

## **Soil Amendment with Humic acid and Phosphate to Promote Sorption and Retard Mobility of Zinc**

**Wing H. Leung and A. Kimaro**, Department of Chemistry, Hampton University, Hampton, VA 23668

### ABSTRACT

This research investigated the effectiveness of soil amendment with phosphate and/or humic acid in immobilizing Zn from soil. The soil treatment involved different amounts of phosphate (0.0075, 0.015, 0.030M) and humic acid (10, 30, and 60 mg/L) and was incubated for a week before being studied by batch and column extractions with (1) DTPA (diethylenetriaminepentaacetic acid) and (2) deionized water. The results show that both humic acid and phosphate are effective in reducing the solubility of Zn from soil. The attenuation of extracted Zn was magnified with increasing concentration of phosphate and humic acid during treatment. The primary mechanism was postulated as surface complexation due to formation of the new functional groups created during treatment. Our results suggest that phosphate and humic acid may provide a cost-effective way to remediate Zn-contaminated soils and wastes.

### INTRODUCTION

Spills, leaks, or subsurface disposal of industrial wastes are known to have contaminated soil and groundwater. Contaminants released into the subsurface are pervasive environmental problems that have proven to be extremely difficult to remediate. Predicting the mobility of contaminants in the subsurface and remediation of contaminated soils and groundwater has proven to be extremely challenging. Recently, increasing attention has been given to in situ remediation of metal-contaminated soils (Czupryna et al, 1989). Numerous field studies have demonstrated that sorption processes recognized as a natural retardation for the migration of metals are important in natural environments. The capacity of a soil to remove metals from solution is one estimate of the effect of that soil on metal availability to plants. Natural organic matter in which humic and fulvic acid are the major components is a very influential factor affecting the properties of soil. Hunter (1980) argued that the adsorbed organic material could mask the properties of the underlying solid and present a surface with very different physicochemical properties. Humic acid, a component of soil organic matter is made of structural units including carboxylic, hydroxylic, phenolic, and aliphatic groups stabilized into aggregates, and may enhance the removal or retard the mobility of contaminants from soil. Also, it has been shown that the geochemical behavior of lead indicates that phosphate, when present in sufficient amount, immobilizes lead (Nriagu, 1974) even at low pH.

It has been shown in this laboratory (Gragg, 1984; Samba, 1989; Eshete, 1995; and Kimaro, 1997), that the adsorption of trace metals (Cd, Ni, Zn) on oxides was facilitated by some anions such as phosphate, sulfate, and humic acid and impeded by calcium ions. It was also interesting to note (Graag, 1984; Eshete, 1995) that adsorption of Cd and Ni could be either enhanced or hindered depending on the concentration of the

anion (phosphate or humic acid). Since solubility, mobility, bioavailability and toxicity are all closely linked (Channey et al, 1989), it was planned in this laboratory to study the feasibility and mechanism of immobilizing zinc as a model metal in soil by the treatment of soil with phosphate or humic acid which would make zinc (and other trace metals as well) less soluble (and so less mobile and less bioavailable). Zn was chosen as a model metal for this study due to its ubiquitous nature and the fact that it is one of the commonly encountered metals of concern. In sludge-amended soil, Cu, Zn, and Ni are the metals mostly likely to cause toxicities in crops (CAST Rep, 1976). Sims et al (1986) reported many in-place treatment technologies such as soil flushing, immobilization (sorption, ion exchange, and precipitation), chemical degradation, biodegradation, and attenuation for contaminated surface soils. Among them, immobilization is a promising technology for cleaning up contaminated soils and wastes.

