

Bioavailability and Toxicity of Extracts from Acid-Mine-Waste-Contaminated Sediments

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Sediments were collected from the Tar Creek-Neosho River confluence, Neosho River, and Grand Lake. Grand Lake sediment core samples contained high concentrations of lead, cadmium, and zinc. Sediment extractions indicated that such extractions of lead, zinc, and cadmium were pH sensitive and related to total initial concentration. Tar Creek-Neosho River confluence and Neosho River sediment extracts were toxic to *Daphnia magna*, whereas Grand Lake sediment extract was not.

INTRODUCTION

Bioavailability of toxic metals is indirectly estimated by measuring a response in organisms or by physicochemical fractionation. The bioavailability of a metal depends not only on speciation or partitioning between water and sediments, but also on the organisms' physiology. Uptake by organisms from surrounding water or in food involves complex interactions such as transport across membranes, metabolism, and elimination. Toxicity and bioconcentration are results of an organism's inability to sequester and/or eliminate deleterious metals.

Chemical extraction approaches (e.g. with acetic acid, hydrochloric acid, ammonium hydroxide) may overestimate bioavailability due to the pH values to which they expose adsorbed, complexed, precipitated, and chelated metals. If adsorption/desorption processes are of major importance in determining solubility of metals, then contacting the sediment with solutions having pH values dissimilar from natural ones will give questionable estimates of bioavailability. In general, extractants used in bioavailability estimation cannot be used in preparing extracts for bioassays, due to their inherent toxicity and complexing or chelation of the metals.

The objectives of the present study were to (a) determine whether sediments from Tar Creek, Neosho River, and Grand Lake are contaminated with metal from acid-mine drainage; (b) develop an extraction procedure that estimates a bioavailable fraction of metals from acid-mine-waste-contaminated sediments; and (c) use the extract directly in *Daphnia magna* bioassays with minimal modification of extract integrity.

STUDY SITE

Surfacing mine water has impacted Tar Creek, located in Ottawa County, Oklahoma (1). The extent of toxic metal contamination of the water that flooded mineshafts in the Picher field, and the potential threat to domestic groundwater supplies, placed Tar Creek near the top of hazardous waste sites nationally.

Sediments were collected from three locations in the Neosho River and the upper end of Grand Lake in northeastern Oklahoma (Fig. 1). The first sampling site, Tar Creek-Neosho River confluence, receives large quantities of acid-mine drainage. This site receives an estimated zinc load from Tar Creek >680 kg/day. The second site, Neosho River site, was approximately seven km downstream from the previous site. Neosho River site represents waters that are well mixed and oxygenated. The third site, upper end of Grand Lake, was below the confluence of Neosho and Spring Rivers.

METHODS

Sediment cores and grab samples were collected from Grand Lake. Core samples were collected with a 5 × 70 cm ballcheck single-tube core sampler (Wildco Model

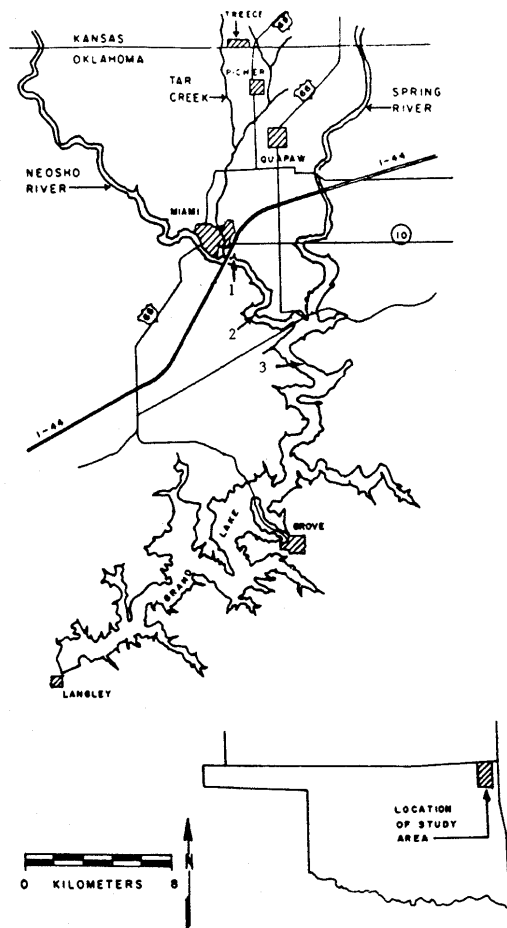


FIGURE 1. Location of sediment sampling sites on the Neosho River and Grand Lake. Neosho River-Tar Creek confluence (1), Neosho River (2), and Grand Lake (3) sediment sampling sites are indicated.

