PRELIMINARY ASSESSMENT OF TIME TRENDS IN BIOAVAILABLE METALS IN THE TRI-STATE LEAD/ZINC MINING DISTRICT THROUGH ANALYSES OF TREE CORES[1]

William J. Andrews, Robert W. Nairn, and William G. Minarik[2]

Abstract. The Tri-State mining district in the central U.S. was a major source of zinc and lead from the early 1800s to 1970, producing 11.7 million tons of zinc, and 2.8 million tons of lead. Soils and streams in more than 70 square miles of the mining district and downstream areas are contaminated by metals. Little environmental monitoring was conducted in the district until the late 1970s, when metals-laden water started to flow from the abandoned mines. To retrospectively determine trends in metals bioavailability during unmonitored decades and recent trends in metals, cores extracted from 36 trees distributed throughout the district were analyzed by laser-ablation-inductively-coupled plasma/mass spectroscopy (LA-ICP/MS). Preliminary analyses indicate that most metals concentrations decreased after cessation of mining. Recent reclamation activities appear to have increased the amount of bioavailable metals in the environment, probably through mobilization in air during disturbance and transport of tailings for use as aggregate, or through runoff of newly-available metals-contaminated fine sediments.

Additional Key Words: dendrochemistry, LA-ICP/MS

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Introduction

This paper describes analysis of metals concentrations in tree rings to evaluate trends in bioavailability of metals in the Tri-State lead-zinc mining district (Fig. 1) and factors which may have affected bioavailable metals in the environment during the 20th and early 21st centuries.

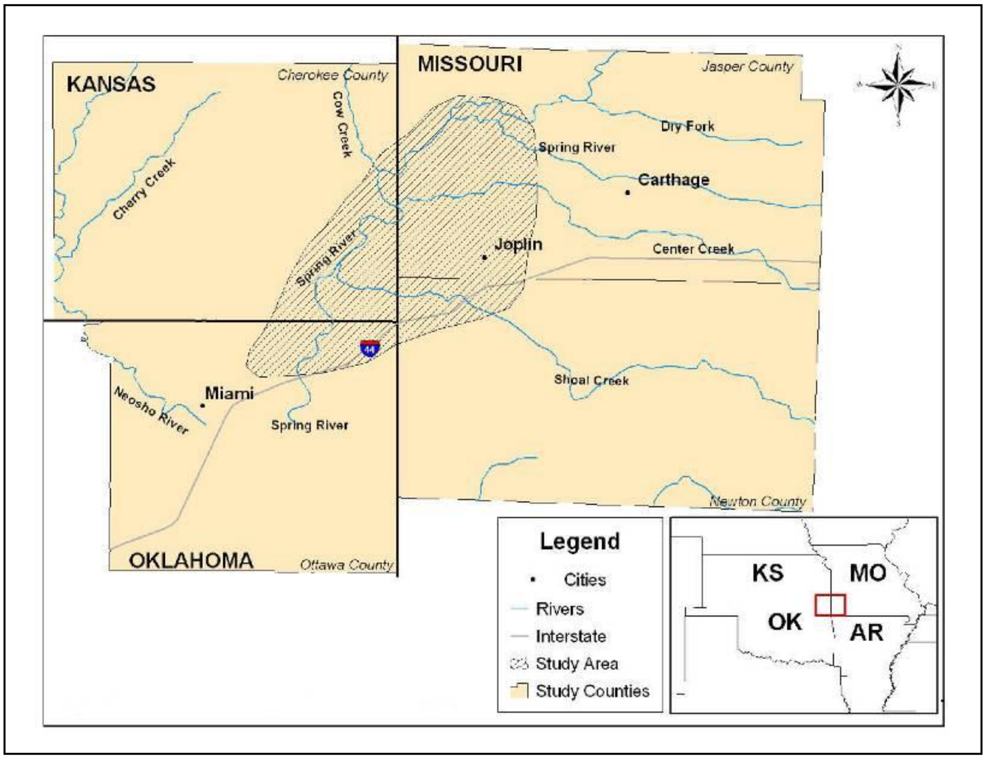

Figure 1. Location of the Tri-State mining district (U.S. Fish and Wildlife Service, 2004).

Features and History of the District

The Tri-State mining district is a 1,188-square-mile area including parts of Jasper and Newton Counties in southwest Missouri, Cherokee County in southeast Kansas, and Ottawa County in northeast Oklahoma that was the site of mining for sulfide ores of Pb and Zn from a matrix of karstic cherty dolomitic limestones from the late 1830s to the 1970's (Gibson, 1972). The district is on the northwest side of the Ozark Uplift, and is drained by numerous creeks and the Neosho, Spring, and Elk Rivers (Gibson, 1972). Topographic relief in the district is gently rolling prairie with small hills and incised stream valleys (Gibson, 1972). Hills in the district are heavily wooded, with white and blackjack oaks (*Quercus alba* L., and *Quercus marylandica*) being the predominant native tree species (Gibson, 1972). In the Oklahoma portion of the Tri-State mining district, known as the Picher mining district, predominant trees near streams include black willow (*Salix nigra*), river birch (*Betula nigra*), and southern catalpa (*Catalpa bignonioides*). On drier land away from stream corridors, the predominant trees are plains cottonwood (*Populus deltiodes* var. occidentalis), green ash (*Fraxinus pennsylvanica*), box elder (*Acer negundo* L.), sycamore (*Platanus occidentalis*), eastern red cedar (*Juniperus virginiana*), Osage Orange (*Maclura pomifera* (Raf.) Schneid) and various species of elms (*Ulma* spp.). The trees that have invaded the more recently-mined Picher mining district in Oklahoma generally are those that propagate by spreading small windblown seeds. There are relatively few trees that bear larger nuts, such as oak or hickory, in the Oklahoma portion of the Tri-State mining district. Much greater numbers of those mast trees can be found in older portions of the mining district and areas surrounding the mining district in Kansas and Missouri.