Chemical extraction techniques, used either to estimate trace element bioavailability or trace element associations in sediments and soils, have been extensively applied in environmental studies, agronomy, and exploration geochemistry. In this study, the chemical extraction method which aims at understanding the mobility and/or bioavailability of zinc involved the use of (1) a modified DTPA (diethylenetriaminepentaacetic acid) sediment extraction procedure (Lee et al, 1978) and also (2) deionized water. All of the trace metals such as lead (Freeman et al, 1992) etc in soil are not in one chemical or physical form and thus may not be uniformly soluble and bioavailable. The rationale for our approach is that the mobility and the bioavailable portion of soil metal can be approximated by the soluble and/or exchangeable fraction, because metal must first be dissolved to be absorbed. Water soluble trace metals usually are used for predicting toxic conditions. Exchangeable soil trace metals have been shown to be related closely to their plant uptake. Chelating agents, e.g., EDTA (ethylenediaminetetraacetic acid) and DTPA have become more popular in recent years. The use of DTPA as a soil test extractant for diagnosing Zn, Fe, Mn and Cu-deficient soils was reported (Linsay and Norvell, 1978). Various chemical extraction procedures have been studied (Lee et al, 1978) at the U.S. Army Engineer Waterways Experiment Station (WES), aiming at predicting plant uptake of toxic metals from sediments. Of these, the DTPA method was the only extraction procedure to show good potential for predicting marsh plant uptake of Zn, Cd, Cu, and to a lesser extent Pb and Cr. Lee et al (1982) argued that total nitric acid digests of sediments indicated the amount of heavy metals present but did not indicate the bioavailability of the heavy metals. In order to get an indication of the mobility and bioavailability of sediment heavy metals, a DTPA extraction procedure should be used.

#### MATERIALS AND METHODS

Humic acid was obtained from Aldrich Chemical Co. (Milwaukee, WI). Before it was used in any experiment, the humic acid was dissolved in water, and then filtered through a 0.45 m filter (Gelman Sciences, GN-6) to remove any particulate material. All other chemicals used were reagent grade supplied by Fisher Scientific.

Soil was obtained from south east of site 3 of Craney Island which is a 2500-acre confined disposal site in Virginia, developed in the early 1940's, initiated in 1954, and completed in 1957 by the Army Corps of Engineers to provide a long-term disposal area for material dredged from channels and ports in the Hampton Roads area. Soils were air dried, crushed, and then sieved through a 1.0 mm pore size and collected

between 1.0 and 0.71 mm pore size. Soils thus prepared were treated with deionized water (and then used as control), phosphate (0.0075, 0.015, and 0.030 M) and humic acid (10, 30, and 60 mg/L), and incubated for seven days, then filtered, dried and sieved. The sieved soils were now subjected to batch and column extraction and then analyzed for indigenous zinc using atomic absorption spectrophotometer (AAS) – a Varian spectrophotometer, SpectrAA-20.

DTPA extraction solution was prepared by (i) dissolving DTPA (1.9668 g/L) in triethanolamine (14.9199 g/L) and diluting to near the proper dilution, (ii) adding  $\text{CaCl}_2$  (1.1099 g/L) to the solution, (iii) buffering the solution to pH 7.3 using HCl or NaOH, and (iv) completing the dilution with deionized water to 1 L. The resulting solution is 0.005 M DTPA.

### Batch Method

For batch extraction of zinc, a 2g portion of soil was placed in a polycarbonate flask and 20 mL of extractant was added. The suspension was shaken in a shaker at 200 revolutions per minute for 24 hours and then filtered. The filtrate was retained for metal analysis using a Varian spectrophotometer.

### Column Method

The column extraction procedure employed a polycarbonate tube (1 cm diameter x 37 cm height). A cork at the bottom provided a conduit for liquid. A 5.0 g sample was placed into the leaching column to a height of 11 cm. The packed column was leached with distilled deionized water or DTPA at a rate of 2.0 mL per minute. Two columns were constructed to allow leaching of two duplicate soil samples simultaneously. Deionized water or DTPA was pumped into the soil through a buret that hung above the column. 20 mL aliquots of the eluant were collected for analysis of Zn using a Varian spectrophotometer.

