SPECTROSCOPIC AND CHEMICAL EVALUATION OF IN SITU CHEMICAL IMMOBILIZATION FOR THE REMEDIATION OF HEAVY METAL CONTAMINATED SOILS

By

LISA L. PHEGLEY

Bachelor of Science

Cameron University

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Thesis Approved:

Thesis Advisor

Warren T Ford

Allen Apblett

Wayne B. Powell

Dean of the Graduate College

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CHAPTER I

INTRODUCTION

A. Background

Contamination of soils with heavy metals (i.e. Cd, Cu, Hg, Ni, Pb, Zn) is a wide spread environmental problem. In a 1993 publication, the U.S. EPA determined that the greatest need for new remediation technologies in the Superfund Program was for metals in soil.[1] Elevated soil metal levels have resulted from a variety of anthropogenic inputs including: metal ore mining and smelting, industrial discharge, automobile emissions and agricultural practices. Concern due to elevated metal levels results from the unfavorable environmental impacts they cause. In general, the concerns are human health, animal health, phytotoxicity, as well as adverse impacts on soil productivity and water quality.[2]

Remediation of metal contaminated soils offers unique challenges. Because metals cannot be degraded, remediation is limited to two main options: removal of the metals or transformation of the metals to less bioavailable or less mobile forms.[3] Metal levels can be reduced by removal and disposal of the contaminated soil or by leaching the metals out of the soil. Metal bioavailability and mobility can be reduced by decreasing the metal solubility through precipitation or sorption reactions.

Currently, excavation and transport of heavy metal contaminated soil is the standard remediation technique.[4] This technique requires removing the contaminated soil, treating it, and disposing of it away from the area of contamination. Removal technologies are costly to practice, destructive to the sites from which the wastes are removed, require disposal of large volumes of metal contaminated soil, and can hardly be viewed as a permanent solution.[5]

Current clean-up action levels are based on the total heavy-metal content of the soil and do not take into consideration the characteristics of the heavy metals within the individual soil matrix. The total metal content of a material may provide a preliminary view of its potential for environmental hazard; however, it is a poor predictor of the risk associated with the metal contaminant because it provides little information on the processes and dynamics which determine the bioavailability and mobility of the metals. Recently, it has been recognized that the bioavailability and mobility of metals at contaminated sites is dependent on the chemical form of the metal.[6] Bioavailability is defined as the possibility that a chemical in the environment will cause an effect to a specific organism.[2] In soils, metals are dissolved in soil solution, held on inorganic soil constituents through adsorption or ion exchange, complexed with soil organic matter, and precipitated as pure or mixed solids.[2] With this in mind, two points become apparent. First, the distribution of metals among these various forms presents a more accurate assessment of the risk associated with a metal contaminated soil than the total metal content. Using metal speciation information to make remediation decisions should lead to more cost-effective solutions by allowing limited clean-up funds to be focused on the most dangerous sites. Second, remediation methods using in situ treatment strategies to convert the metal to less soluble and therefore less bioavailable forms may provide an effective and cost efficient alternative to restore soil productivity and quality.

Soils are particularly important in the attenuation of heavy metals in the environment because they act to reduce heavy metal solubility through interactions with the mineral and humic constituents they contain. Immobilization of metals by adsorption, ion exchange, complexation or precipitation can reduce metal solubility and prevent movement through the environment. When a soil becomes contaminated, the excess metal saturates the soils ability to hold metals relatively insoluble, leaving the excess to be held in more soluble forms. Addition of natural or synthetic chemical additives similar to the phases present in soil, would enhance the soils metal immobilizing capacity without producing any detrimental by-products. The chemicals used for immobilization may also increase soil fertility and eliminate toxicities to plants and soil organisms. Growing a plant cover physically holds the soil and their contaminants in place, minimizing soil erosion and off site movement of the soil.