R232 A10), PVC core tubes, and core catchers to prevent mixing when the core was withdrawn. Core tubes were withdrawn, endcapped, packed on ice, and the contents frozen until analyzed. Grab samples were collected from the mouth of Tar Creek, the Neosho River, and the upper end of Grand Lake. The samples were obtained from the upper 15 cm of sediment by using a standard Ekman dredge, packed on ice, and transported to the laboratory, where they were frozen until analyzed. The core samples were extruded and cut into 5-cm sections. All sediments were passed through a #30 sieve to insure homogeneity and dried at 50 °C for 8 hr prior to use. Total metals concentrations were determined by digesting 1 g of sediment in boiling concentrated nitric acid. Hydrogen peroxide (30%) was added to promote oxidation of organic matter (2). Organic carbon was determined in each of the sediments by dichromate oxidation and ferrous ammonium sulfate titration of excess dichromate (3).

Sediment leachates were obtained from the sediment grab samples in reconstituted water. Reconstituted water (RCW) was prepared in accordance with USEPA guidelines (4). The leachate procedure was performed at pH values of 3, 4, 5, 6, 7, 8, and 9. Tar Creek-Neosho River confluence, Neosho River, and Grand Lake sediments were added to the RCW and the pH adjusted with dilute acid or sodium hydroxide. Five-gram samples of sediment were placed into 125-mL polyethylene bottles and 100 mL of the pH-adjusted RCW added to the sediment. This suspension was agitated for 48 hr on a rotary residue extractor. The pH was readjusted at 1, 6, and 24 hr and

tested at 47 hr to insure maintenance of the desired pH during extraction. At 48 hr the samples were centrifuged ($1475 \times g$ for 10 min) and filtered with Whatman #42 filter paper. Filterable metal concentrations were determined by atomic absorption spectrophotometry.

Sediment extractions were also performed for use in *Daphnia magna* LC_{50} determinations. One hundred-gram portions of sediment were suspended each in 2 L of RCW adjusted to pH 6. Two liters of each such suspension were placed in two 1-L dark polyethylene bottles. Control treatments were pH-adjusted RCW. Extraction was for 48 hr at room temperature (25 °C) in the rotary residue extractor. Sediment suspensions were centrifuged as before, and filtered, and filterable metals determined. The leachate water was adjusted to pH 7 prior to use in *Daphnia* bioassays.

Daphnia magna LC_{50} bioassays were performed according to standard methods (4). Dilutions of leachate water were performed to give final concentrations of 90, 55, 30, 15, and 8% by volume. The mortality was recorded at the end of each 24-hr period and the 48-hr LC_{50} calculated by the Litchfield and Wilcoxon method (4).

RESULTS AND DISCUSSION

Sediments from Grand Lake, Neosho River, and mouth of Tar Creek were digested and analyzed for total iron, lead, zinc, cadmium, chromium, and percent organic carbon (Table 1). Iron and zinc concentrations were highest in Tar Creek samples while lead and cadmium concentrations were highest in Grand Lake sediments. Chromium was used as a control metal since deposits of accessory minerals containing chromium are not reported for the area (5). In the present study, sediment iron concentrations at the Tar Creek-Neosho River confluence were much higher, zinc and lead similar, and cadmium lower than previously reported by the Oklahoma Water Resources Board (6). Neosho River and Grand Lake sediments contained significant metal contamination, due to acid-mine wastewater. Grand Lake sediments were much higher in iron, lead, zinc, and cadmium than at a similar site sampled by OWRB (6). The higher concentrations of lead and cadmium in Grand Lake sediments, compared to the other sites, was attributed to increased sedimentation of particulate-associated metals.