### Total Zn Content extracted by $\text{HNO}_3/\text{H}_2\text{O}_2$

The total amount of zinc in the treated soil was studied by digesting 1 g of soil sample in 15 mL of 3M nitric acid and 2.5 mL 30% hydrogen peroxide on a hot plate in a temperature range of 85-96°C. Additional 30% hydrogen peroxide, if needed, was added until the digestion was complete as seen by the lightening of the sample's color. After filtering, the solution was analyzed for Zn using a Varian spectrophotometer. The total zinc content in the soil extracted by this method was 24900 µg/g.

## RESULTS

The results showing the amount of zinc in µg per gram extracted from soils with and without treatment are summarized and illustrated in Figures 1-4.

As shown in these figures, the result of these studies indicated that the extracted amount of zinc was decreased with soil amendment and the extent of attenuating zinc in the extract was further enhanced with increasing concentration of either phosphate or humic acid during treatment.

Results of Phosphate Treatment: From batch extraction (Figure 1) with deionized water as the extractant, the concentration of extracted zinc decreased as compared with control (soil without treatment) by 69.7, 90.1 and 92.5% for the soil treated with phosphate of 0.0075, 0.015 and 0.030 M respectively. With DTPA as extractant, the extracted zinc concentration decreased by 11.9, 18.3 and 24.4% respectively. In column

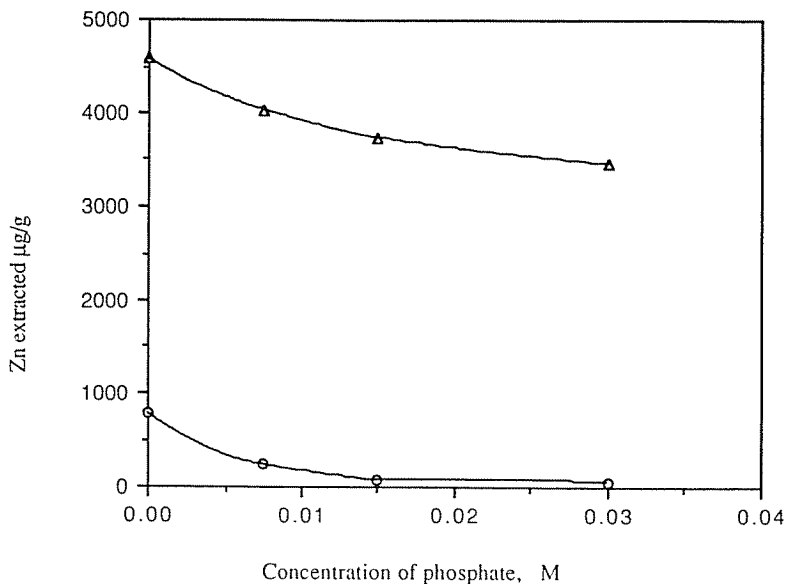


FIGURE 1. Plot for the batch extraction of Zn from soil treated with phosphate using distilled deionized water (o) and DTPA ( $\Delta$ ) as extractants.

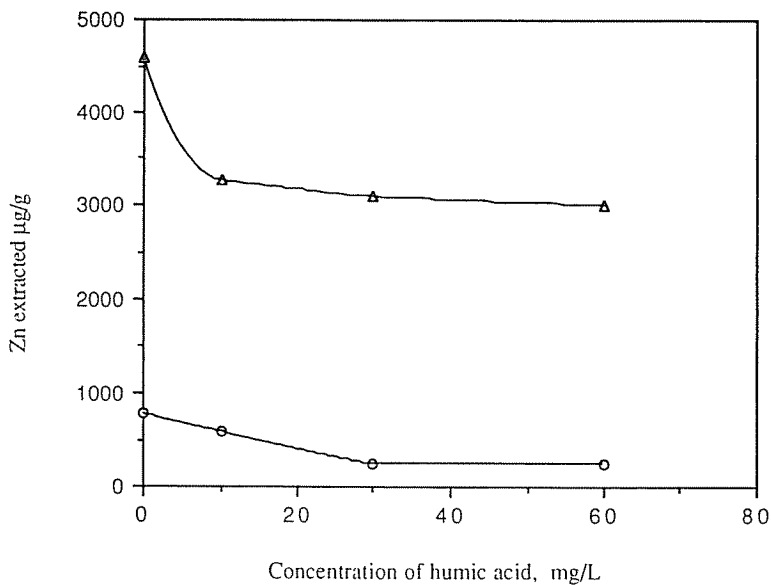


FIGURE 2. Plot for the batch extraction of Zn from soil treated with humic acid using distilled deionized water (o) and DTPA ( $\Delta$ ) as extractants.