In-situ chemical immobilization is a promising technology for remediating heavy metal contaminated soils while leaving the soil and metal in place. In-situ chemical immobilization involves adding a substance (an amendment) to the soil which chemically stabilizes the metal contaminants through the formation of metal phases with reduced solubilites. Chemical stabilization can involve a continuum of reaction types, from sorption of metals to solid surfaces, through the formation of new surface metal precipitates to the formation of discrete heterogeneous or homogeneous metal precipitates.[2,7]

Currently, many chemicals are being evaluated for their ability to immobilize heavy metals in situ.[7] These include: lime,[8-10] iron and manganese oxides,[8,9] zeolites,[9,11] phosphates,[7,12-13] biosolids,[8,15,16] and manure.[8] These amendments have been evaluated on soils contaminated from pesticides,[12] paint spills,[13] battery recycling,[7] and smelter waste.[8,9,15,16] A variety of techniques are currently being used to evaluate the effectiveness of these treatments. These include single[7] and sequential extraction,[14,15,16] plant growth and uptake,[8,9,15,16] microbial activity,[17] and spectroscopic techniques including XRD and SEM.[12, 13]

B. Purpose of Study

This study evaluated the ability of six in situ chemical immobilization treatments to remediate smelter contaminated soils. The approach taken to characterize smelter contaminated soils and evaluate the effectiveness of soil amendments for in situ immobilization of Cd, Pb and Zn in those soils involved a suite of chemical and spectroscopic methods. Each of these methods provided specific and complementary information. Sequential extraction provided a tool to evaluate the effectiveness of the amendments by monitoring changes in metal extractability. Spectroscopic techniques were used to identify new metal containing phases in the amended soils which could be used to explain the reduced metal extractabilities. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) provided information on both crystalline and amorphous phases present in the soils, amendments, and soil-amendment mixtures. X-ray powder diffraction (XRD) provided information on bulk crystalline phase minerals. Solid state nuclear magnetic resonance spectroscopy (NMR) enabled the determination of the chemical environment of phosphorous and protons in the soils and amendments.

As the study evolved, three principal objectives developed. The initial objective was to compare the effectiveness of phosphate, organic, and/or alkaline amendments for immobilizing Cd, Pb and Zn in contaminated soils using sequential extraction. A second objective was the evaluation of three phosphate amendments of varying solubilities for the immobilization of Cd, Pb, and Zn in soils using sequential extraction. The final objective was the application of spectroscopic techniques, DRIFTS, XRD, and NMR, to identify the formation of new metal containing phases in the treated soils. In addition, to support the principal objectives two underlying assumptions had to be tested. The first was that the proposed immobilized phases extracted in the anticipated step of the sequential extraction scheme. The second was to establish that spectroscopy could be applied to characterize these soil-amendment systems.

C. Overview of Research

In Chapter 2, the experimental details will be presented. This chapter includes detailed descriptions of the process used to evaluate the amendments, instrumentation and protocols used for data collection, and methods used to synthesize model compounds. Chapter 3 will provide an overview of the soils and amendments used in this study. The chemical and physical properties of the soils and amendments will be described and spectroscopic characterization of the materials will be presented. Chapter 4 provides a brief overview of the sequential extraction method used to evaluate the amendment effectiveness. Also included in Chapter 4 are the results for the sequential extraction of model compounds used to confirm the extractability of the proposed immobilized forms of the metals. Chapter 5 will present the sequential extraction results for both remediation studies. Chapter 6 will focus on the results of the spectroscopic studies of the remediated soils. Chapter 7 summarizes the results of the sequential extraction and spectroscopic studies. In addition, the conclusions of the study and suggestions for future work will also be presented in Chapter 7.

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CHAPTER II

EXPERIMENTAL

A. General Information

Chemicals used in these experiments were purchased from Aldrich Chemical Co., unless otherwise noted, and were of reagent grade and required no further purification before use. Hydrochloric (HCl) and nitric (HNO_3) acids were of trace metal grade or better. All water used was purified and deionized (to 18 MΩ) using a Barnstead E-Pure purification system.

B. Batch Remediation Process

1. Field Moisture Capacity

The three soils used in these experiments were collected from sites contaminated by zinc smelting operations in Oklahoma [Bartlesville (B4), Blackwell (BW), Henryetta (H12)]. The soils were air-dried, sieved to pass 2 mm, and stored in plastic tubs until use. Four chemical immobilization amendments were examined in these experiments: 1. North Carolina rock phosphate (RP) obtained from PCS Sales, Skokie, IL; 2. municipal biosolid-alkaline admixture blend marketed as N-Viro soil (NV) obtained from N-Viro Soil, Columbus, OH; 3. anaerobically digested municipal biosolid (SS) obtained from the city of Tulsa; and 4. lime stabilized municipal biosolid (LS) obtained from Oklahoma City.

