ASSESSMENT OF A SEQUENTIAL EXTRACTION PROCEDURE FOR PERTURBED LEAD CONTAMINATED SAMPLES WITH AND WITHOUT PHOSPHORUS AMENDMENTS

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INTRODUCTION

Many sequential extraction schemes are modifications stemming from a procedure developed by Tessier et al. (*1*). These procedures were originally developed for the examination of aquatic sediments but gained wide acceptance as tools for the speciation of metals in soils. In the mid-1980s, an increasing number of researchers began to question the validity of sequential extraction procedures for metal speciation in solid samples. Amongst the chief concerns were sampling/preservation procedures, chemical properties of the target element and sample chemical composition, little specificity for the solid phase attacked, lack of reference standards for quality control, and lack of standardized procedures. While sampling techniques and actual extraction routines can be standardized to some degree, results from sequential extraction procedures may vary widely in complex matrices such as soils and sediments. Lack of specificity on the fractions attacked by a particular extractant can mobilize elements that are associated with solid phases other than the phase targeted by the extraction.

Soils are seldom, if ever, in equilibrium. Thus, the assumption of equilibrium is often a convenience to simplify an experimental design, which is typically the case for sequential extraction procedures that operate under the premise of equilibrium. Tessier et al. (*1*) presuppose that sequential extraction procedures will *conceptually* work under ideal equilibrium conditions. Immobilization of Pb as pyromorphite via soil amendments (phosphate with inorganic phases of biosolids and/or industrial iron byproducts) is a case-in-point of a non-equilibrated, perturbed environmental system that may lead to erroneous results when examined by sequential extraction procedures. As a result of such findings, some researchers have declared that the soils are safe (both environmentally and biologically) since pyromorphite is highly insoluble and biologically inert. However, few studies (*2,3*) have ever applied advanced spectroscopic methods to establish the presence of pyromorphite before the extraction procedure or if the extraction procedure itself causes a release of Pb and P into solution with subsequent formation of pyromorphite. We believe that literature studies that observe significant amounts of Pb in the residual fraction is a result of the sequential extraction chemicals releasing Pb and P into solution, thus, creating favorable conditions for the precipitation of pyromorphite. Pyromorphite formed early in the extraction sequence would tend to pass through the extraction procedure to the residual fraction customarily attributed to insoluble phases such as pyromorphite and galena. As a result, a false assumption is implied that residual forms of Pb dominate in the soil prior to the sequential extraction procedure but, in fact, are probably formed during the extraction process for these perturbed systems.

Previous studies have interpreted the term re-sorption to include complexation, precipitation, coprecipitation and adsorption (*4*). The work presented here refines the phenomenon of re-sorption by focusing on precipitation of Pb during the selective extraction process. The objectives of the experiments were to investigate the potential formation of pyromorphite during sequential extraction steps and examine the effects of the presence of P on the distribution of Pb in the operationally defined fractions. These experiments aim to illustrate that sequential extractions redistribute Pb from more soluble forms to residual phases (usually considered more recalcitrant forms of metal) by precipitation processes. If this hypothesis is correct, sequential

extraction experiments on Pb-contaminated soils with significant sources of potentially soluble phosphorus (i.e. granular fertilizer, runoff sources, etc.) will tend to overestimate the overall stability of the Pb in the system.