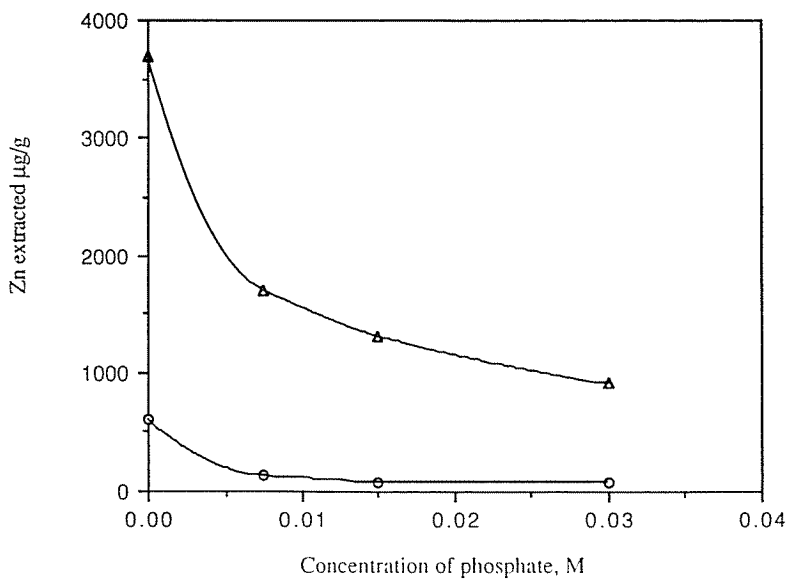


FIGURE 3. Plot for the column extraction of Zn from soil treated with phosphate using distilled deionized water (o) and DTPA ( $\Delta$ ) extractants.

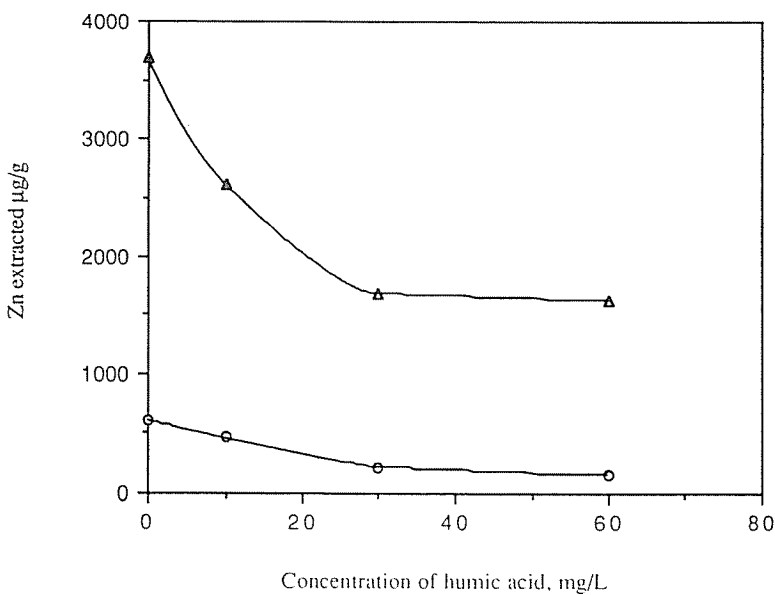


FIGURE 4. Plot for the column extraction of Zn from soil treated with humic acid using distilled deionized water (o) and DTPA ( $\Delta$ ) as extractants.

extraction (Figure 3) with deionized water as the extractant, concentration of extracted zinc decreased as compared with the control by 77.0, 86.8 and 87.4% for the soil treated with phosphate of 0.0075, 0.015 and 0.030 M respectively. With DTPA as extractant, the extracted zinc concentration decreased by 43.4, 56.4 and 69.7% respectively.