Three hundred grams of each amendment were added to 3 kg of each soil contained in plastic tubs (loading of 100 g of amendment per 1 kg of soil).[1] Triplicate 1 kg subsamples of each amended soil and 1 kg of non-amended soil (control) were placed in plastic trays. After adding water to the soils to obtain an optimal moisture content of 25 %[2] by weight, the soils were stored at 27 °C for 90 days in a Percival temperature controlled room. During the remediation process, water was added to maintain soil moisture and the soils were mixed by hand at weekly intervals. The soil pH was measured at the completion of the remediation process with a Corning Model 350 pH/ion meter equipped with a Corning flat surface combination pH electrode. To measure soil pH, a 1:2 soil to 0.01 M calcium chloride ($CaCl_2$) slurry method was chosen.[3] Ten milligrams of soil were mixed with 20 mL 0.01 M $CaCl_2$ and stirred for 15 min. The suspension was allowed to settle for 15 min, and the pH of the clear supernatant was measured. At the completion of the remediation process, the soils were air dried and stored in plastic tubs until further chemical and spectroscopic analyses.

2. Slurry

Four soils were chosen for the slurry study: two soils from the previous study [BW(b), H12(b)] and two soils collected from sites in the Western United States which were heavily contaminated with lead (Pb) as a result of arsenic smelting activities (S5, C1). The soils were air-dried, sieved to pass 2 mm, further sieved to pass 250 µm, and stored in plastic tubs until use. Three chemical immobilization amendments were examined in these experiments: 1. North Carolina rock phosphate (RP) from the previous study, 2. hydroxyapatite ($Ca_5(PO_4)_3OH$) (HA), and 3. calcium monohydrogen phosphate ($CaHPO_4$) (CaP) obtained from Fisher.

Each amendment was thoroughly incorporated into three 100 g samples of each soil contained in acid rinsed 250 mL Nalgene polypropylene bottles, at a loading of 2 % phosphorous (P) by weight. Two percent P loading corresponds to a 15.3, 10.8, and 8.8 % by weight loading of RP, HA, and CaP, respectively. Three 100 g samples of each soil were not amended and used as controls. Water was added to each soil sample to obtain a 1:1 soil to H_2O slurry. The soils were capped, shaken intermittently, end-on-end at 150 cycles/min (low setting) using two Eberbach reciprocating shakers, and maintained at room temperature during the two week remediation process. The soil pH was measured at the completion of the remediation process. The soil pH was measured directly from the 1:1 soil to H_2O slurry[3] by allowing the suspension to settle for 15 min and measuring the pH of the clear supernatant, using the pH meter described above. After the remediation process was completed, the samples were opened, dried in a 60 °C oven for 4 days, capped and stored in the Nalgene bottles for further chemical and spectroscopic analyses.

C. Sequential Extraction[2]

Triplicate 1-2 g samples of soil or model compounds were placed in acid rinsed 50 ml polycarbonate centrifuge tubes and 20 mL of 0.5 M calcium nitrate tetrahydrate ($Ca(NO_3)_2 \bullet 4H_2O$) was added. Stoppered tubes were shaken for 16 hr using the reciprocating shaker described above. The samples were then centrifuged at 12,000 rpm for 12 min using a Sorval Instruments model RC5C centrifuge. The supernatants were decanted and filtered through 0.45 μm membrane filters, acidified with 0.5 mL concentrated HCl, and stored at 4 °C until analysis. Next, 20 mL of 1 M sodium acetate

(NaOAc), adjusted to pH 5 with concentrated HCl, was added to the residue in the centrifuge tubes and shaken for 5 hr. After extraction, the resulting supernatants were prepared for analysis as above. Next, 20 mL of 0.1 M disodium ethylenediamine tetraacetate (Na_2EDTA), adjusted to pH 7 with sodium hydroxide (NaOH), was added to the residue in the centrifuge tubes and shaken for 6 hr. Resulting supernatants were treated as previously, but not acidified with HCl as acidification causes precipitation of EDTA salts. For the final step of the procedure, 20 ml of 4 M HNO_3 was added to the residue in the tubes and shaken for 16 hr at 80 °C in a Fisher shaking water bath model 129. These extracts were prepared as above with the exception of the HCl addition. Metals analyses were conducted by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

D. Instrumentation

1. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

The concentrations of metal ions in solution were determined using a Fisons Maxim ICP-AES. Analytical standards (1000 µg/mL Pb and Cd, and 10,000 µg/mL Zn) were obtained from Radian International. Calibration curves were prepared over a linear concentration range of 0 to 50 ppm for Cd, 0 to 100 ppm for Pb, and 0 to 1,000 ppm for Zn. The calibration standards were prepared using known concentrations of the analytical standards in each particular extracting solution studied, (i.e. matrix matching was used for all experiments). The emission lines monitored were 226.500 nm for Cd, 220.355 nm for Pb, and 206.198 nm for Zn. Sample introduction into an argon plasma was accomplished using a concentric nebulizer. The $Ca(NO_3)_2$ extracts were introduced with a modified Babbington-type nebulizer (V-groove), due to the high salt content. Between samples, dilute HNO_3 rinses were used for all extracts except Na_2EDTA, for which a 0.01 M NaOH rinse was used. The calibration of the instrument was verified after every tenth sample by running blank, low, and high standards.

2. Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS)

DRIFTS spectra were recorded on a Nicolet Magna 750 infrared spectrometer equipped with a Spectra Tech "Collector" diffuse reflectance accessory from 4000 to 400 cm^{-1}, at 4 cm^{-1} resolution over 32 to 128 scans. Samples were ground using a mortar and pestle or Wig-L-Bug amalgamator model 3110-3A (Crescent Dental MFG Co.). Samples were run diluted to 5 % by weight with dried KBr to prevent the Reststrauhlen effect in the 1000 cm^{-1} region.[4] Powdered samples were hand packed in 13 mm round sample cups and the upper surface was smoothed with a spatula. The background was KBr, and the samples were purged with dry air or N_2 during data collection. The DRIFTS spectra were analyzed using the computer program Omnic, provided by Nicolet. All spectra were background corrected to normalize the data for spectral subtractions. The $CO_{2(g)}$ band at 2360 cm^{-1} has been removed from all the DRIFTS spectra for clarity.

3. Solid State Nuclear Magnetic Resonance (NMR)

Solid state NMR measurements were carried out on a Chemagnetics CMX-II 301 MHz (7.07T) spectrometer. Chemagnetics 5 mm CMP300P2-3035 and 7.5 mm 300VXP-144 double resonance (H-X) magic-angle spinning probes were used for data collection. Samples were packed in pencil-type rotors made of zirconia with vespel drive tips, and spun at speeds of 5 KHz using dry air. Both single pulse and cross-polarization[5] experiments were conducted. The spectra were collected at resonance frequencies of 301.0, 121.8, and 75.8 MHz for ^{1}H, ^{31}P, and ^{13}C, respectively. Chemical shifts were reported in ppm relative to 85% phosphoric acid for ^{31}P and tetramethylsilane (TMS) for ^{13}C and ^{1}H. The NMR spectra were analyzed using the Chemagnetics program, Spinsight. Specific experimental details, such as pulse delays and applied line broadening, will be presented in the discussion or figure captions describing the spectra. Spinning sidebands will be denoted with an asterisk in the figures.

4. Powder X-ray Diffraction (XRD)

All XRD analyses were conducted on a Philips X-ray diffractometer using Cu Kα radiation at 40 kV and 40 mA. Samples were ground using a mortar and pestle and run as randomly oriented sample mounts. Measurements were made using a step scanning technique with a fixed time of 0.5 or 1.0 s per $0.02^{\circ}\,2\theta$. The XRD patterns were obtained from 2 to $50^{\circ}\,2\theta$.

E. Model Compounds

1. Cadmium Montmorillonite[6,7]

Montmorillonite KSF clay was first Na exchanged using a modified salt-acid treatment.[5] Initially, a 5% (wt/vol) suspension using 2 M NaCl and 100 g clay was prepared and stirred for 15 min. The suspension was allowed to settle and the supernatant decanted. The clay was resuspended in 2 M NaCl to obtain a 1 % suspension, treated with sufficient HCl to make a 0.1 M solution and stirred for 0.5 hr.

The solid suspension was separated by centrifuging and decanting. Finally, the clay was resuspended in 2 M NaCl to prepare a 5 % suspension and stirred for 0.5 hr. The solid solution was separated as described above, the clay was then washed several times with H_2O and transferred to dialysis tubing (Spectra/Por 7, MWCO 1,000). The dialysis tubing was suspended in a large beaker of H_2O which was periodically replenished until no Cl^- ions were detected by the $AgNO_3$ test. The clay was removed from the dialysis tubing and added to sufficient H_2O to make a 1.5 % suspension.