Concentrations of cadmium and lead in all sediments exceeded the numerical criteria goals for sediments established by the Oklahoma Water Resources Board (7).

Two sediment cores taken from Grand Lake were analyzed for iron, lead, zinc, cadmium, chromium, and percent organic carbon. Little vertical variation existed in the concentrations of iron, chromium, and percent organic carbon with average values of 3.0×10^4 mg/kg, 3.15 mg/kg, and 2.11 percent, respectively. Regressions for lead, zinc, and cadmium with depth were calculated and plotted for each metal (Fig. 2). Lead levels were highly correlated with those of zinc and cadmium ($r = 0.90$ and $r = 0.87$, $p = 0.001$).

Sediment cores taken from Grand Lake showed high concentrations of lead, zinc, and cadmium even at depths greater than 50 cm. Walters et al. (8) reported on sediment core metal content from Lake Erie and Iskander and Keeney (9) analyzed cores from eutrophic Wisconsin lakes (e.g. Mendota and Monona). In both cases, metal content reached precultural levels below 25 cm. In contrast, Grand Lake sediment cores showed increased zinc, lead, and cadmium at depths >50 cm. The relatively young age of Grand Lake suggested that the elevated quantities of metals in the sediment core probably resulted from higher sedimentation rates. Landsat (August, 1973) and high-altitude infrared photographs (April, 1980), obtained from the Oklahoma State University Center for Remote Sensing, indicated high turbidities in the upper end of Grand Lake. The existence of a common source of the metals, e.g. acid-mine drainage, was supported by the significant correlation of lead, zinc, and cadmium with depth, and with each other, and the lack of significant correlation of chromium with any parameter.

Aliquots of Grand Lake, Neosho River, and Tar Creek sediments were extracted with reconstituted water at various pHs and filterable iron, lead, zinc, cadmium, and

TABLE 1. Total metals and organic carbon in sediments from Tar Creek-Neosho River confluence, Neosho River, and Grand Lake.

Sampling Location	Metal concentration, mg/kg					Organic Carbon (%)
	Iron	Lead	Zinc	Cadmium	Chromium	
Mouth of Tar Creek	9.8×10^4	84	3.5×10^3	7.4	10.4	1.64
Neosho River	8.8×10^4	64	2.6×10^3	3.7	6.7	1.36
Grand Lake	4.8×10^4	132	1.2×10^3	9.9	9.0	1.47

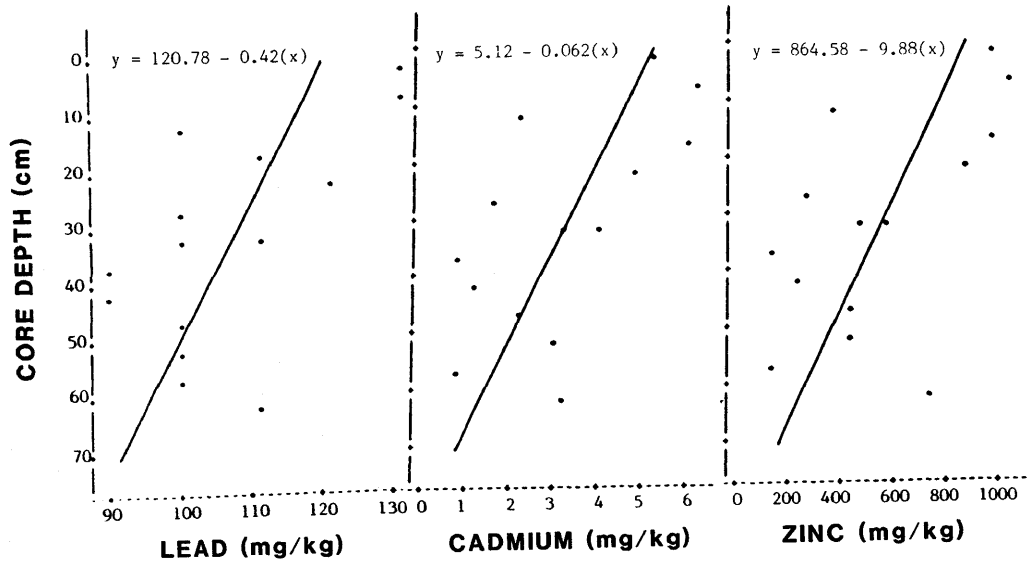


FIGURE 2. Regression of mean total lead, cadmium, and zinc versus depth (cm) in sediment cores from Grand Lake.