Results of Humic acid Treatment: For the soil treated with humic acid (10, 30, and 60 mg/L), in batch extraction (Figure 2) with deionized water as the extractant, the concentration of extracted zinc decreased as compared with the control by 25.1, 68.6 and 69.3% respectively. With DTPA as the extractant, the extracted zinc concentration decreased by 28.7, 32.5 and 34.5% for the soil treatment with 10, 30 and 60 mg/L humic acid respectively. In column extraction (Figure 4), the decrease in concentration of extracted zinc was 23.3, 63.7 and 75.4% respectively when deionized water was used as an extractant. When DTPA was used the decrease in concentration of extracted zinc was 12.9, 44.1 and 46.2 respectively.

#### DISCUSSION

The fate of trace metals in soils and in natural systems is largely controlled by adsorption/desorption processes (Spoito, 1984; Sigg, 1987). Transformations such as

Particulate metal  $\longleftrightarrow$  dissolved metal

are of fundamental relevance for the mobility of the involved metal ions in the particular reservoir. In soil, desorption leads to mobilization and to transfer from soil to the ground water system. The above results in this work on the extraction of Zn from soils indicate that soil properties can be modified by amendment to reduce mobility and thus plant availability of zinc, and that both phosphate and humic acid on association with soils have potential ability to hold zinc on soil. As a result of recent studies (Kimaro, 1997) in this laboratory, of the treatment of silica with phosphate solution, the sorptive capabilities for lead were greatly enhanced and increased with increasing concentration of phosphate used in treatment. This provides useful results for comparison with soil amendment. It has been known that both humic acid and phosphate are readily adsorbed by oxides (Gragg, 1984; Samba, 1889; Eshete, 1995; Kimaro, 1997; Tipping, 1982; and Stumm et al, 1979) and soil (Barrow, 1983). Adsorption occurs by complex formation between surface hydroxyls and the acidic functional groups of the organic molecules and phosphate anion. The association with phosphate and/or humic acid is expected to have a great influence on subsequent sorption of inorganic cations and anions. Adsorption of humic acid covers surface hydroxyls and provides new functional groups (Davis, 1982) for further complexation reactions with metal ions. Since humic acids are large adsorbing molecules, not all their anionic groups can be involved in the ligand exchange interactions on adsorption. The excess anionic groups (e.g., carboxylic and phenolic) are still available for complexation reactions with metal ions, thus providing new functional groups for complexation reactions with Zn, and affecting the fate of zinc and other metal ions as well in solution. Addition of phosphate as well as humic acid to the system reduced the pH of the zero point of charge (zpc), and thus also increased Zn sorption. Therefore, the enhancement of sorption capability for zinc can be attributed to the presence of the newly created carboxylic and phenolic and phosphate chelating groups at the surface. Complexation of Zn with the functional groups of adsorbed organic matter and phosphate is expected to be stronger and

therefore more effective to immobilize the metal than complexation with uncovered surface hydroxyls.

A batch extraction method involves the mechanical mixing of a unit volume of water or an alternative extractant with a unit mass of soil. In Column extraction method there is a continuous flow of extractant through a fixed bed of soil. While the batch extraction method is easy to operate and has low experimental variation, leachate generated by the column method is more representative of the leachate derived from the disposal site than is the leachate from the batch method. The column method is more realistic in simulating leaching processes which occur under field conditions.

Thus we can conclude, based on the above information, that either humic acid or phosphate adsorbed on soil can interact with Zn, possibly forming surface complexes and are important factors controlling the mobility and fixation of Zn in soils, thus reducing Zn solubility as well as bioavailability. It is suggested that such soil amendment with phosphate or humic acid may be used to improve the retardation capabilities of soils and aquifer materials and also to enhance the containment capabilities of clay landfill liners and slurry walls.

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