Next, the clay was cation exchanged using an Amberlite IR-120(plus) resin, sodium form, with an exchange capacity of 1.9 meq/g. The resin was converted to the H form by treating with a sufficient volume of 0.5 M HCl for 1 hr, filtering, and rinsing with H_2O until no Cl^- ions were detected by the $AgNO_3$ test. The 1.5 % Na montmorillonite suspension was then treated with four times the amount of resin required to convert the clay to the H form, assuming a cation exchange capacity (CEC) of 1.0 meq/g for the clay. The clay-resin suspension was stirred for 1 hr at room temperature. The clay was separated from the resin using a 250 μm sieve.

The H clay was converted to the cadmium (Cd) form[6] by mixing the 1.5 % H montmorillonite suspension with sufficient 0.3 M cadmium chloride ($CdCl_2$) to obtain a dopant levels of 0.9 mmol Cd/g clay. The Cd doped suspension was subdivided and the pH adjusted to 4 and 10 with NaOH or HNO_3. The suspensions were stirred for 15 hrs, centrifuged and the supernatant decanted. The samples were air dried, ground by hand with a mortar and pestle, and stored in airtight containers for further analyses. The Cd content of the clays were determined by graphite furnace atomic absorption spectroscopy.

2. Goethite, (α-FeOOH): Neat, Coprecipitated, and Sorbed[8,9]

Goethite was prepared by adding 200 mL 2.5 M KOH to 50 g $Fe(NO_3)_3 \cdot 9\ H_2O$ in 825 mL H_2O while stirring to give a final pH of 12. The red precipitate formed turned yellow after aging for 24 hr in a 60 °C oven. The supernatant was decanted and the precipitate rinsed by repeated centrifuging with H_2O. The sample was dried in a 60 °C oven and stored in an air tight container for further analysis. XRD confirmed that the synthesized material was α-FeOOH, with no other detectable crystalline impurities.

Coprecipitated goethite samples were prepared by the method described above with the addition of Pb^{+2} or Cd^{+2} to the $Fe(NO_3)_3 \cdot 9\ H_2O$ solution at a ratio of 100:1 Fe^{+3} to M^{+2}. Specifically, 25 g $Fe(NO_3)_3 \cdot 9\ H_2O$ and 0.215 g $Pb(NO_3)_2$ or 0.198 g $Cd(NO_3)_2 \cdot 4\ H_2O$ were dissolved in 400 mL H_2O. Surface sorbed goethite samples were prepared by mixing approximately 3 g of wet FeOOH with 30 mL of 9×10^{-5} M $Pb(NO_3)_2$ or $Cd(NO_3)_2 \cdot 4H_2O$. The pH of the suspension was adjusted to 7 with HNO_3 and stirred for 72 hr. These samples were isolated and stored as described above.

3. Lead and Cadmium Phosphates, ($Pb_3(PO_4)_2$, $Cd_3(PO_4)_2$)[10,11]

$$3\ XCl_2 + 2\ Na_2HPO_4 \rightarrow X_3(PO_4)_2 + 4\ NaCl + 2\ HCl \quad (X=Pb \text{ or } Cd)$$

Lead and cadmium phosphates were precipitated from a solution prepared by adding 100 mL of 0.1 M Na_2HPO_4 to 1 L of 0.0185 M $PbCl_2$ or 200 mL of 0.2 M $CdCl_2$, respectively. The precipitates were allowed to settle and the supernatants removed by decanting. The precipitates were filtered and rinsed four times with H_2O. The solid samples were transferred to dialysis tubing and stored in large beakers of H_2O which were periodically replaced until no Cl^- ions could be detected using the $AgNO_3$ test. The samples were removed from the dialysis tubing and dried in an 80 °C oven overnight. These procedures resulted in metal phosphate yields of 71 % (2.910 g) and 61 % (1.560 g) based on the metal nitrate added for Pb and Cd, respectively. The identity of these samples were confirmed to be Pb and Cd phosphates through characterization by DRIFTS, solid state NMR and XRD (Pb only).

4. Cadmium Phthalate, $(Cd(C_8H_4O_4) \bullet H_2O)$[12]

To a stirred solution (1 L) of 5×10^{-3} M phthalic acid and 5×10^{-3} M $Cd(NO_3)_2 \bullet 4 H_2O$ (pH=2.6), concentrated NaOH (6 M) was added drop wise to obtain a final solution with a pH of 7. The clear solution was slowly evaporated at room temperature for one week. Colorless crystals of Cd phthalate precipitated and were removed from the bulk solution. The procedure resulted in a 41 % yield of Cd phthalate (1.111g), based on the initial phthalic acid added. DRIFTS and sequential extraction experiments were used to confirm the identity of this material.