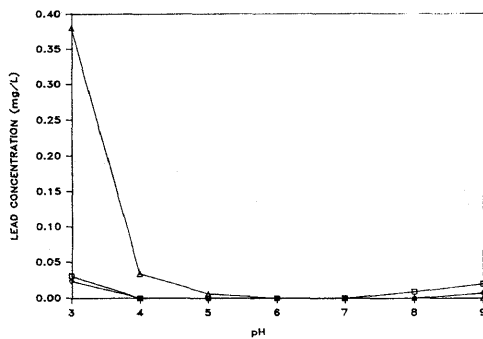


FIGURE 3. Extracted, filterable lead for pH values ranging from 3 to 9. Grand Lake (Δ), Neosho River (\diamond), and Tar Creek-Neosho River confluence (\square) sediment extracts are shown.

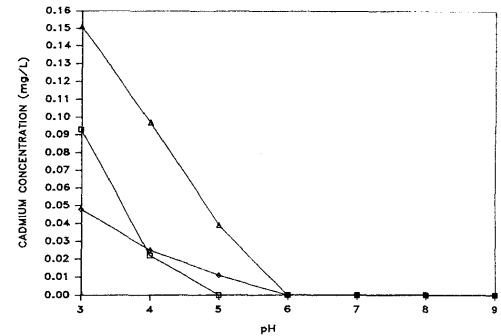


FIGURE 4. Extracted, filterable cadmium for pH values ranging from 3 to 9. Grand Lake (Δ), Neosho River (\diamond), and Tar Creek-Neosho River confluence (\square) sediment extracts are shown.

chromium concentrations determined.

Total filterable iron and zinc extracted from Tar Creek sediments were significantly higher than from Neosho River or Grand Lake sediments ($p = 0.05$). Extractable metals concentrations, except iron, were positively correlated with increasing acidity of the extractant (Figures 3-5). At $pH > 7$ a slight increase of iron, lead, and zinc in the filtrate was noted. This was believed related to adsorption of lead and zinc to iron oxyhydroxide particulates < 0.45 in diameter.

Extracted, filterable lead, cadmium, and zinc were related to total sediment concentration and extractant pH. Grand Lake sediments had the highest total sediment cadmium and lead and the largest quantity of each was extracted from these sediments. Tar Creek-Neosho River sediments had the highest initial zinc content and greatest filterable zinc extracted. Lead extractability was least sensitive to pH, that of cadmium was intermediate, and that of zinc very

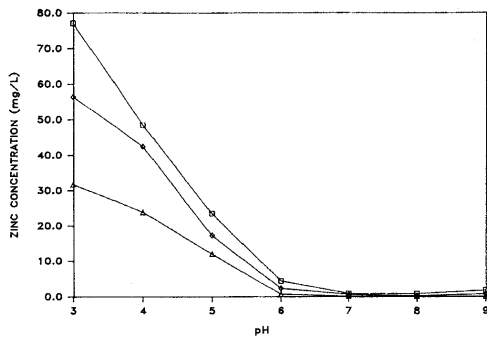


FIGURE 5. Extracted, filterable zinc for pH values ranging from 3 to 9. Grand Lake (Δ), Neosho River (◊), and Tar Creek-Neosho River confluence (◻) sediment extracts are shown.

sensitive. Mouvet and Bourg (10) estimated that the surface binding constants for zinc, cadmium, and lead on sediments were $10^{-3.6}$, $10^{-3.7}$, and $10^{-1.7}$, respectively. They concluded that binding of all three metals was controlled by adsorption processes, with lead more strongly bound to particulates and organic matter in the sediment, than was cadmium or zinc. Figura and McDuffie (11) found that cadmium and zinc were in very labile and moderately labile forms and lead in slightly labile and inert forms. These results, together with Mouvet and Bourg (10), support the conclusion in the present study that concentration of zinc, cadmium, and lead extracted by pH-adjusted reconstituted water was controlled by adsorption on the sediments of Grand Lake, Neosho River, and Tar Creek. Further, the higher concentration of

lead detected in Grand Lake sediments reflects this adsorption/mobility relationship, e.g. it is adsorbed to and deposited with particulates. Zinc is much more mobile and is transported greater distances before removal from the water column.