Health Effects and Environmental Legacies of the Mining

The legacies of nearly a century of mining in the district as of 2007 include: more than 300 miles of underground tunnels, more than 30 million tons of metals-contaminated mine tailings (Fig. 2), 1,320 mineshafts, and tens of thousands of 4-8 inch diameter test holes, extending down to 400 feet below land surface (Gibson, 1972; State of Oklahoma, 2000). Subsidence is an ongoing problem in the mining district, with hundreds of sinkholes reported in Kansas, Oklahoma, and Missouri in areas underlain by mine workings (Luza, 1986; Subsidence Evaluation Team, 2006). The small mountains of mine tailings that remain in the district (Figure 2) only represent a portion of the material originally removed by miners. From 1942-50, more than four million tons of tailings were removed annually for use as railroad ballast and concrete (Gibson, 1972). Removal of mine tailings increased in the 1990s into the 2000s.

Figure 2. Photograph of mine tailings piles near Picher, OK, 2004.

Water quality also remains impaired as a relict effect of the mining. Pumping of millions of gallons of water per day was required to drain the mine workings. After mining stopped, ground-water levels recovered to their natural levels near the land surface, and in late 1979, water contaminated by large concentrations of sulfate (>500 mg/L) and combined metals (>10 ppm, dominated by Fe and Zn) began discharging to local streams from the mine workings. During the decades of mining and up to the present, the air, water, soil, plants, wildlife, and tens of thousands of people living in the mining district have been exposed to silica dust and metals including Pb, Cd, and Zn.

Potential for Application of Dendrochemistry to Examine the History of Metals Contamination

Analyses of metals concentrations in tree rings can be useful for estimation of historical bioavailability of metals in soils and to determine tree species which might be best suited for phytoremediation of local soils. Many different species of trees that grow in the mining district have been sampled for metals, with varying degrees of success, including: white oak (*Quercus alba*) (Baes and Ragsdale, 1981), northern red oak (*Quercus rubra*) (Brabander et al., 1999), tulip poplar (*Liriodendron tulipifera*) (Baes and Ragsdale, 1984; Farrish et al., 2000), hickory (*Carya* spp.) (Baes and Ragsdale, 1984), sycamore (*Platanus occidentalis*) (Watmaugh and Hutchinson, 2003), common ash (*Fraxinus excelsior* L.) (Watmaugh and Hutchinson, 2003), and eastern red cedar (*Juniperus virginiana*) (Connor et al., 1972; Guyette et al., 1991).

Methods

Tree cores and soil samples were collected at 36 sites distributed across the mining district (Fig. 3) from February 2005 to June 2006. Time-series concentrations of Cd, Pb, and Zn in cores collected from nine of those trees are described in this paper.

Tree Coring

To evaluate the usefulness of varying tree species and possible translocation of metals in trees, a variety of species and sizes of trees were cored, including: plains cottonwood (*Populus deltoides* var. monilifera), river birch (*Betula nigra*), American elm (*Ulmus americana*), sycamore (*Platanus occidentalis*), eastern red cedar (*Juniperus virginiana*), green ash (*Fraxinus pennsylvanica*), black oak (*Quercus velutina*), post oak (*Quercus stellata*), bur oak (*Quercus macrocarpa*), northern red oak (*Quercus rubra*), Osage orange (*Maclura pomifera* (Raf.) Schneid), pecan (*Carya illinoensis*), and acacia (*Acacia* sp.).

Trees were selected for coring in a manner to provide a range of species, a range of tree sizes (ages), and a range of antecedent and current land uses. Trees were cored by hand using a Mora 8 x 0.25 inch stainless steel hand corer. Cores were kept in a cooler containing dry ice for transport back to the University of Oklahoma Center for Restoration of Ecosystems and Watersheds laboratories.

Analyses of Metals Content of Tree Cores

The tree core samples were analyzed by LA-ICP/MS at the Department of Earth and Planetary Sciences at McGill University in Montreal, Canada. That laboratory used a NewWave UP-213 ultraviolet laser system with He as the carrier gas. The He gas and ablation particles are combined with Ar makeup gas before entering the injector of the PerkinElmer Elan DRCplus ICP/MS. Flow rates are optimized for maximum counts and minimum molecular isobaric interferences, and are typically 600-800 mL/minute for He and 850-950 mL/minute for Ar. The NewWave UP-213 is a frequency quintupled Nd:YAG laser with an output wavelength of 213 nm. Spot size is controlled by an aperture imaged on the sample, with apertures selectable in the range of 8 to 120 μM. Typically the laser is pulsed at 5 to 10 Hz with an energy density of 5 to 12 J/cm^2. The pulse duration of this system is 5-7 ns, resulting in a fluence to the sample surface of over a gigawatt per pulse. This power, combined with the ultraviolet wavelength, is sufficient to ablate material directly from the solid state into a gas plasma plume. Helium is used as a carrier gas due to its high thermal conductivity, which promotes rapid re-condensation of the plasma plume with resulting small particles.