MATERIALS AND METHODS

Sample Preparation. Samples were prepared from the <250 µm size fraction of Pb compounds and a cleaned quartz sand (U.S. Silica, Ottawa, IL) at a concentration of 2000 mg Pb/kg sand to represent a contaminated soil. In one experiment, the Pb spiked solid matrices contained calcium phosphate amendments while the other experiment did not. For XRD studies, amorphous silica from the Huber Corporation (Cleveland, OH) was used to eliminate the intrusive XRD pattern of quartz in order to observe pyromorphite emergence. XAFS studies were conducted at Beamline X-11A of the National Synchrotron Light Source, Brookhaven National Lab. The Pb mineral/chemical samples include: 1) Pb-acetate (ACS Certified, Fisher Scientific, Fair Lawn, NJ), 2) $PbSO_4$ (anglesite) (Aldrich Chemical Company, Milwaukee, WI), 3) $PbCO_3$ (cerussite) (Aldrich Chemical Company, Milwaukee, WI), 4) PbS (galena) (GFS Chemicals, Columbus, OH), and 5) $Pb_5(PO_4)_3Cl$ (pyromorphite, aged 1 month) from a previous study. These materials were examined individually, in one-to-one combinations, and in a mixture of all materials in equal amounts both in the presence and absence of a phosphorus amendment, calcium phosphate (ACS Certified, Fisher Scientific, Fair Lawn, NJ). For the phosphate containing samples, 1000 mg/kg calcium phosphate amendment was spiked into the samples just prior to starting the extraction procedure and this concentration of P was selected to mimic a well-fertilized agricultural soil.

Sequential Extraction Procedure. The procedure described by Tessier et al. (*1*) was employed with slight modifications.

> **Fraction 1 - Exchangeable:** The samples were extracted at room temperature for 1 h with 8 mL of magnesium chloride solution (1 M $MgCl_2$, pH 7.0) with continuous agitation.
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> **Fraction 2 - Bound to Carbonates:** The residue from Fraction 1 was leached at room temperature with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained and the time necessary for complete extraction was evaluated based on Pb carbonate prior to experimental trials and was determined to be 3 hours.
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> **Fraction 3 - Bound to Iron, Manganese Oxides:** The residue from Fraction 2 was extracted with 20 mL of 0.04 M $NH_2OH{\bullet}HCL$ in 25% (v/v) HOAc. This fraction experiment was performed at 96 ± 3 °C with occasional agitation for 6 hours.
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> **Fraction 4 - Bound to Organic Matter:** To the residue from Fraction 3, 20 mL of 7 M NaOCl (adjusted to pH 8.5 with HCl) was added, and the mixture was heated to 90 ± 2 °C for 2 hours with occasional agitation. After centrifuge separation, a second 20-mL aliquot of NaOCl (adjusted to pH 8.5 with HCl) was then added and the sample was heated again to 90 ± 2 °C for 2 hours with intermittent agitation.
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> **Fraction 5 – Residual:** The residue from Fraction 4 was digested with concentrated HNO_3 in a microwave digester according to EPA method 3051 and diluted 50:1 with 18 mΩ DI water.

After the prescribed time interval for each extraction (fractions 1-4), samples were and the supernatant filtered through a 0.45 µm filter. The remaining solid sample was washed twice with Millipore DI water before continuing with the next extraction step. For fraction 5, the final dilution was filtered through a 0.45 µm filter and stored at 4^0C. Once an entire sequential extraction replication was completed, the samples were analyzed for Pb by inductively coupled argon plasma spectrometry (ICAP) according to EPA Method 6010B.

RESULTS AND DISCUSSION

The expected solubility of the Pb compounds used in this study predicted the following trend of Pb-acetate > $PbSO_4$ > $PbCO_3$ > PbS ˜ pyromorphite based on known solubility data. Likewise, we anticipated the steps (fractions) of the sequential extraction procedure to possess varying degrees to induce solid-phase solubility as exchangeable (F1) < carbonate (F2) < Fe/Mn oxide (F3) < organic matter (F4) < residual (F5). These assumptions were confirmed in Figure 1 for the sequential extraction of the Pb-spiked sand samples without calcium phosphate to examine the fractionation of just the Pb minerals/compounds with recoveries from 91% to 103%. The Fe/Mn oxide fraction step had some Pb extracted primarily from the pyromorphite and galena samples and could be as a result of either oxidative dissolution of galena or desorption of exterior crystal metal sites from reaction with the extraction solution. In terms of the pure compounds individually, Pb-acetate and anglesite were predominantly extracted in the exchangeable phase and cerrusite was primarily removed in the carbonate step. The majority of pyromorphite and galena was removed in the residual extraction step, as expected, but 33% to 40% of the extracted Pb is distributed among the exchangeable, carbonate, and Fe/Mn oxide fractions indicating that relatively stable minerals that would normally be associated with residual phases can undergo desorption/dissolution in the milder extraction solutions. The fact that Pb was removed during the Fe/Mn oxide step is a good indication that extraction procedures are not as well defined as some may hope since Fe/Mn oxides were not present in our samples. The Pb-spiked samples without calcium phosphate in one-on-one combinations (Figure 1) show that they essentially behaved additively based on each individual component. For example, the Pb-acetate-anglesite sample (containing equal amounts of both components that were individually extracted in the exchangeable fraction), was 94% extracted in the exchangeable phase. The anglesite-galena combination also showed scaled attributes from each mineral as examined separately. These trends were observable throughout the data shown in Figure 1. The mixture of all the Pb minerals/compounds exhibited amounts of extractable Pb that correlated well to the sum of the individual extraction experiments. In short, the extraction sequence performed suitably for Pb in these laboratory created samples.

