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# Lead and zinc bioavailability to *Eisenia fetida* after phosphorus amendment to repository soils

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*Phosphorus form and pH were controlling factors in the effectiveness of phosphorus amendment in decreasing Pb and Zn bioavailability.*

**Abstract**

Four phosphorus forms were investigated as potential soil amendments to decrease the bioavailability of Pb and Zn in two repository soils to the earthworm, *Eisenia fetida*. Treatments were evaluated by examining differences in bioaccumulation factors between amended and non-amended soils. Triple super phosphate at 5000 mg P/kg decreased both Pb and Zn bioavailability in both soils. Rock phosphate at 5000 mg P/kg decreased Zn bioavailability, but not Pb bioavailability in both repository soils. Monocalcium phosphate and tricalcium phosphate at 5000 mg P/kg did not significantly decrease Pb or Zn bioavailability to earthworms in either repository soil. In order to optimize phosphorus amendments, additional phosphorus (up to 15,000 mg P/kg) and lowered pH were used in a series of tests. The combination of lowering the pH below 6.0 and increasing phosphorus concentrations caused complete mortality in all triple super phosphate amended soils and partial mortality in the highest rock phosphate amended soils. Results indicate that triple super phosphate and rock phosphate are viable soil amendments, but care should be taken when optimizing amendment quantity and pH so that adverse environmental effects are not a by-product.


*Keywords:* Lead; Zinc; Earthworm; Bioavailability; Soil amendments

## 1. Introduction

Environmental and human health problems worldwide can be attributed to past metal mining and smelting activities. Soil samples obtained from southeast Kansas, southwest Missouri and northeast Oklahoma, collectively known as the tri-state mining area, contain elevated levels of Pb, Zn, and Cd from tailings and smelting activities. Elevated metal concentrations cause harm to local children and ecosystems. The quantity of Pb in soils has been directly linked to elevated blood Pb concentrations (Lewin et al., 1999) and the abatement of Pb levels to decreases in blood Pb concentrations in 6 to 72-month old children (Lanphear et al., 2003). Residents of the tri-state mining area have exhibited a decline in human health. High levels of Pb have been found in children along with increased prevalence of kidney and heart disease in the tri-state mining area (Nueberger et al., 1990). Exposure to metals can also be hazardous to wildlife and plants. Little or no vegetation exists in old mining regions, causing wind and water erosion to continually increase metal dispersal (Pierzynski et al., 1994).

Soil excavation, solidification, vegetative remediation and phosphorus remediation are used in remediation of

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metal contaminated sites. Locating hazardous waste landfills and high cost are disadvantages to soil excavation. Solidification consists of a cement mix that physically solidifies sediment, while chemically stabilizing and immobilizing contaminants. Although human contamination is reduced, land is rendered unavailable for many flora and fauna. In vegetative remediation, metals may be removed from soils, but they still pose a threat through food web transfer to herbivores. Phosphorus has been shown to immobilize Pb and reduce bioavailability (Ma et al., 1995; Ma and Rao, 1997; Pearson et al., 2000; Hettiarachchi et al., 2001; Cao et al., 2002; Yang et al., 2002; Melamed et al., 2003; Brown et al., 2004). Phosphorus amendments added to contaminated soil can lead to the formation of pyromorphites, an insoluble Pb-phosphate complex. Pyromorphite complexes remain stable in soil as a secondary mineral with phosphate as the limiting formation agent (Maenpaa et al., 2002). High phosphorus treatments reduce the bioavailability of Pb and Zn to earthworms presumably due to the metal-phosphate complexes formed in amended soils (Maenpaa et al., 2002). Ma and colleagues have published many papers on the usefulness of rock phosphate in immobilizing Pb from contaminated soils (Ma et al., 1995; Ma and Rao, 1997; Cao et al., 2002; Cao et al., 2003; Melamed et al., 2003).

Recently, a commercially available biosolid, triple super phosphate (TSP), rock phosphate, and phosphoric acid were utilized alone and in combination in field studies. Addition of 3.2% TSP and 1% phosphoric acid were the most effective treatments for reducing tall fescue grass concentrations of Pb and Zn and in vitro extractable Pb (Brown et al., 2004). Other potential amendments that have been used in an attempt to stabilize Pb in contaminated soils include lime, activated carbon, clay, zeolite, sand, and cement. Lime and cement were significantly effective, while activated carbon, clay, and zeolite were not effective in Pb immobilization as measured by the toxicity characterization leaching procedure (Alpaslan and Yukselen, 2002).

Due to their life history and place in the food web, earthworms are an important soil biota and an effective biomonitoring tool (Neuhauser et al., 1985). Through soil burrowing, earthworms mix organic matter and aerate soils; thereby, increasing their exposure to soil contaminants by direct dermal contact and ingestion. Earthworm bioaccumulation of metals aids trophic transfer of metals and elevated earthworm metal concentrations have been found in worms inhabiting contaminated soils (Spurgeon and Hopkin, 1996b). Studies have shown decreased earthworm bioaccumulation of Pb and Zn from lab-spiked (Pearson et al., 2000) and field-collected soils amended with TSP or $KH_2PO_4$ (Maenpaa et al., 2002).

This study was performed in two phases. The first phase evaluated the potential usefulness of a suite of phosphorus forms in decreasing Pb and Zn uptake by the earthworm, *Eisenia fetida*. The second phase took two phosphorus forms that were successful in Phase I and varied the amendment conditions to optimize pH and phosphorus concentrations for limiting Pb and Zn availability.

## 2. Methods

### 2.1. Soils and amendments

Test soils from two contaminated repository sites from the Tri-State Mining Region were collected in May 2002. Both the active repository soil (ATR) and time critical repository (TCR) soil were collected from waste landfill sites near Joplin, MO where metal-contaminated soil was stored from nearby urban areas. Soils varied in metal concentrations, but were similar in carbon content (LECO C/N 2000 combustion analyzer, Leco Corporation, St. Joseph, Michigan, USA) and pH (Table 1). Other characteristics that were similar for ATR and TCR soils included %Clay (14 and 18%), cation exchange capacity (13.5 and 13.6 meq/100 g), calcium (2878 and 3035 mg/kg), and potassium (223 and 222 mg/kg). Initial Bray-1 P concentrations for ATR and TCR soils were 136.5 and 467 mg/kg, respectively. Cadmium is a secondary contaminant in ATR and TCR soils (32 and 22 mg/kg). Preliminary studies indicated little affect of P amendments on bioavailability and other authors have found little evidence of Cd immobilization by P addition (Basta et al., 2001), so Cd was not included as an analyte throughout these studies.

Soils were collected in large seed boxes and homogenized by mixing. Soils were transported in 190-L plastic containers from the site and stored at Southern Illinois University (Carbondale, IL, USA) until used for

Table 1
Mean soil total and calcium exchangeable metal concentrations ($n=3$, $\pm 1$ standard deviation), pH and total carbon in active repository (ATR) and time critical repository (TCR) soils

| Soil | Total Pb (mg/kg) | Calcium exchangeable Pb (mg/kg) | % Pb exchangeable | Total Zn (mg/kg) | Calcium exchangeable Zn (mg/kg) | % Zn exchangeable | pH | % Total C |
|---|---|---|---|---|---|---|---|---|
| ATR | 1103 ± 68 | 107 ± 6 | 9.7% | 6592 ± 503 | 594 ± 22 | 9.0% | 7.0 | 4.74% |
| TCR | 1741 ± 70 | 117 ± 4 | 6.7% | 4655 ± 1925 | 399 ± 21 | 8.6% | 7.0 | 3.90% |