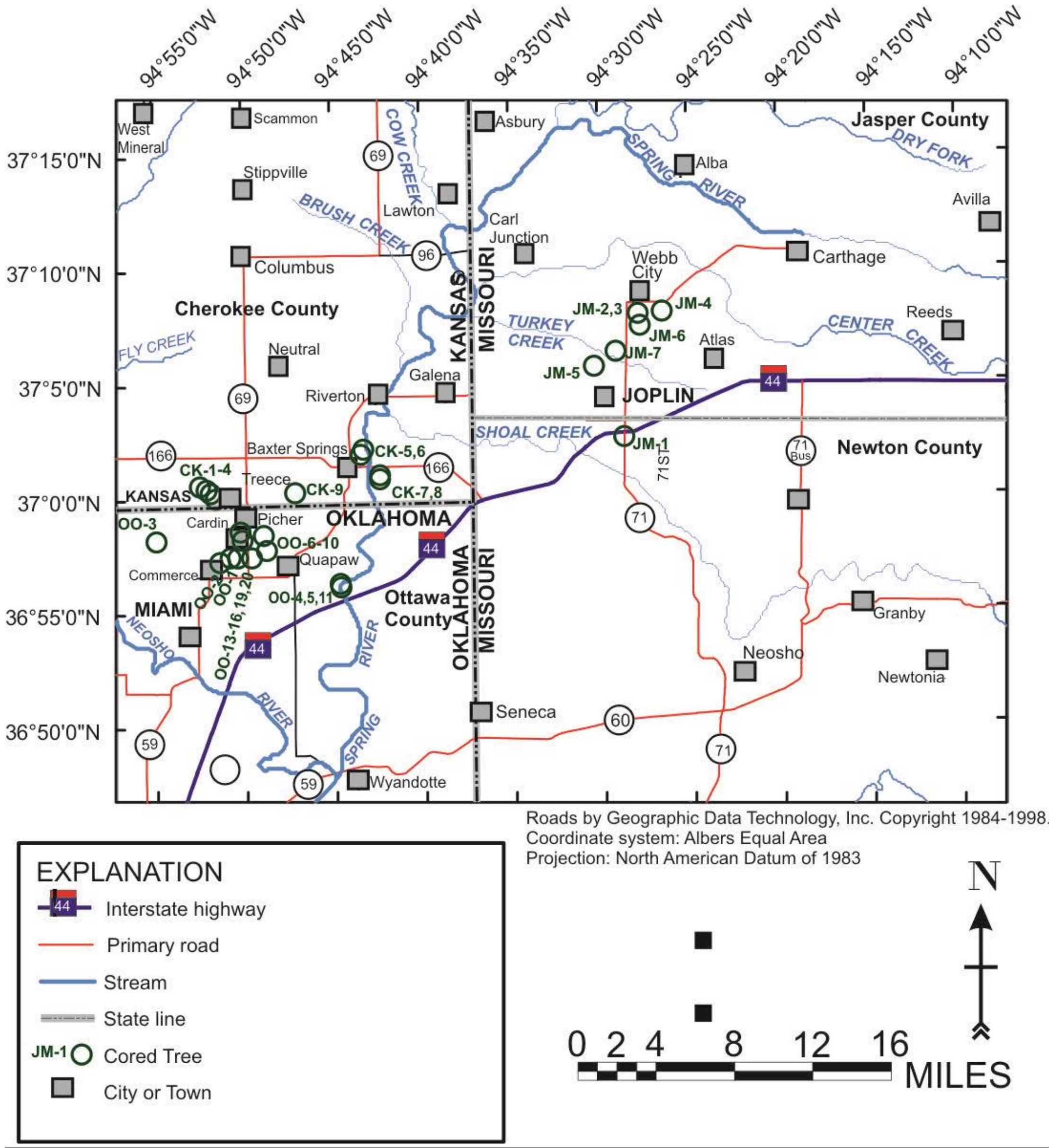

Figure 3. Map showing location of cored trees.

Data Analysis

Dates of each LA-ICP/MS analysis were estimated through measurement of tree-core widths and amortization of the LA-ICP/MS readings for each year over the average growing season (March 15-September 15). Limitations to this method include small errors in measurement of tree-ring thicknesses and assumption that tree growth was evenly spread over each growing season. Differences in tree-ring thickness measurements and ring thicknesses analyzed in sanded core sections may have led to errors in estimation of analyses dates of up to six months.

Results

Analyses of Cd, Pb, and Zn in the selected tree cores indicate that concentrations of those metals generally decreased after cessation of mining, with recent increases in some metals that may be due to disturbance from widespread remediation activities (Fig. 4-11). Each tree, however had unique patterns of metals uptake due to factors such as tree location relative to mining activity, tree species, tree health, competition from other vegetation, and local soil characteristics. Trees with ring-porous wood, such as ashes, oaks, and pecans, are believed to be more likely to preserve metals concentrations in their annual growth rings (Brabander et al., 1999). Trees with diffuse-porous structures (non-ring-porous), such as elms, birches, and cottonwoods are believed to be more likely to transfer fluids and entrained substances such as metals between growth rings. Zinc concentrations typically were two or more orders of magnitude greater than lead concentrations in the tree cores (Fig. 4-11). Zinc is a micronutrient for plants that is involved in carbon metabolism, and is a co-factor of enzymes that regulate plant metabolism, the formation of chlorophyll, and plant growth (Zekri and Obreza, 2003). Metals concentrations substantially greater than typical concentrations in parts of some tree cores may be due to segregation of metals into vacuoles in the boles of trees. Cadmium tends to have similar chemical affinities as Zn and commonly substitutes for Zn in concentrations less than one percent in sphalerite, the zinc sulfide ore common in the Tri-State mining district. Lead typically has relatively small rates of uptake due to it being relatively immobile in soils and the lack of uptake of lead as a plant nutrient (Siccama and Smith, 1978; and Friedland and Johnson, 1985).