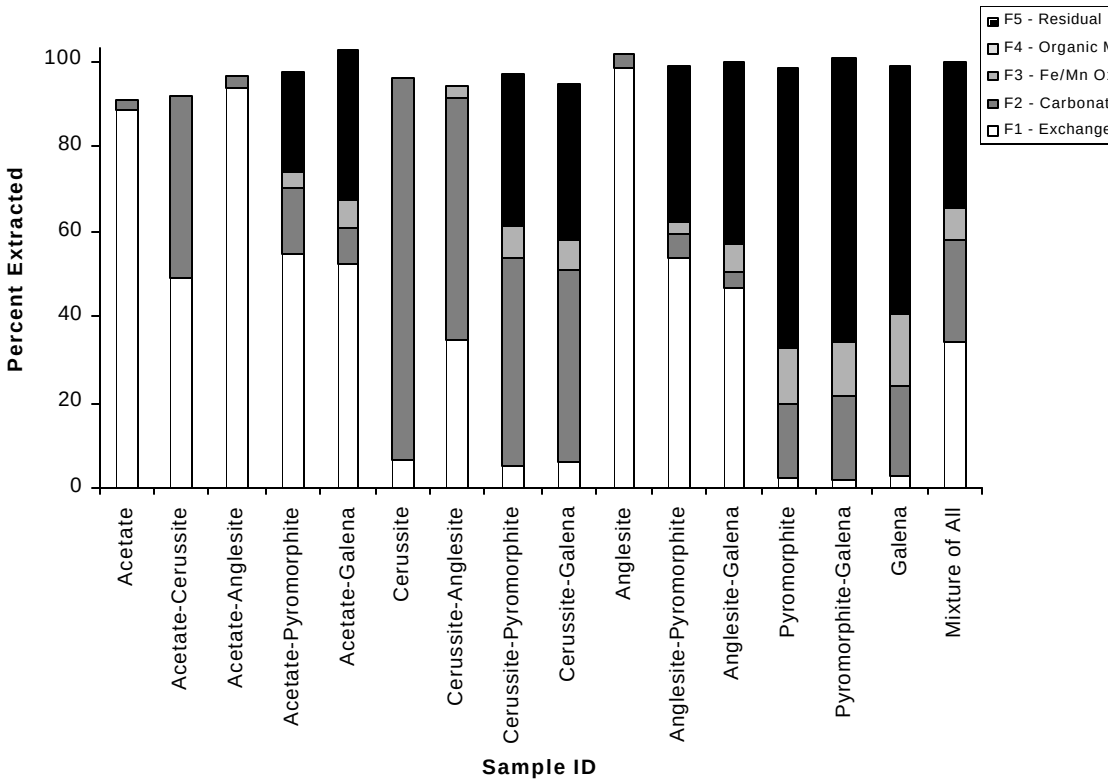

Figure 1. Sequential extraction results of 2000 ppm Pb-spiked samples.

