

## RELEASE OF ARSENIC AFTER APPLICATION OF PHOSPHATES INTO LEAD AND CADMIUM CONTAMINATED SOIL

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### **Abstract**

In lysimeter experiments, it was observed that application of triple superphosphate greatly diminished concentrations of lead and cadmium in soil solution, but enhanced concentration of arsenic. This phenomenon was correlated with acidification of soil solution. The goal of the present paper was to find an additive that could be applied to the soil along with triple superphosphate in order to lower the resulting arsenic concentration in soil solution. In batch experiments, it was found that application of 0.80% lime with the superphosphate reduced arsenic concentrations in water extracts by 22% compared to superphosphate treatment alone. At a higher rate of lime (3.30%), arsenic in the water extracts was reduced by 73% compared to superphosphate treatment alone. Incorporation of lime also raised the pH of water extracts and was associated with an increased immobilization of lead and cadmium by superphosphate.

### **Introduction**

Immobilization of toxic elements is a promising method for remediation of heavily contaminated soils. One approach to immobilization is the application of amendments to contaminated soil. Anthropogenic contamination often exists as complex mixtures. For example, the mining and smelting of lead or zinc is often associated with environmental contamination not only by lead and zinc, but also by cadmium and arsenic. A literature reviewed shows, however, that most research concentrates on stabilization of one heavy metal at a time (1, 2).

Our previous investigations have focused on stabilization of lead and cadmium in contaminated soil associated with a lead and zinc smelter. In lysimeter experiments, it was observed that application of triple superphosphate resulted in greatly diminished concentrations of lead and cadmium in soil solution (i.e., reduced environmental mobility), but enhanced concentration of arsenic. The aim of the present investigations was to find an additive that could be applied to the soil along with superphosphate in order to lower arsenic concentration in soil solution.

### **Methods**

Soil was collected from a site near a former lead and zinc- smelter in southern of Poland near the town of Katowice. The soil used in these experiments was characterized as shown in Table 1.

Table 1. Properties of contaminated soil used in lysimeter and batch experiments

pH - KCl	OM <sup>a</sup> %	CEC (cmol+/kg)	Pb <sup>b</sup> (mg/kg)	Cd <sup>b</sup> (mg/kg)	As <sup>b</sup> (mg/kg)
6.7	8.52	6.6	9927	541	213

<sup>a</sup>OM, soil organic matter

<sup>b</sup>Total soil element concentrations determined in an Aqua regia destruction

#### Lysimeter Experiment

Lysimeters (diameter of 25 cm and a height of 60 cm) were filled with air-dried soil that had been homogenized and sieved (< 4 mm). Superphosphate (5 % w/w) was mixed with contaminated soil before filling the lysimeters. In each lysimeter (n=3), 2 Rhizon soil moisture samplers (artificial roots) were installed to take up soil solution (3).

Soil solution was sampled twice, two months (first sampling event) and three months (second sampling event) after the lysimeters were initialized. The concentration of lead, cadmium and arsenic as well as pH were measured in soil solution as described below.

#### Batch Experiment

Conical flasks were filled with 10 g of contaminated soil. The soil was then mixed with one of the following combinations of additives (in triplicate):

- Soil without additives (control)
- 5 % w/w triple superphosphate
- 5 % w/w triple superphosphate + 0.80 % w/w lime
- 5 % w/w triple superphosphate + 3.30 % w/w lime.

Soil in flasks was moisten with deionized water and flasks were covered with aluminum foil. After seven days of incubation at room temperature 25 ml of deionized water was added to each flask and after 24 hours pH and concentration of lead, cadmium and arsenic was measured in water extract.

#### Analytical procedures

The solutions (soil solutions and water extracts) were analyzed for metal content by atomic absorption spectrophotometer (Varian Spectra AA300). The pH of solutions was measured with pH-meter (CPC-551, Elmetron) and pH-electrode (OSH 10-10, Metron).

Data reported in this paper were analyzed using Statistica software. A probability of 0.05 or less was considered to be statistically significant.

## Results

Lysimeter studies showed that triple superphosphate 5 % w/w mobilizes arsenic from contaminated soil and resulting in large increases of this element in soil solution (figure 1).

