

X-ray Fluorescence Microprobe Analysis of a Contaminated Soil

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INTRODUCTION

Contaminated soils present a major global health problem especially in urban areas with dense populations. Heavy metals are common contaminants and understanding their behavior in soils is central to our ability to predict the extent of their environmental hazard. The environmental and health consequences of elevated concentrations of soil Pb resulting from human activities is of great concern because of its toxicity at very low concentrations, especially to children.

The solubility and potential biological availability of Pb and other heavy metals in soils is influenced by a number of mechanisms including solid phase interactions with soil constituents and spatial distributions both on a micro-scale and larger. Lead, e.g., can adsorb to soil phyllosilicates, hydrous oxides, and organic matter as well as form separate solid phase compounds like lead phosphate.¹ Identifying elemental associations on a micro-scale is important for assessing these solid phase forms. Understanding spatial distribution of Pb and other toxic elements in soil is also very important since hazardous conditions from contamination may not be related to an averaged concentration found in bulk soil but to possible exposure to extremely high concentrations in micro regions.

The sampling site was a heavy metal contaminated, residential area in Oakland, CA. Apparently, paint from old buildings that burned down in the late 1960's resulted in soil contamination. Initially, the site was investigated because local residents expressed a desire to develop a community garden on this plot of land. Preliminary x-ray fluorescence (XRF) analysis of the soil yields the following ranges of concentrations for a number of various locations at the site: 195-64510 mg Pb/kg, 243-32414 mg Zn/kg, 45-165 mg Ni/kg, 164-10414 mg Cr/kg, and 5900-110,000 mg Ti/kg soil. In comparison, the range of means for U.S. soil as it pertains to Pb, Zn, Ni, Cr, and Ti are 7-26, 34-84, 13-30, and 20-85 and 1800-3600 mg/kg respectively^{2,3}. In general, the site had heavy metal concentrations far greater than the means for the U.S. and showed a very heterogeneous distribution dependent on location.

The objectives of this project are to determine the spatial distribution and elemental associations of Pb as well as other potentially toxic metals in a contaminated urban soil. These results will provide important information which will help in our interpretation of the chemical solubility and biological availability of these elements studied in another part of this overall project. The high spatial resolution and low detection limits of the x-ray fluorescence microprobe at Beamline 10.3.1 at the Advanced Light Source provides excellent capabilities for the detection of elemental association in undisturbed soil systems.

EXPERIMENTAL

Intact soil cores were collected from various locations in a contaminated residential area in Oakland and at various soil depths. The cores were imbedded with LR White acrylic resin. Samples were cut into approximately 2 cm wide x 0.5 cm thick x 3 cm long blocks, polished, and mounted on the microprobe stage. Using the x-ray fluorescence microprobe, four vertical scan lines spaced 0.18 mm apart horizontally, ran vertically along the sample in 0.18 mm steps. Data for only one core is presented in this report.

Figure 1 shows the Pb, Cr, and Ti distributions and concentrations in an Oakland soil sample that was collected 22.5 to 25.4 cm below the soil surface. The x, y, and z axes are in units of mm, cm, and $\mu\text{g}/\text{cm}^2$ respectively. Figure 2 shows linear regression analyses of a) Cr vs. Ti, b) Ti vs. Pb, and c) Cr vs. Pb with R^2 values of 0.733, 0.389, and 0.485, respectively. Ti and Cr concentrations were the most highly correlated in the soil matrix. Figures 1b and 1c show the actual distribution of Cr and Ti. It can be seen that Cr and Ti were concentrated between 25.0 and 25.4 cm below the soil surface.

