PRELIMINARY ASSESSMENT OF FLOODPLAIN SOIL METAL CONCENTRATIONS, NEOSHO RIVER, OKLAHOMA[1]

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Abstract. The lower Neosho River watershed has been negatively affected by intensive Pb and Zn mining that took place from the late 1800's through the mid-1900's. The nearby region is recognized with several of the U.S. Environmental Protection Agency's Superfund Sites.   The Tar Creek Superfund Site in Oklahoma is contaminated with ecotoxic metals such as lead, zinc, cadmium, and iron. In addition, millions of tonnes of mine tailings have been left on the surface near the neighboring towns of Picher and Cardin. Tar Creek is the main drainage through the Oklahoma portion of the mining area and a major source of contamination leading into the Neosho River and subsequently Grand Lake O' the Cherokees. Completion of the Pensacola Dam forming Grand Lake is a cause of backwater flooding in the Neosho River basin, which could lead to sediment and dissolved metals transport into the surrounding riparian areas. Due to the increased frequency of upstream flood events since construction of Grand Lake, a floodplain area on the Neosho River upstream of Tar and Elm Creeks was investigated for possible transport of mining-related metals using sediment core sampling and analysis techniques. Metals analysis showed total metals concentrations to have strong correlations with elevation in the floodplain area. Other relationships regarding metals concentrations and distance from the riverine area and particle size were inconclusive. Further study should be employed to characterize the quantities of metals on the remaining downstream stretch of the Neosho River.

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Introduction

The Tar Creek Superfund Site (Tar Creek SS), part of the former Tri-State Mining District (TSMD), is an area containing the towns of Picher, Cardin, Commerce, and Quapaw in Ottawa County, Oklahoma. The Tar Creek SS had been mined extensively for Pb and Zn from the mid-1800s through the 1960s. Visual evidence of the mining includes numerous mine tailings (chat) piles, generally located near the towns of Picher and Cardin. The chat piles are the contaminated waste products of the milling operations required to process the Pb and Zn ores. The angular chert fragments in the chat piles usually range in diameter from 16 mm to less than 75 μm, with the finest particles containing the highest concentrations of Pb, Cd, and Zn (Datin and Cates, 2002). Runoff from the chat piles partly contributes to the metal loads in Tar Creek; however, artesian-flowing abandoned mines have been the primary source of contamination. The cessation of mining led to increasing water levels in the mines and created surface seeps that flowed downstream into Tar Creek and other local streams. Dissolved metals and contaminated sediment are constantly loaded into Tar Creek, a stream characterized by its red and yellow iron oxyhydroxides and degraded habitat (Parkhurst, et al., 1988).

The point of focus in this study was an area on the Neosho River, which is one of two main tributaries to deliver a significant contaminant load from the TSMD into Grand Lake. Grand Lake was formed from the construction of the Pensacola Dam on the Neosho River in 1940 (Juracek and Becker, 2009). The lake is one of the largest reservoirs in Oklahoma, supporting five state parks and providing for numerous recreational activities, as well as supplying water to local communities. The Neosho River is impacted by Tar Creek near the town of Miami, approximately 12 miles upstream of Grand Lake (Fig. 1).

The region on the Neosho that was examined was a floodplain approximately one half mile upstream from the Elm Creek confluence and approximately 8 miles upstream of the Tar Creek confluence (Fig. 1). On a larger scale, the site is situated in the northeast corner of Oklahoma, approximately 11.3 km (7 mi.) south and 29 km (18 mi) west of the Kansas and Missouri borders, respectively (36°53' N; 94°56' W). The area was sought out due to its position upstream of Tar Creek and Elm Creek. During periods of extensive rainfall, the Neosho River may reach flood-stage nearby largely from the backing up of water from Grand Lake and its tributaries.

Figure 1 Map showing a portion of the Grand Lake Watershed; the sampling location is marked upstream of Elm Creek on the Neosho River

The possibility exists that dissolved metals and sediment could be transported upstream from Tar Creek. The region is part of the Grand River Dam Authority's (GRDA) Carbon Sequestration and Ecosystems Research and Restoration Area (CSERRA). The goal of the project was to acquire a better understanding of the area by examining the sediment near the active channel, in the near floodplain, and in the far floodplain by taking and analyzing sediment core samples. Sediment core sampling was chosen to give a baseline for future studies on sediment and metals transport in the floodplains. In a broader context, the study could show the extent to which surface water backflow can contribute to the transport of contaminants.