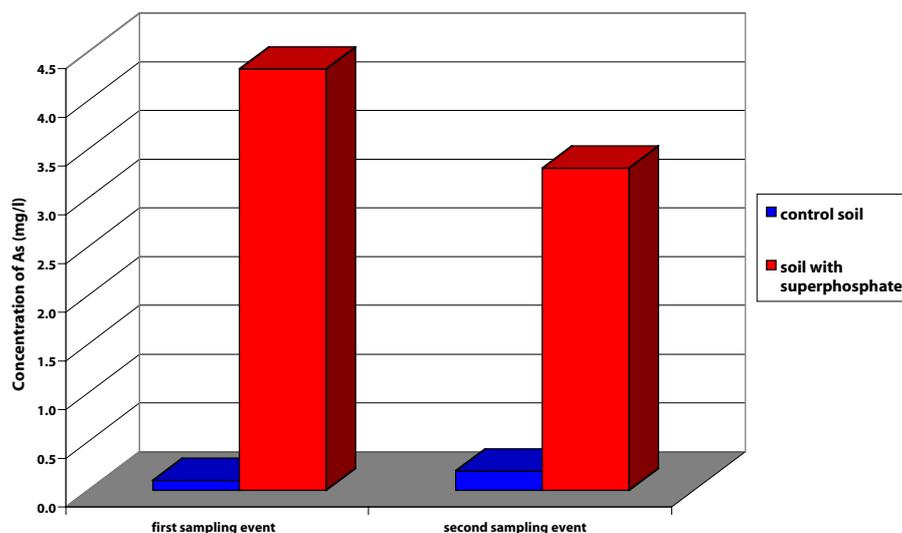


Fig. 1 Effect of superphosphate application to contaminated soil on As concentration in soil solution.

In the current study soil solution pH dropped after addition of superphosphate fertilizer (figure 2).

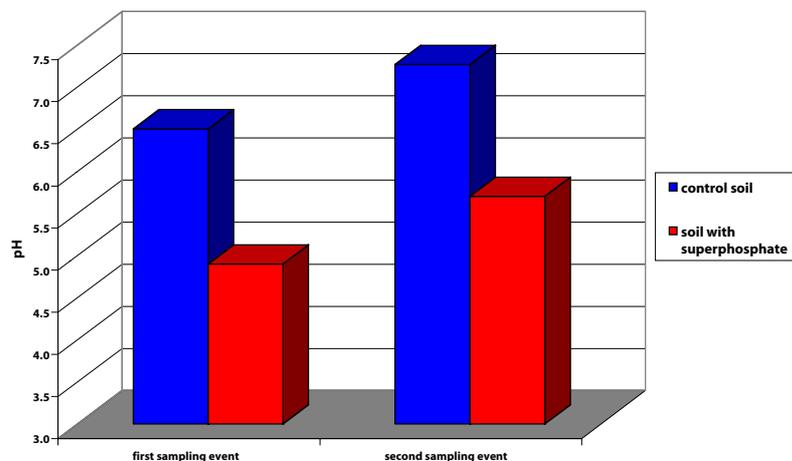


Fig. 2 Effect of superphosphate application to contaminated soil on pH of soil solution.

It was hypothesized that high concentrations of arsenic in soil solutions after application of superphosphate were the result of reduced soil solution pH. To verify this hypothesis a batch experiment was conducted.

In the batch experiment, it was found that the application of lime in conjunction with superphosphate reduced arsenic concentration in soil water extracts (figure 3) and enhanced the effect of superphosphate on lead and cadmium immobilization (data not shown).