Figure 2 shows the results of the sequential extraction procedure for the Pb-spiked samples with the calcium phosphate amendment. Total Pb recovery ranged from 90% to 103%. These results are drastically different than those present in Figure 1 for the same samples sequentially extracted without phosphate. First, the presence of phosphate totally eliminates any indication of an exchangeable phase. Furthermore, Pb observed in the residual phase increased dramatically. This was the result of Pb extracted during the exchangeable step reacting with P from the calcium phosphate amendment to form pyromorphite (Figure 3). The other combinations exhibited in Figure 2 (carbonate-cerrusite, Fe/Mn oxide-pyromorphite, and residual fractions-galena, pyromorphite) show an increased concentration of Pb in the residual phase with the P amendment than the samples without P (Figure 1). With P present, acetate and anglesite also had Pb concentrations increase in the carbonate fraction, cerrusite showed a decrease in Pb extracted in the carbonate step, and Pb in the carbonate fraction remained roughly the same for galena and pyromorphite. For the Fe/Mn oxide fraction, Pb increased drastically for the acetate, anglesite, and cerrusite samples and slightly decreased in the galena and pyromorphite samples. Every sample observed an increase in residual Pb. It should be noted that increases in residual phase Pb occurred for pyromorphite (9% increase) and galena (14% increase) with the P amendment. This shift towards residual Pb was due to the formation of pyromorphite as confirmed by XAFS (Figure 3) and XRD analyses.

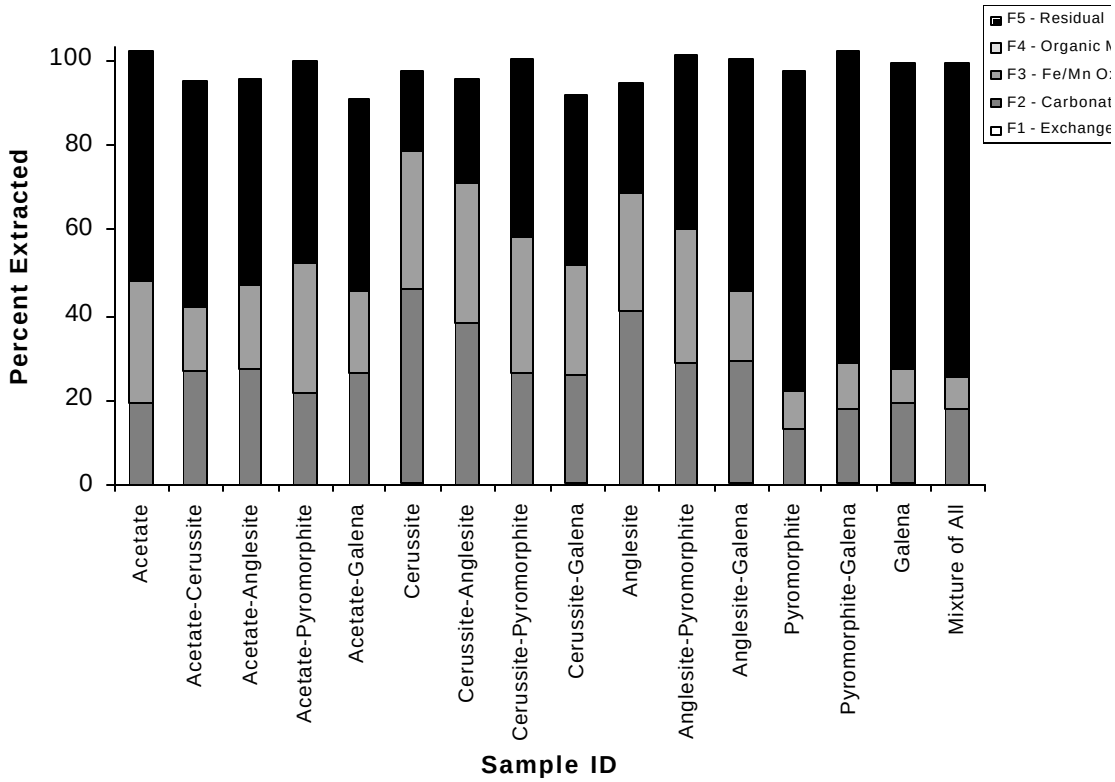

Figure 2. Sequential extraction results of 2000 ppm Pb-spiked samples amended with 1000 ppm of calcium phosphate.