In addition to human health risks, the terrestrial and aquatic life forms in some areas of the Grand Lake watershed have been affected by metal mining. The Neosho madtom (*Noturus Placidus*) is one species of catfish listed as threatened in the Spring River Basin, which is linked to the area via Grand Lake (Juracek, 2007). In Tar Creek and the Neosho River, toxic conditions in sediment for the freshwater flea (*Daphnia magna*) also exist (McCormick and Burks, 1987). Mussels (Angelo, 2005), waterfowl (Carpenter and Merwe, 2008), amphibians, and fish in the Grand Lake watershed could also be at risk.

Methods

Sediment core samples were taken along a mapped transect starting at the bank of the Neosho River. A total of 6 sample sites were planned by mapping out a due North-South transect. The area consists of an active channel gravel bar, riparian areas, and open floodplains. Sites were chosen based on visual landscape changes and their location relative to the active channel (Fig. 2). Surface samples were collected, taking the first 7.6 cm (3 in) of soil. A bucket auger was used to take three soil cores from each site, two of which were comprised of the first 25.4 cm (10 in) of soil and the third, which contained a soil core starting at a depth according to the extent of the previous soil core depth. Cores were capped to prevent moisture leakage and stored in a cooler. Decontamination of the soil corer and equipment was performed between each sampling routine.
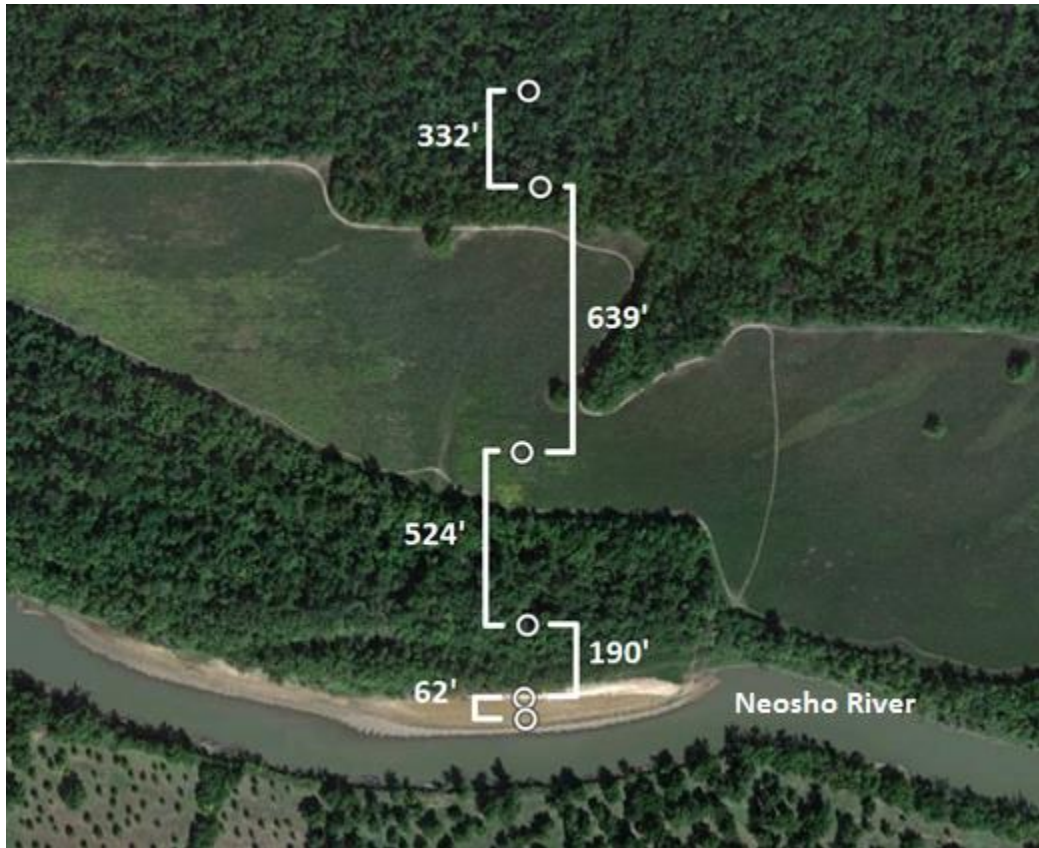