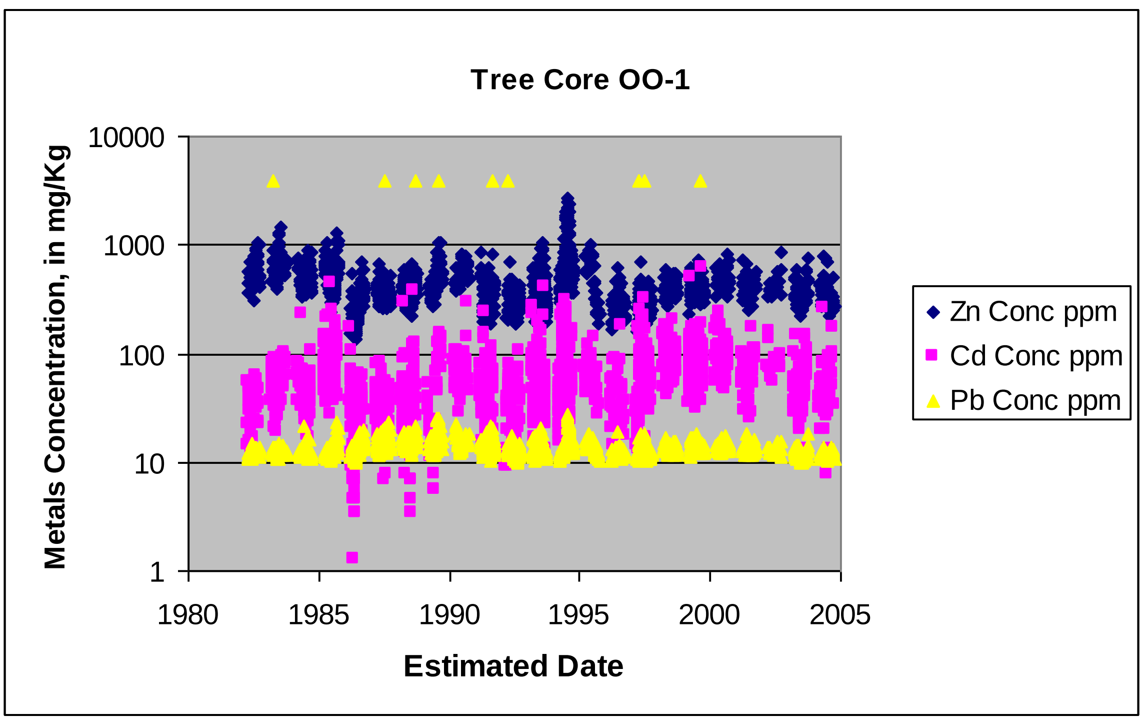

Figure 4. Concentrations of Cd, Pb and Zn versus estimated date in a core from tree OO-1, a plains cottonwood located next to an abandoned ore mill near Douthat, OK.

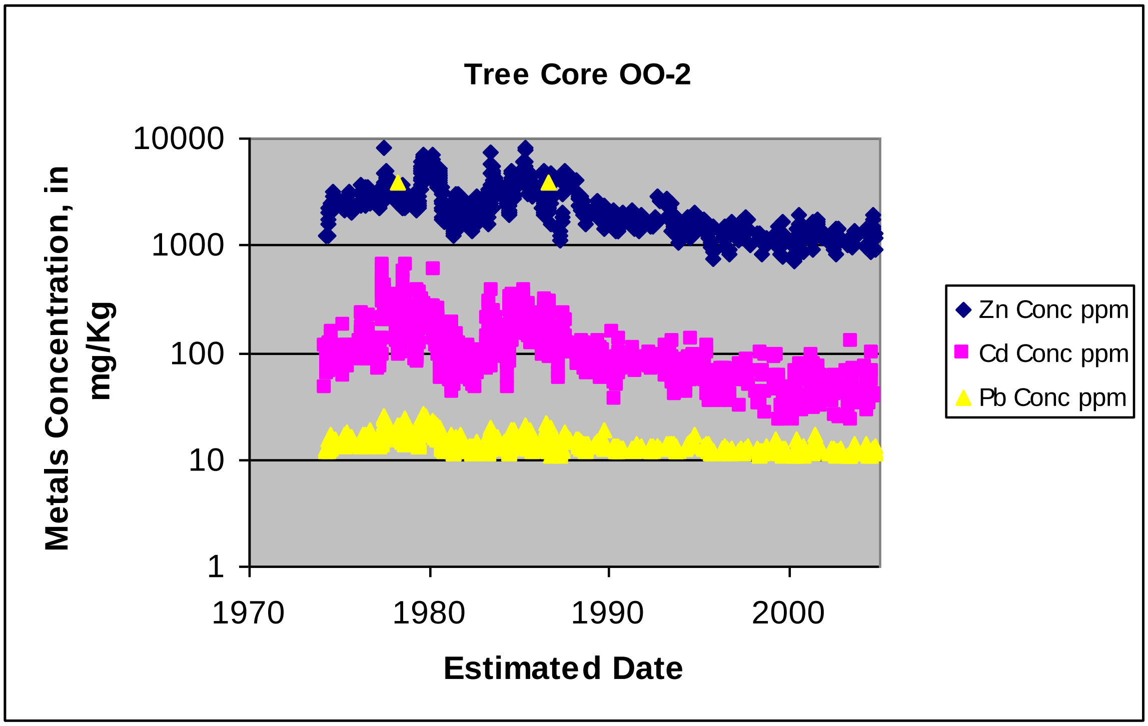

Figure 5. Concentrations of Cd, Pb and Zn versus estimated date in a core from tree OO-2, a river birch located next to Tar Creek, which drains much of the Picher mining district, at Douthat, OK.

