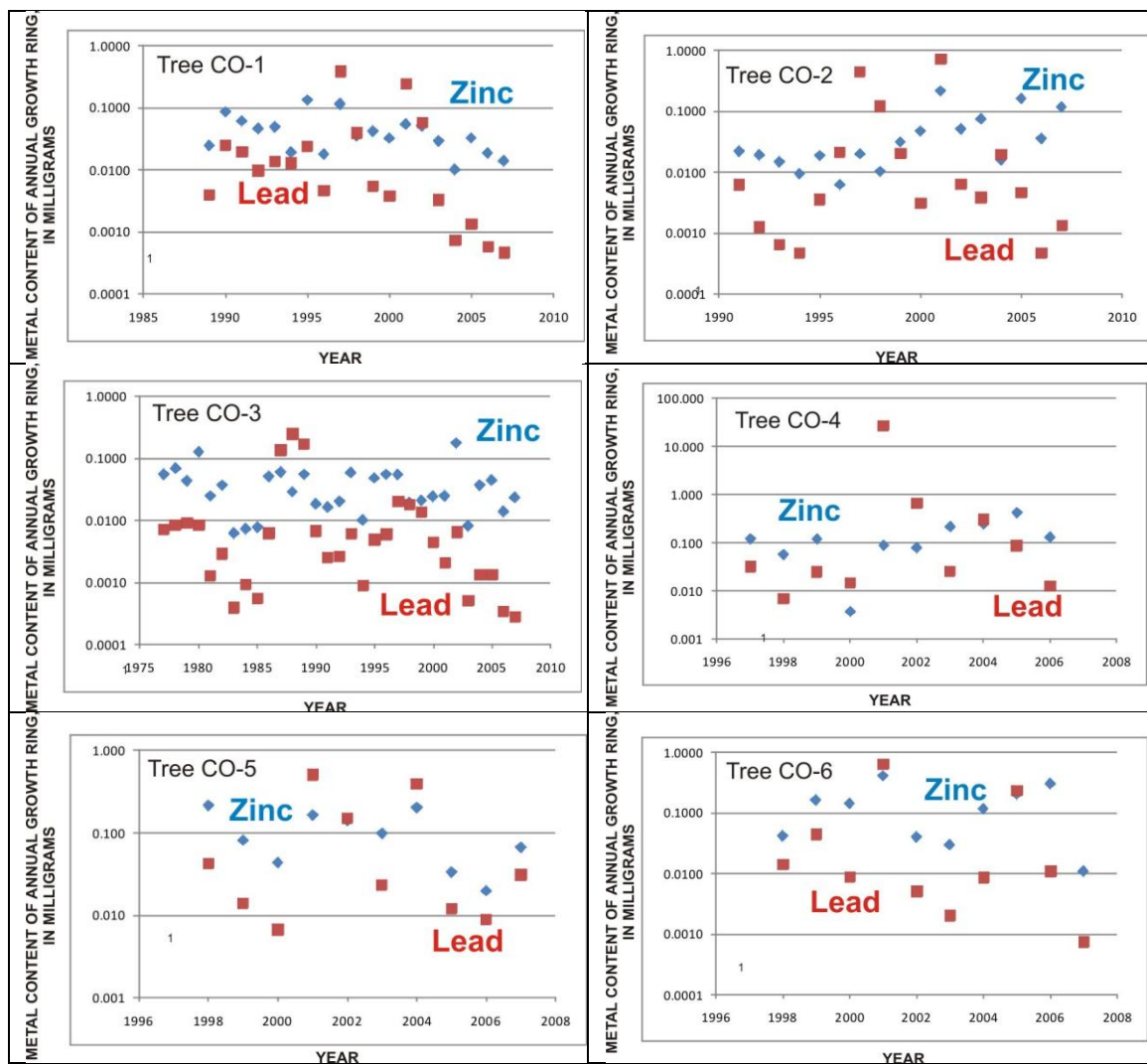


Figure I.1 Graphs showing estimated annual log₁₀ mean trimmed lead and zinc concentrations in tree cores collected in the Tri-State mining district and Cleveland County, Oklahoma, 2005-2007, continued.