Figure 2 Aerial map showing the six sampling locations with respect to the Neosho River

Core sediment samples were analyzed for total metals, the leachable fraction of metals, organic matter (as loss on ignition), moisture content, and particle size. A field leach test (FLT) was performed to gain an additional form of data. There are several steps to the FLT. First, finer

particles were separated from larger particles by grinding and sifting. A small portion (5 g) of the finer soil particles and 100 mL of deionized water were added to a capped plastic bottle. The bottles were shaken (5 min) and solids allowed to settle (10 min). Supernatant samples were transferred to beakers to measure pH and specific conductivity. Preserved samples were filtered through 0.45 μm filters for further analysis. Methods were taken from the U.S. Geological Survey due to their proven effectiveness in a variety of investigations (Hageman, 2007). FLT extract samples were digested using a CEM Microwave Accelerated Reaction System (MARS) following procedures 3015 from the U.S. EPA's SW-846 (USEPA, 2011). The samples were then analyzed on a Varian Vista-Pro Charged Coupled Device (CCD) Simultaneous Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) using method 6010b for the metals (Al, Ca, Cd, Co, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn).

Soil core samples were cut into 5 cm (2-in.) sections, while larger clumps of soil were ground into smaller particles using a Humboldt soil grinder. These samples were similarly digested and analyzed using methods 3051a and 6010b from U.S. EPA's SW-846 (USEPA, 2011). Additionally, methods for determining moisture content using a forced air oven and methods for determining organic matter content by loss on ignition (LOI) were used to gain a deeper perspective on the mass percent of water and total organic material (Dean, 1974). A particle size analysis (PSA) test was also completed using a RO-TAP test sieve shaker. Sieve sizes (U.S.) used in the PSA included 0.420 mm, 0.149 mm, 0.074 mm, 0.053 mm, 0.044 mm, and 0.037 mm.

Results and Discussion

Metals concentrations were analyzed by plotting the trace metals and leachable portion of trace metals versus the distance from the active channel (Fig. 3). Total Zn increases with distance as the FLT leachable Zn mainly decreases with distance from the active channel.

Metals concentrations in the floodplain and riverine area were much lower than typical trace metal concentrations that would be found in a mining district (Table. 1) (Andrews et al., 2009). The tailings concentrations of trace metals, including Cd, Pb, and Zn are typically found at levels near 50 mg/kg, 700 mg/kg, and 10,000 mg/kg, respectively (Schaider et al., 2007). The floodplain sites showed a strong correlation in (decreasing) total metals concentrations with increasing elevations from the riverine area, implying that the frequency of metal loading

associated with flooding decreased with distance.   Other relationships between metals concentrations and distance from the riverine area or particle sizes were not found.
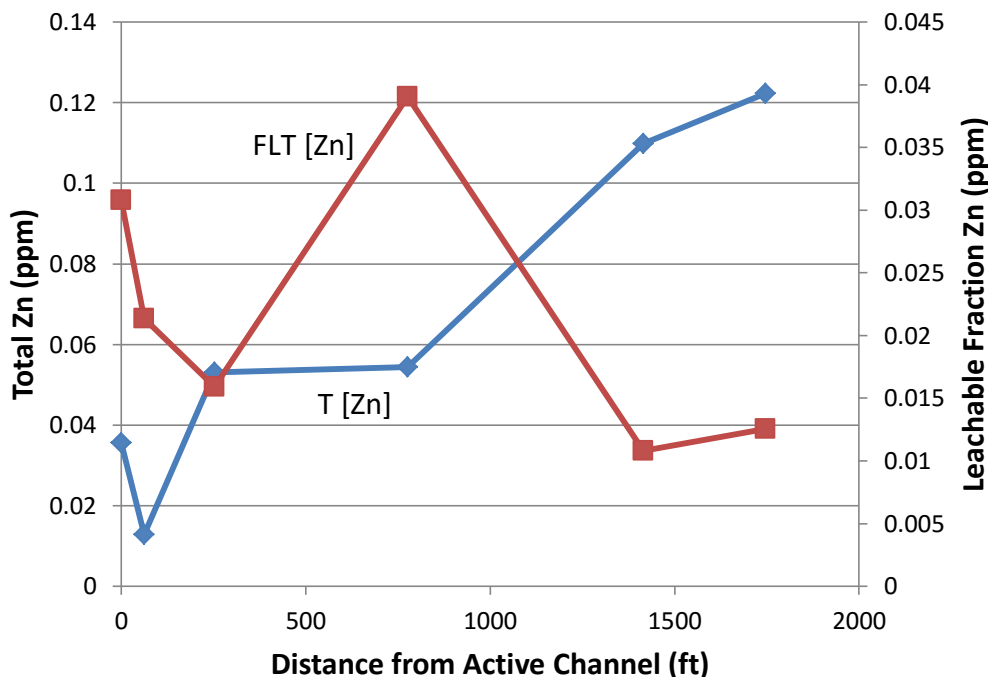