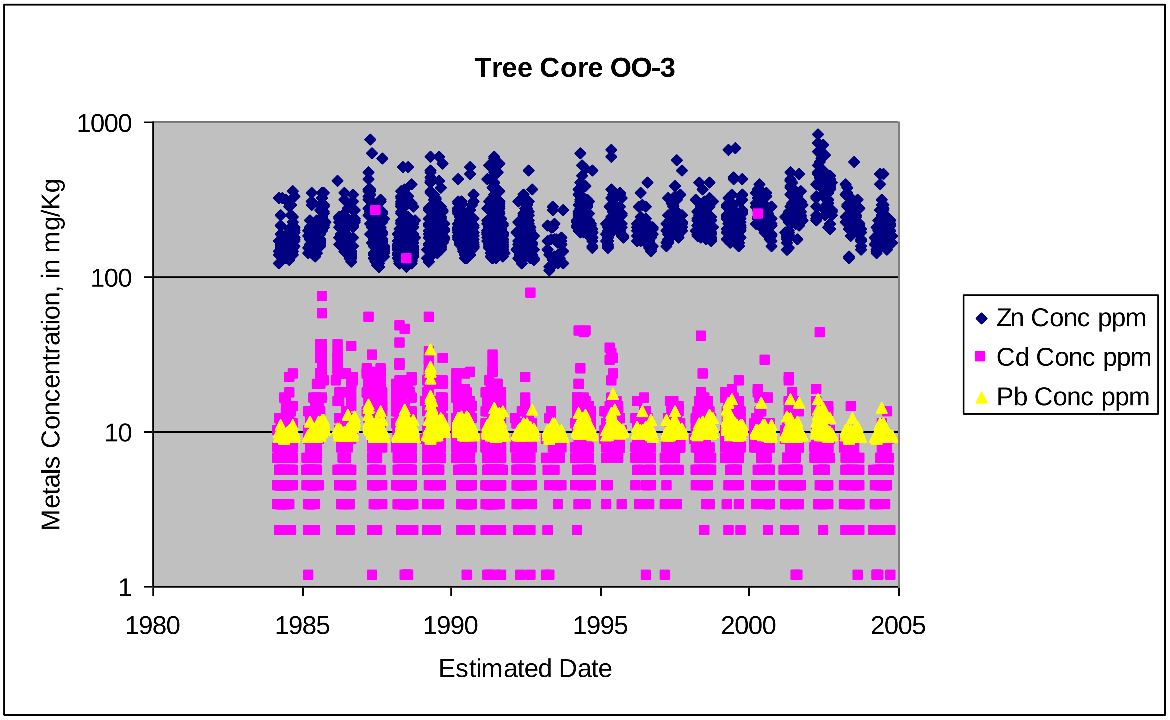

Figure 6. Concentrations of Cd, Pb and Zn versus estimated date in a core from tree OO-3, an American elm located outside of the mining areas, two miles west of Douthat, OK.

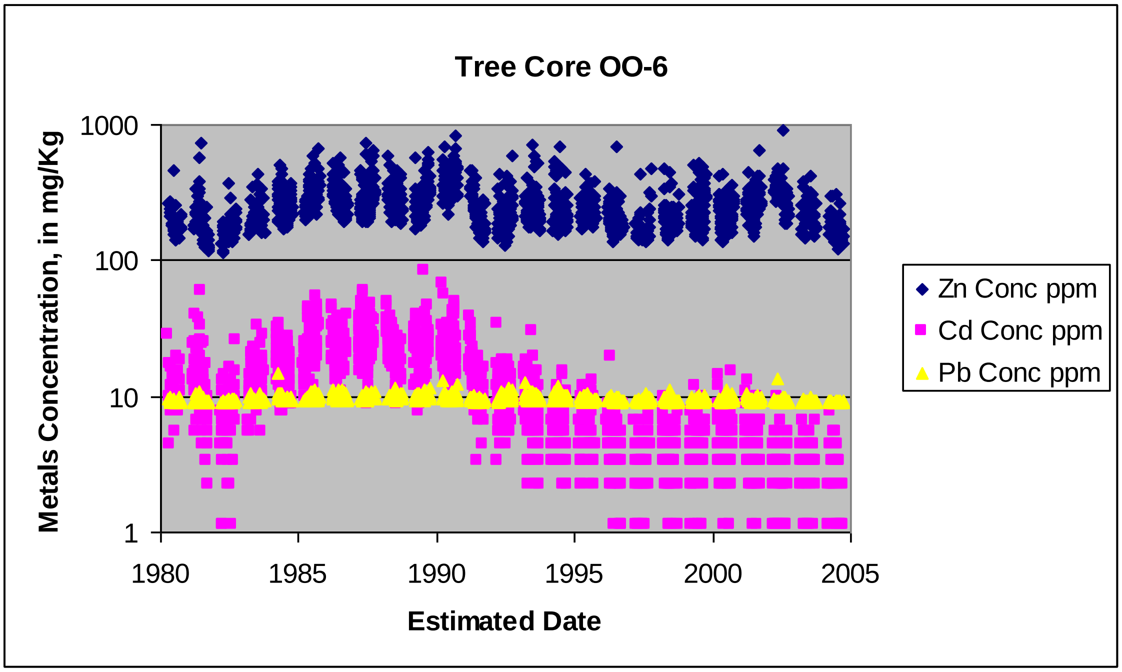

Figure 7. Concentrations of Cd, Pb and Zn versus estimated date in a core from tree OO-6, an American elm located 100 meters east of large tailings piles south of Picher, OK.

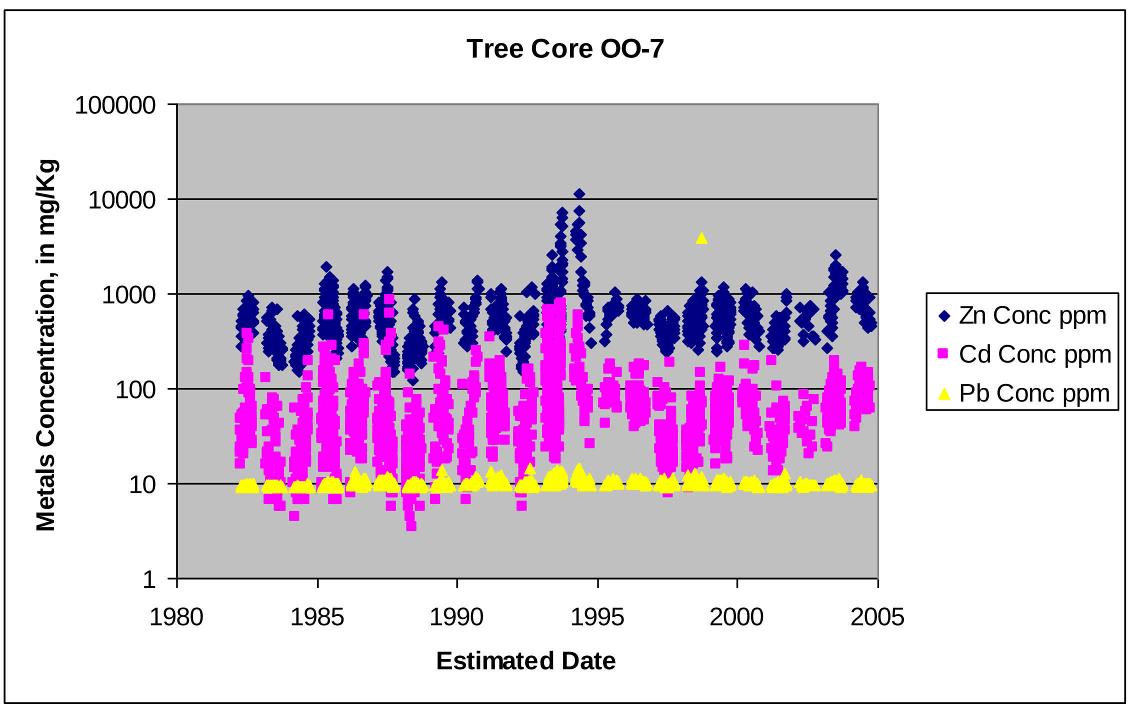

Figure 8. Concentrations of Cd, Pb and Zn versus estimated date in a core from tree OO-7, a plains cottonwood located in an abandoned mining area one mile east of Picher, OK.