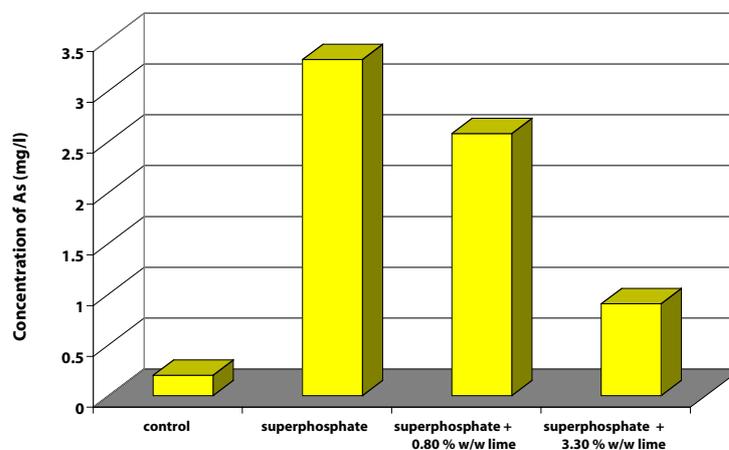


Fig. 3 Effect of application of lime and superphosphate to contaminated soil on As concentration in soil water extracts.

Addition of lime (3.30 % w/w) increased the pH of soil water extract to that of control treatments (figure 4).

### Discussion

Immobilization of heavy metals is a promising method for treatment of heavily contaminated soils. Literature data showed that most researchers concentrate on stabilization one heavy metal at a time such as lead (1) and cadmium (2). However anthropogenic contamination often exists as complex mixtures. For example, soils contaminated with lead and cadmium from lead/zinc smelter activity often contain high concentrations of arsenic.

Hydroxyapatite and phosphate rock have been proposed as amendments for stabilization of lead in soils surrounding lead-zinc smelters (4, 5), however the concentration of arsenic in these soils was not investigated. We observed in lysimeter experiments that application of triple superphosphate to

soils highly contaminated with lead and cadmium, greatly enhanced the concentration of arsenic in the soil solution (figure 1).

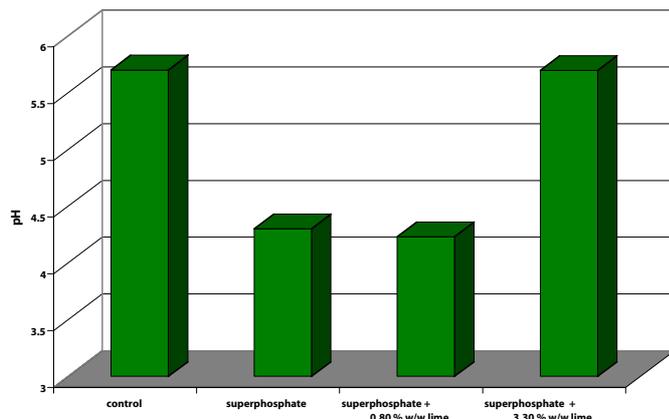


Fig. 4 Effect of application of lime and superphosphate to contaminated soil on the pH of soil water extracts.

This phenomenon was correlated with acidification of soil solution (figure 2). Our results suggest that the application of triple superphosphate to stabilize Pb or Cd in smelter-contaminated soils should be conducted with great caution. It is proposed that concentration of arsenic (and possibly other toxic metals) has to be assessed and that soil pH should be monitored.

Yang et al. (6) reported that phosphoric acid can be used for immobilization of lead in smelter-contaminated urban soil. They observed that addition of 5000 mg of phosphorus as  $H_3PO_4$  per kg of soil lowered the soil pH from 7.22 to 4.34 (6). However, they did not report arsenic concentration in the soil. The results of this study show that reducing soil pH to 4.5 would result in the release of arsenic from solid phase to solution (figures 1 and 2). The application of lime along with superphosphate prevented the reduction of soil pH and, thus, the release of arsenic (figures 3 and 4). Based on the results presented in the current study, it is suggested that if phosphoric acid is to be used for lead immobilization in smelter-contaminated soils, pH changes associated with that use should be considered. In situations where pH reductions are likely, that lime or other compounds that increase soil pH should be used in order to prevent the unintentional mobilization of arsenic.

## Conclusions

- Addition of triple superphosphate to lead and cadmium contaminated soil can lower soil pH and mobilize arsenic from solid phase into soil solution.
- Application of lime in conjunction with triple superphosphate can prevent this pH reduction and arsenic mobilization.
- Higher concentration of lime (3.30 % w/w) was more effective in reducing arsenic concentration and increasing soil pH.
- When phosphoric acid is used for stabilization of lead or other heavy metals in smelter-contaminated soils, it should be applied with lime to prevent soil pH reduction and arsenic mobilization.

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