Figure 3 Zn plotted against distance from the active channel. Zn is a trace metal typically found in larger concentrations in the Tri-State Mining District (Andrews et al., 2009). The total Zn increases with distance from the channel as the FLT Zn mostly follows a decreasing pattern with distance. An exception is site NR4, at a distance of 240 m (786 ft.) from the active channel, where the historical agricultural tilling of the soil may play a role.

Table 1 Cd, Pb, and Zn concentrations in surface layers of three locations.

Location	Cd (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Floodplain	0.0010 – 0.0019	0.1600 – 0.1951	0.0531 – 0.1223
Riverine area	0.0004 – 0.0011	0.0799 – 0.1987	0.0129 – 0.0356
Tailings near Cardin, OK	12.9 - 119	369 – 9180	3630 - 22300

There are several factors that promote the mobility or immobility of trace metals. An increasing amount of organic matter generally will increase the surface area available for metal

sorption. The percentage of clays, as well as Al, Mn, and Fe oxides will also give trace metals negatively charged binding sites. Some mining-related metals concentrations are correlated with one another in the surface samples, such as Cd and Zn. In Fig. 3, the leachable fraction of Zn decreases with distance, perhaps due to the main increase of organic matter content with distance from the active channel (Fig. 4). Site NR-4, at a distance of 240 m (786 ft.) from the active channel, deviates from the trend of decreasing leachable Zn with distance. This location was a historical agricultural area. Several factors could have contributed to the increase in mobility of Zn in that area, such as the amount of dissolved organic matter, possibly from the addition of organic fertilizers or crop residues (Robinson et al., 2006). A soil with a higher cation exchange capacity will usually support the immobility of trace metals. Phosphates in soil can also promote insolubility of trace metals, especially with Pb by forming lead phosphates (Cao et al, 2003). Phosphate does not have as much of an immobilizing effect on Cd and Zn as it can have on Pb (Cao et al, 2002).
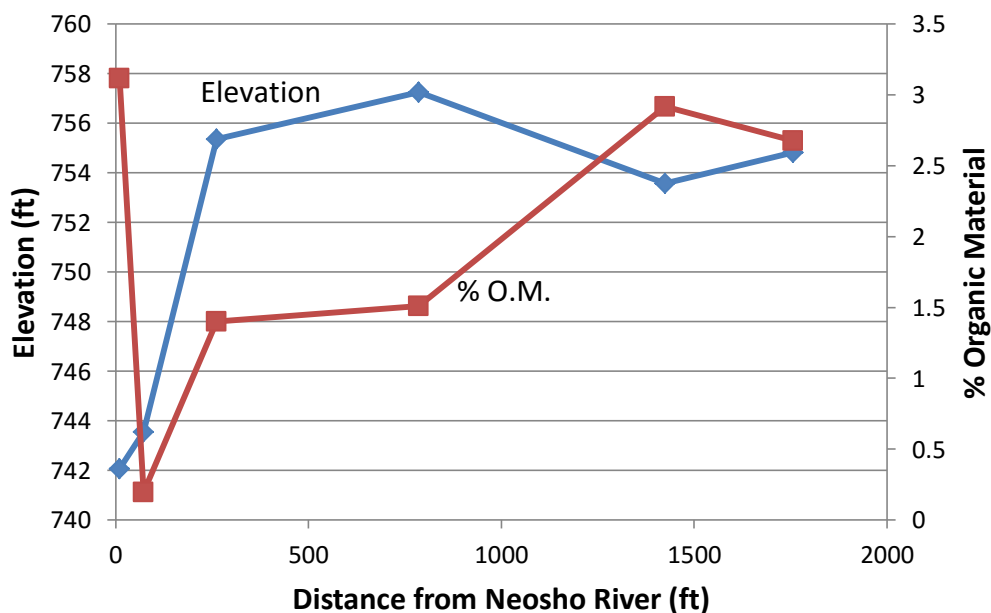

Figure 4 Elevation and the percent organic material plotted against the distance from the active channel. Organic content in the samples show a main increase with distance, with exception to site NR-1 at a distance of 3 m (10 ft) from the active channel and an elevation of 226.2m (742.07 ft).