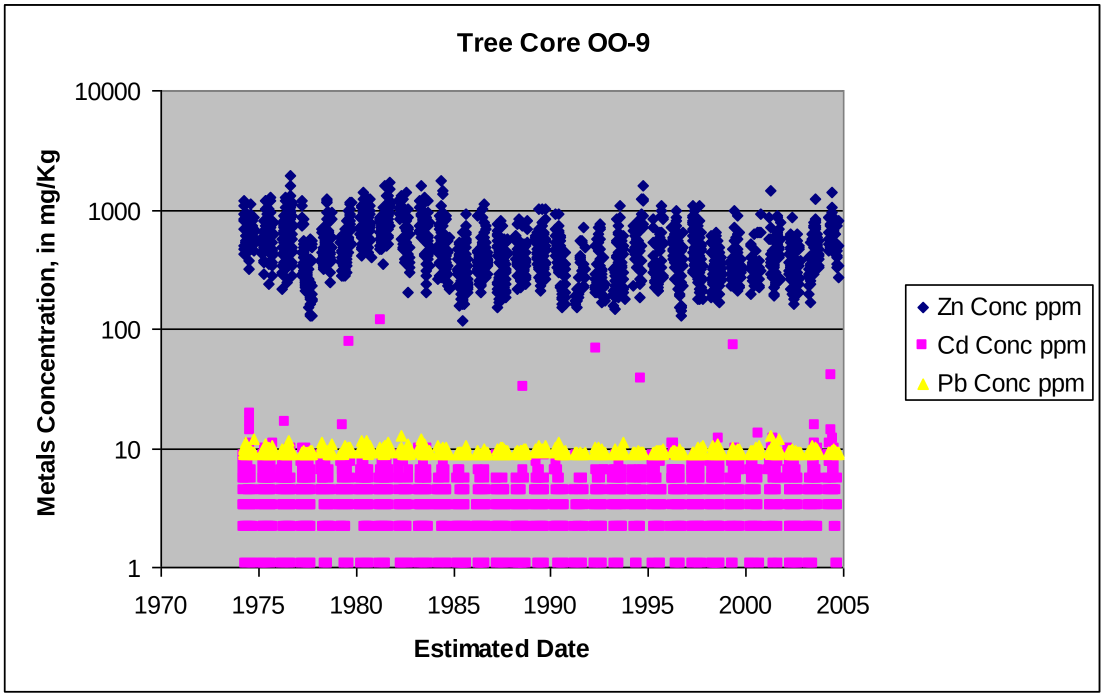

Figure 8. Concentrations of Cd, Pb and Zn versus estimated date in a core from tree OO-7, a green ash located in an abandoned mining area at Douthat, OK.

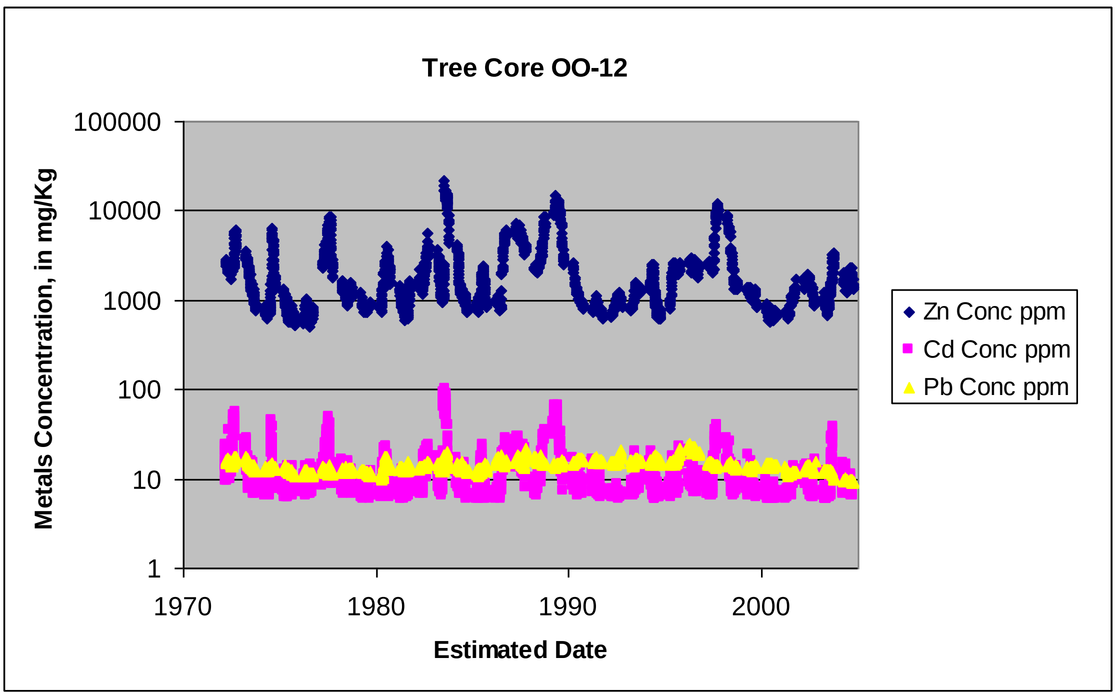

Figure 9. Concentrations of Cd, Pb and Zn versus estimated date for a core from tree OO-12, a pecan located next to a unnamed stream receiving discharge from mine seeps near Commerce, OK.