The aim of this research is to alert users of sequential extraction procedures to be aware of precipitation processes as well as re-sorption phenomena. The research presented here shows quite clearly that the results of a sequential extraction on identical materials is severely altered by the presence of P (as either a fertilizer input or soil amendment). Phosphorus chemistry is quite complex and P is ubiquitous in soils as well as sediments. Application of sequential extraction procedures for Pb, Cd, Zn, Co, Cr and Ni contaminated soil and sediment samples, especially for those with large sources of P, should be avoided. Extreme caution should be employed

in interpreting data from the sequential extraction of Pb from any soil or sediment. Ideally, one would support and verify sequential extraction data with other speciation techniques (e.g. molecular-level spectroscopic techniques such as X-ray absorption fine structure and X-ray diffraction spectroscopies). This would allow the researcher to examine the sample in-situ to identify metal species without physicochemical alteration of neither the target analyte nor constituents, such as P, that will react with the target analyte.

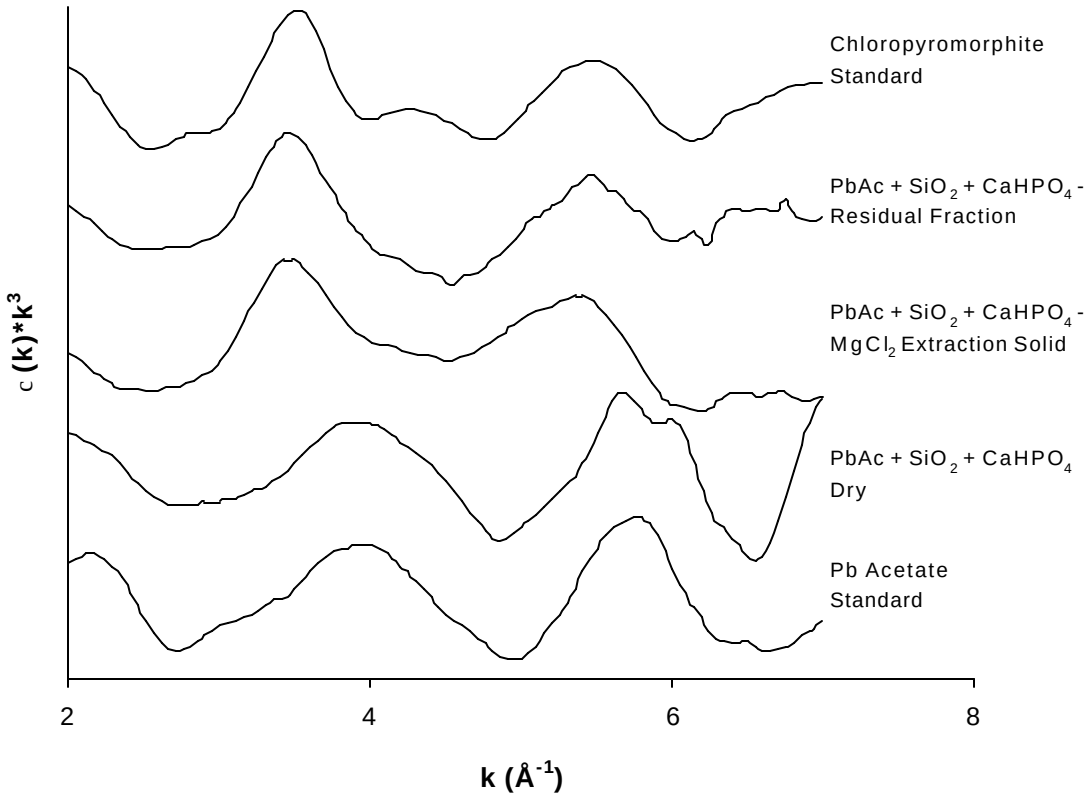

Figure 3. Normalized $Pb_{(LIII)}$-EXAFS k^3-weighted chi (χ) functions of Pb acetate sequential extraction and reference (chloropyromorphite and Pb acetate) samples.

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