Since Pb concentrations are elevated in the finest particle sizes of tailings piles, the relationship in Fig. 5 would be expected to show a positive correlation. This plot shows that

there is no significant relationship of Pb to the smallest particles of soil in the floodplain. However, this is a relatively small data set and further study is suggested to fully understand the situation.
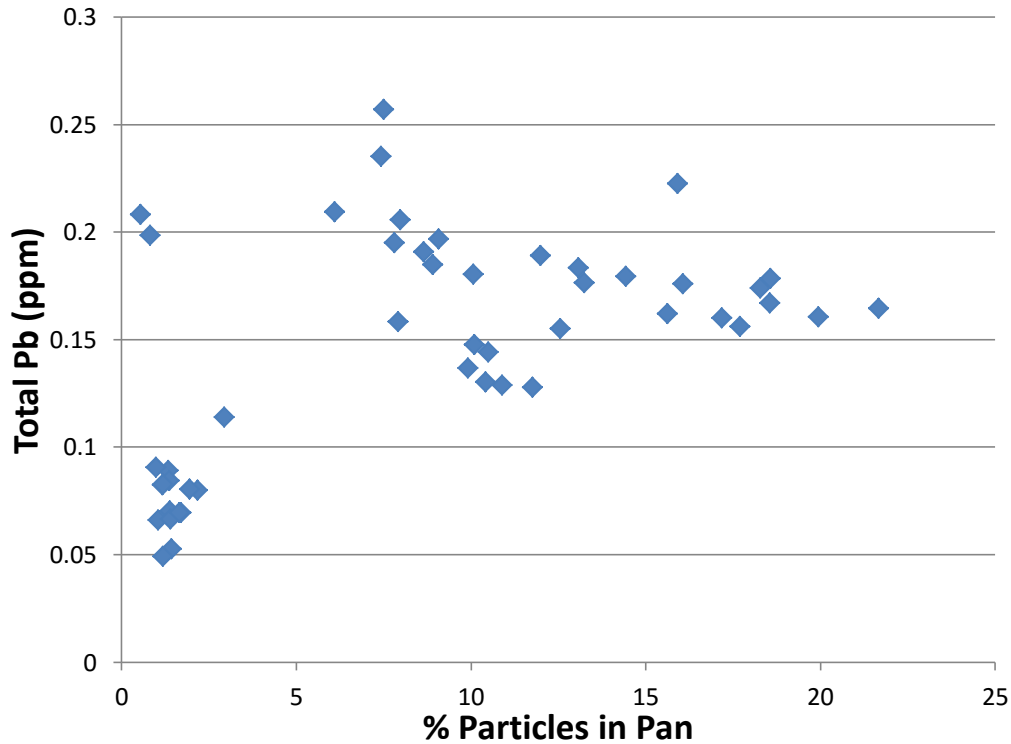

Figure 5 Pb concentrations plotted against the percent mass of fine particles collected in the pan after passing through the finest sieve (400 divisions per linear inch). A separate group of data points is visible; the small group in the lower left of the graph is comprised mostly of samples from the riverine area. No relationship was present (i.e., linear coefficient of correlation $R^2 = 0.3073$). Lead is found in much higher concentrations within the Tri-State Mining District (Andrews et al., 2009).

The notion of measuring dissolved organic matter may also be of interest in the future, since dissolved organic matter can show strong correlations with the solubility of metals. Other constituents that could help to characterize the soil would be to measure cation exchange capacity, nutrient concentrations, or by taking sequential extractions. Adsorption edges for trace metals have been studied by taking sequential extractions. Changes in solution metal concentrations have been examined for trace metals, such as Cu, Pb, Zn, and Cd (Webster et al, 1998). Another factor to investigate would be the seasonal differences. Flow rates in the channel may differ in the colder months, which may cause changes in the resulting data of the

riverine area. Continued studies on sediment cores on the Neosho River area should be considered for more evaluation.

Acknowledgements

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