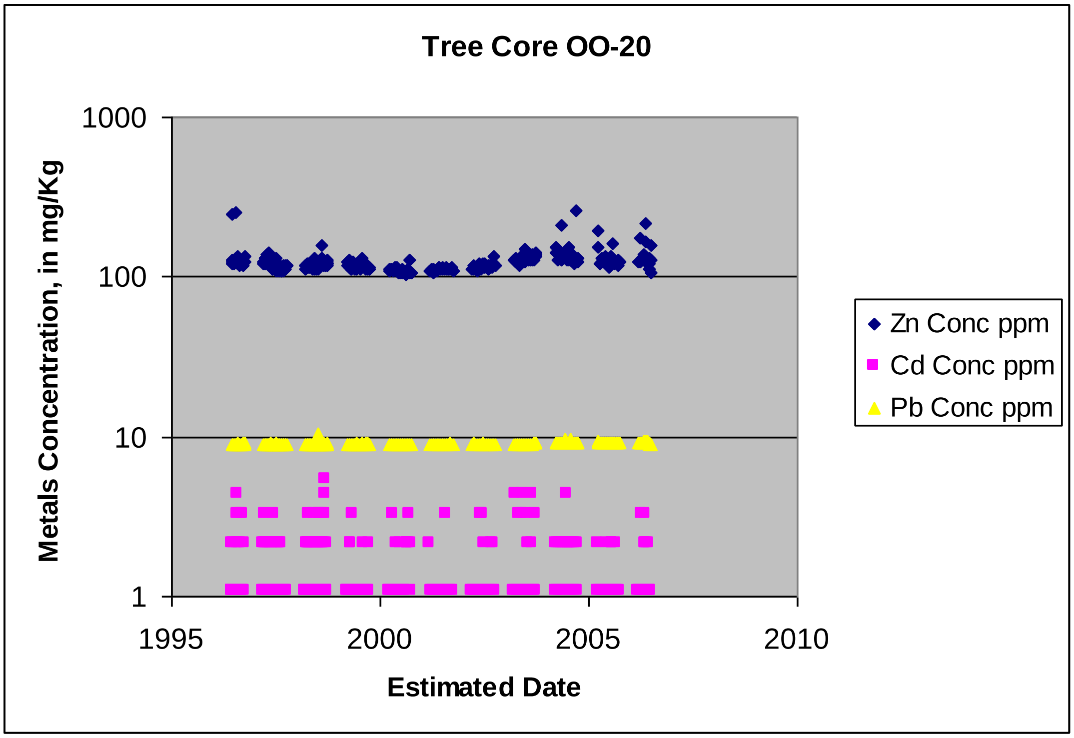

Figure 10. Concentrations of Cd, Pb and Zn versus estimated date for a core from tree OO-20, a pin oak located next to a settling pond for mill wastes at Douthat, OK.

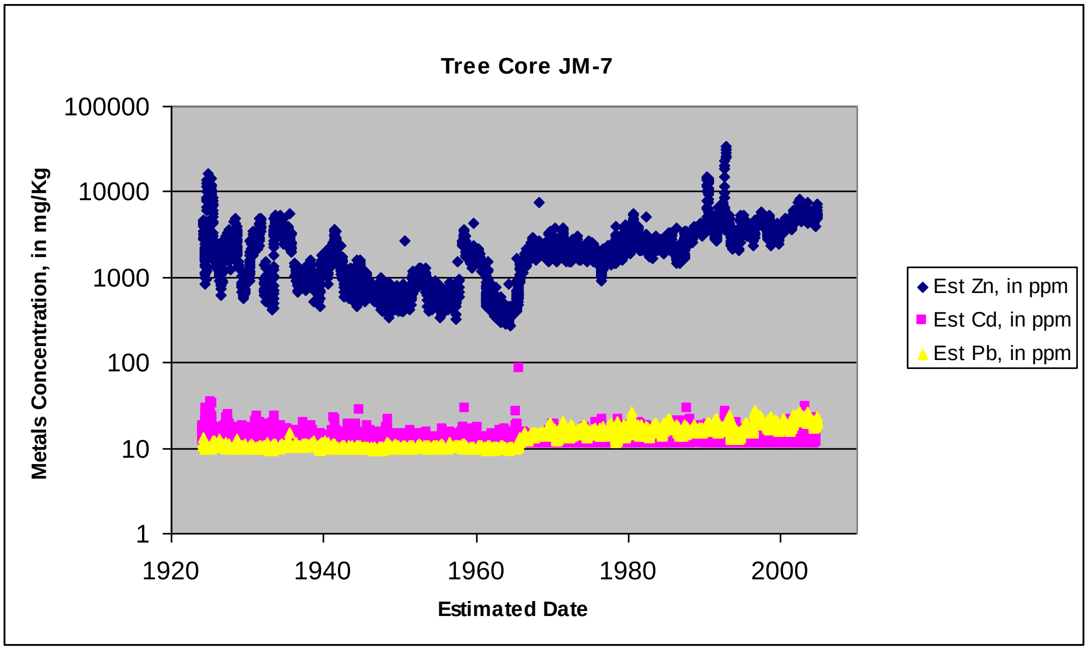

Figure 11. Metals concentrations versus estimated date for a core from tree JM-7, a post oak located next to a highway and Turkey Creek, the site of some of the earliest mining in the district.

Each of the sampled trees has different current and historical land uses which can contribute to variations in uptake of bioavailable metals. Although tree OO-1 is a plains cottonwood, with diffuse-porous wood, some patterns in metals concentrations occurred over time (Fig. 4). Removal of a tailings pile about 100 meters west of this tree started in 2004. An apparent increase in metals content starting about 1994 may be due to up take of metals from fine dust caused by increased tailings removal activities starting in the Picher mining district in the mid 1990s. Although removal of a tailings pile about 100 meters west of this tree started in 2004, the most recent metals concentrations in the core from this tree appear to be starting to decrease.

As the mine workings in the Picher mining district filled up with water after pumping stopped, seeps of metals-laden water started to flow in the district in the late 1970s. Eventual equilibration of water in the mine workings with exposed metallic sulfide minerals and gradual reductions in runoff of metals-rich tailings fines may be the principal causes of decreasing metals concentrations in the core from tree OO-2 (Fig. 5), a river birch located on the banks of Tar Creek, one of the major streams draining the mining district. Recent small increases in Zn and Cd concentrations (Fig. 5) may be due to removal of large tailings piles occurring since 2003 immediately upstream of this tree.