Bioavailability of metals refers to the quantity of metals available to organisms and has been reviewed by Luoma and Bryan (12) and Luoma (13). In the present study, extraction of sediments at pH 6 was performed to simulate potential bioavailability of sediment metals to overlying water. For a more detailed rationale see McCormick (14).

The chemical characteristics of sediment extracts produced, as described in the Methods section, are shown in Table 2. Lead and cadmium were below detection limits in all test waters. The hardness was significantly higher for Grand Lake extracts than for the other sediment extracts ($p = 0.05$). Grand Lake sediment extracts produced no significant toxicity to *Daphnia*. However, Neosho River and Tar Creek sediment extracts were significantly toxic and LC_{50} values were determined.

The absence of toxicity of Grand Lake sediment extracts can be explained by the relatively low concentration of zinc and the elevated hardness. A regression calculated relating LC_{50} zinc concentration to hardness produced the following equation: $LC_{50} = 2.98 \cdot (\text{hardness}) + 113.55$, $r = 0.89$ (14). Based on this regression, the zinc concentration in Grand Lake extracts (0.66 mg/L) was ap-

TABLE 2. Analysis of aqueous sediment extracts used in toxicity determinations with *Daphnia magna*.

Water quality parameter	Extract			
	Reconstituted water	Tar Creek	Neosho River	Grand Lake
pH*	7.0	7.0	7.0	7.0
Hardness	133	160	202	388
Alkalinity	124	80	128	320
Calcium (mg/L)	22.7	30.0	35.2	101.6
Magnesium (mg/L)	16.5	13.4	15.8	17.3
Iron (mg/L)	0.07	1.73	0.47	0.29
Zinc (mg/L)	0.09	4.16	2.56	0.66
Lead (mg/L)	<0.005	<0.005	<0.005	<0.005
Cadmium (mg/L)	<0.005	<0.005	<0.005	<0.005
Chromium (mg/L)	0.01	<0.01	<0.01	<0.01

*Extraction was performed at pH 6

proximately one-half of that estimated from the regression value (1.270 mg/L).

The calculated 48-hr LC₅₀ for the Neosho River extract was 26.4 percent, corresponding to 0.676 mg/L zinc. The LC₅₀ zinc concentration estimated from regression was 0.715 mg/L at a hardness of 202 mg/L. Therefore, LC₅₀ concentrations calculated for zinc in Neosho River sediments explained the observed toxicity.

The calculated 48-hr LC₅₀ for Tar Creek extract was 25.6 percent, corresponding to 1.065 mg/L zinc. The LC₅₀ for zinc at the hardness of the extract was estimated at 0.590 mg/L based on the previous regression equation. The zinc content corresponding to the 48-hr LC₅₀ is almost twice that expected from the estimated value. The higher 48-hr LC₅₀ concentration of zinc might be attributed to adsorption to particulates <0.45 μm in diameter or formation of less toxic species of zinc due to the filterable iron content, which was approximately four times that of the Neosho River extract.

SUMMARY

Sediment core analysis showed that elevated concentrations of cadmium, lead, and zinc were deposited in the upper end of Grand Lake. The metals concentration at >50 cm indicated that the sediment deposition in the upper end of Grand Lake, since impoundment, was relatively rapid. Elements whose availability is primarily controlled by adsorption/desorption processes were extracted with pH-adjusted reconstituted water. The pH-sensitive concentrations of metals extracted typified the mobility of zinc, cadmium, and lead reported for aquatic systems. Reconstituted water sediment extraction appears to reflect bioavailability of sediment-associated metals.

The 48-h LC₅₀ for Neosho River and Tar Creek sediment extracts was 26.4% and 25.6%, respectively. The toxicity was attributed to bioavailable zinc in Neosho River extracts and zinc plus an unidentified contaminant(s) in the Tar Creek extracts.

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