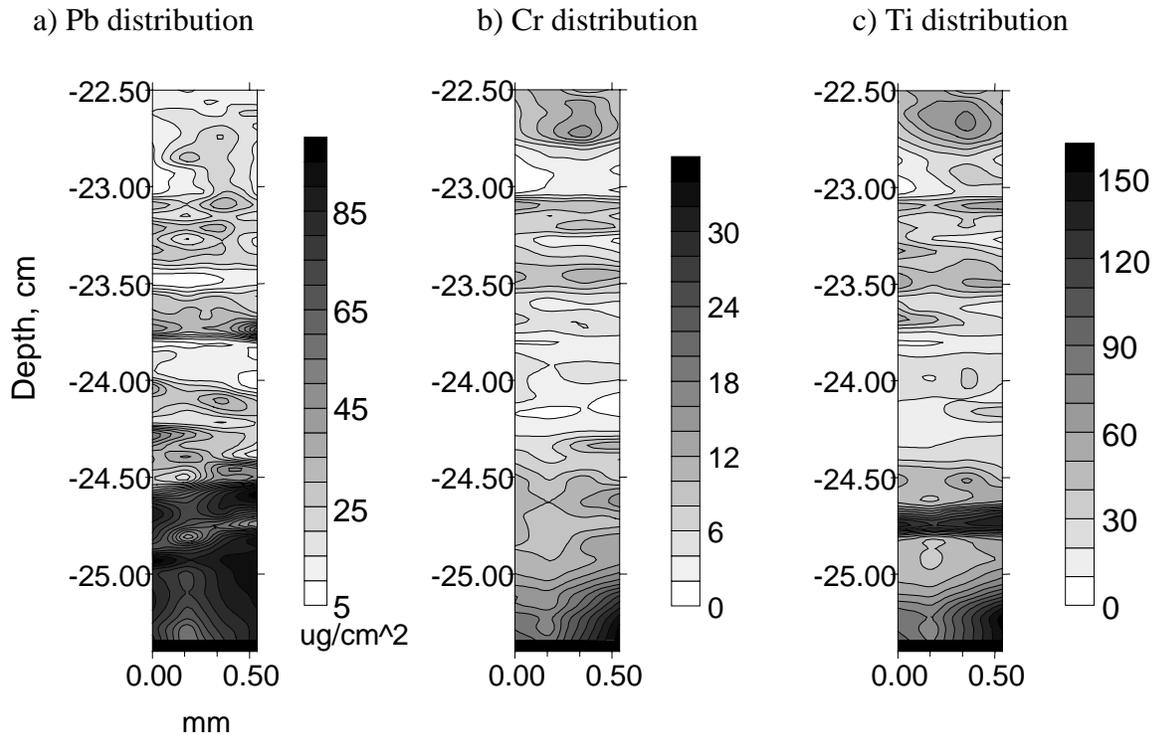
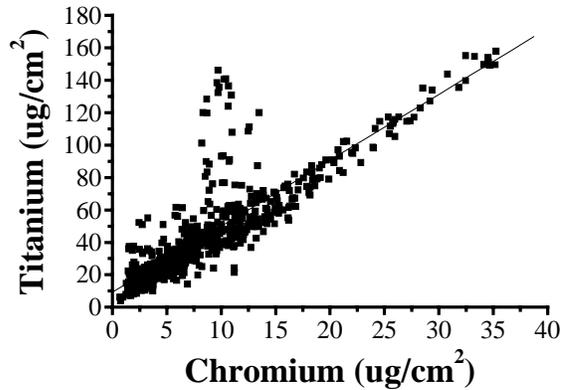
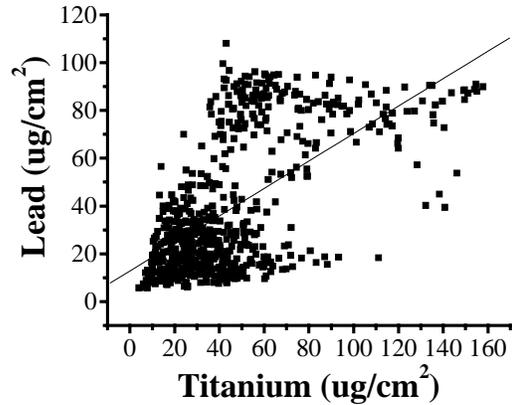


Figure 1. a) Pb, b) Cr, and c) Ti distributions in a soil sample which was collected approximately 22.5-25.4 cm below the soil surface.

a) Cr vs. Ti



b) Ti vs. Pb



c) Cr vs. Pb

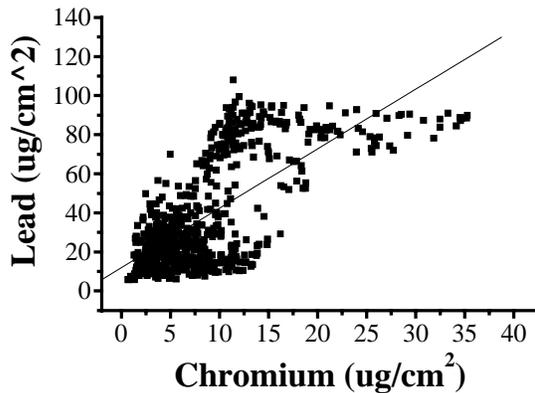


Figure 2. Linear regression analysis of a) Cr vs. Ti ($R^2=0.733$), b) Ti vs. Pb ($R^2=0.389$), and c) Cr vs. Pb ($R^2=0.485$) from x-ray microprobe analysis.

However, at approximately 24.7 cm, Ti had an elevated concentration which was independent of Cr. This suggests that these metals originated from two sources or that Cr is more mobile than Ti and has migrated from its previous location which was in close proximity with the Ti at 25.0 cm. Pb and Ti were concentrated in the area between 24.5 and 25.4 cm below the soil surface as shown in Figures 1a and 1c. However, Pb was fairly dispersed in this region and Ti was localized. These two metals were not as well correlated ($R^2=0.389$) as Cr and Ti ($R^2=0.733$). These results imply that the Pb and Ti contamination originated from two sources or that lead is slightly more mobile than titanium in the soil.

The titanium in the soil is likely to have originated from titanium dioxide which comes in two crystalline forms, both of which are used for interior and exterior paints.⁴ Titanium dioxide is a very stable compound. Through the use of a sequential extraction technique⁵, Pb has been found to be highly associated with carbonates. Lead carbonate and other lead pigments are used in paint pigments and usually prevents the growth of microorganisms.⁴ Crocoite (PbCrO₄) that is associated with litharge (PbO), a drier used in nails and varnishes, are possible sources of Cr and Pb.⁶ Thus, these results along with the support of other chemical and biological methods provide an important tool for accessing potential hazards from heavy metal contamination of soils.

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