Tree OO-3, an American elm located on the western fringe of the Picher mining district, had lesser concentrations of Zn and Cd than were in cores of trees OO-1 and OO-2, probably due to lesser concentrations of bioavailable metals at that location (Fig. 4-6). A slight increase in Cd, Pb, and Zn concentrations in the core from tree OO-3 in 2002 may correspond to increased removal of tailings in neighboring mining areas during that time. Although trees OO-6 and OO-7 were located relatively close to abandoned mining areas, they had metals concentrations similar to those in tree OO-3. Trees OO-6 and OO-7 also had increases in Cd and Zn concentrations from 2002-2003, perhaps due to tailings removal activities in the area (Fig. 7 and 8). Metals concentrations in cores from trees OO-9 and OO-12 also have had increases in metals content since 2002 (Fig. 8 and 9). After an apparent decline in metals concentrations in the mid to late 1970s, metals concentrations in the core from tree OO-12 increased starting in 1980, when nearby seeps started to discharge from the mine workings. The core from tree OO-20 (Fig. 6) indicated increasing trends of uptake of Zn since 2003, coincident with the beginning of removal of a large tailings pile approximately 200 meters to the north of that tree.

The longest tree-ring record of this group was obtained from tree JM-7, a post oak growing on the north side of Joplin, MO (Fig. 11). Metals concentrations in the core from that tree tended to decrease after the peak of mining in the early to mid 1920s. Subsequent increases in metals content in the mid 1960s may be due to increased development and traffic in the area. Metals concentrations commonly have been found to be elevated within 75 feet of roads, particularly on the downwind sides of roads (Lagerwerff and Specht, 1970; and Connor et al., 1971). Ongoing increases in lead content in that tree core since the phased out of lead in gasoline in the 1970s through the 1980s, may be due to remediation activities, particularly disturbance/removal of mine tailings in the north Joplin and Webb City areas since that period or due to a lag effect of metals gradually seeping through soils into this trees root zone.

Summary

The Tri-State mining district was a major source of Pb and Zn ores during the first half of the 20th century. Many decades after cessation of mining, substantial degradation of environmental quality exists due to the presence of millions of tons of mine tailings, contaminated soils, and seeps of metals-contaminated water in the district. Trees can act as recorders of long-term time trends of bioavailable metals in the environment. Concentrations of Cd, Pb, and Zn in tree cores tended to decrease with decreases in mining activity, but discharges from seeps connected to the mine workings in the late 1970s and reclamation activities focused on removal of tens of millions of tons of mine tailings since the early 1990s caused increases in amounts of metals available for uptake by trees in the Tri-State mining district. Determination of long-term trends of metals in tree cores can provide increased understanding of how natural attenuation and active remediation can affect the bioavailability of metals in the environment.

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Literature Cited

Argonne National Laboratory, 2002, Peconic River remedial alternatives—phytostabilization: Brookhaven National Laboratory, 4 p.

Baes, C. F., III, and Ragsdale, H. L., 1981, Age-specific lead distribution in xylem rings of three tree genera in Atlanta, Georgia: Environ. Pollut. Ser. B., vol. 2, p. 21-35. http://dx.doi.org/10.1016/0143-148X(81)90005-7

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, vol. 96, no. 25, p. 14635-14640. http://dx.doi.org/10.1073/pnas.96.25.14635.

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.

Farrish, K., LaChastity, F., Gilliand, 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 1/19/2005 at URL: www.wcu.edu/ubms/pdf%5C200@5Clead.pdf

Friedland, A.J., and Johnson, A.H., 1985, Lead distribution and fluxes in a high-elevation forest in northern Vermont: Journal of Environmental Quality, vol. 14, no. 3, p. 332-336 http://dx.doi.org/10.2134/jeq1985.00472425001400030006x

Gibson, A.M., 1972, Wilderness bonanza, the Tri-State district of Missouri, Kansas, and Oklahoma: University of Oklahoma Press, Norman, Oklahoma, 362 p.

Gray, K.A., 2004b, Section 3: General phytoremediation: Northwestern University, 4 p., at URL: http://www.civil.nwu-edu/ehe/HTML_Kag/Kimweb/MEOP/section3.htm accessed on 9/5/2004

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, vol. 20, p. 146-150. http://dx.doi.org/10.2134/jeq1991.00472425002000010022x.

Lagerwerff, J.V., and Specht, A.W., 1970, Contamination of roadside soil and vegetation with cadmium, nickel, lead, and zinc: Environmental Science and Technology, vol. 4., no. 7, p. 583-586 http://dx.doi.org/10.1021/es60042a001

Luza, K.V., 1986, Stability problems associated with abandoned underground mines in the Picher Field, northeastern Oklahoma: Oklahoma Geological Survey, Circular 88, 113 p.

Siccama, T.G., and Smith, W.H., 1978, Lead accumulation in a northern hardwood forests: Environmental Science and Technology, vol. 12, no. 5, p. 593-594 http://dx.doi.org/10.1021/es60141a004

State of Oklahoma, 2000, Governor Frank Keating's Tar Creek Superfund Task Force, Final Report: Office of Secretary of Environment, October 1, 2000, 27 p.

Subsidence Evaluation Team, 2006, Picher mining field, northeast Oklahoma, subsidence evaluation report: U.S. Army Corps of Engineers, Tulsa District, 149 p.

U.S. Fish and Wildlife Service, 2004, Region 6 Environmental Contaminants, Cherokee County, Kansas, at URL: http://mountain-prairie.fws.gov/nrda/CherokeeCounty.htm accessed on 2/5/2005

Watmaugh, 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, vol. 146, nos. 1-4, p. 225-241 http://dx.doi.org/10.1023/A:1023952417583

Zekri, M., and Obreza, T.A., 2003, Plant nutrients for citrus trees: Soil and Water Science Department, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida, SL 200, 8 p.