5. Metal Humates[13,14]

Solid Pb and Cd humate complexes were prepared by two procedures, sorption (using insoluble humic acid) and precipitation (using soluble humic acid), assuming a 350 meq/100 g cation exchange capacity (CEC) for humic acid. Approximately twice the stoichiometric amount of metal ion required to completely exchange the humic acid was used in each preparation. For the sorption experiments, 3 g of humic acid (Fluka) were added to 40 mL of 0.3 M $Pb(NO_3)_2$ or 0.21 M $Cd(NO_3)_2 \bullet 4 H_2O$ and stirred for 62 hr. For the precipitation experiments, 4 g of humic acid, sodium salt (Acros), were added to 50 mL 0.3 M $Pb(NO_3)_2$ or 0.21 M $Cd(NO_3)_2 \bullet 4 H_2O$ and stirred for 46 hr. The sodium humate samples were then precipitated by acidifying the solutions with concentrated HCl, until the pH dropped below 2. The solid samples were separated by centrifuging, rinsed four times with H_2O, dried at 115 °C in an oven, and stored in airtight containers for further analysis. These samples were confirmed to be exchanged with Cd and Pb by DRIFTS and sequential extraction.

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CHAPTER III

SURVEY OF SOILS AND AMENDMENTS

A. Introduction

The purpose of the research described in this chapter is to provide a characterization of the soils and amendments used in this study and to investigate the feasibility of using spectroscopy to study soil-amendment interactions. In section B, the chemical and spectroscopic characterization of the soils used in this study will be presented. In section C, the chemical and spectroscopic characterization of the amendments will be presented. Experimental details for analyses conducted outside of this study will be presented in the discussion of the soil and amendment properties. The instrumentation and protocols used for spectroscopic data collection were presented in Chapter II.

B. Soils

Five different soils were investigated in this study. The soils were selected for their degree of Pb and Zn contamination. Surface (0 – 15 cm depth) samples of the soils were collected from three sites adjacent to zinc smelters in Oklahoma; Bartlesville (B4), Blackwell (BW), and Henryetta (H12) and two sites adjacent to arsenic smelters in a Western state; S5 and C1. All soils were air-dried, lightly crushed and sieved to pass 2 mm. The U.S. Department of Agriculture (USDA) defines soil as having particle sizes smaller than 2 mm.[1] For the greenhouse incubation study, the $\leq$ 2 mm fractions of the soil were used. For the slurry incubation study, the soils were further sieved, and the $\leq$

250 μm fractions were used. This size fraction was chosen because the smaller particle sizes generally contain higher metal contents and have been determined to be in the particle size range most likely to become ingested.[2] The ≤ 250 μm fractions of BW and H12 soils are denoted with a (b).

1. Chemical and Physical Properties

The physical and chemical properties of the soils used in this research were characterized using standard methods.[3,7-11] The chemical properties included soil pH, organic carbon content, total metal content, electrical conductivity and total iron content. The physical properties included a textural analysis. The results of the soil characterization of are summarized in Table 1.

Total metal content was considered to be the metals extracted by the USEPA Method 3050B.[3] This method employs a three step heated digestion with HNO_3, H_2O_2 and H_2SO_4. If 3050B data were not available, the sum of the four fractions from the sequential extraction analyses was used as an estimate of total metal content. Other authors have reported a close agreement between the sum of the sequential extracts and the total metal extracted by acid digestion.[4,5] Normal metal levels in non-contaminated soils are presented in the Table 2.[6] Heavy metal contents in all the smelter site soils greatly exceed "normal " levels and the soils are described as contaminated.

Soil pH was measured in 1:2 soil to 0.01 M $CaCl_2$ slurry.[7] Typically, soils are neutral to moderately acidic in pH (5.5 to 7.5). With the exception of the C1 soil, which would be categorized as acidic, all soils in this study would be categorized as neutral.

Soil electrical conductivity (EC) was measured using a 1:2 soil to water saturation extract.[8] The soil EC is related to the soluble salt content or salinity of the soil.

Electrical conductivity values > 4 dSm^{-1} (decisiemens per meter) indicate a saline or salt affected soil. None of the soils in this study were salt affected.

The organic carbon (OC) content of the soils was determined by dry combustion.[9] A 25 g sub-sample of each soil was analyzed by dry combustion in a Carlo-Erba NA 1500 high temperature induction furnace. Typical soils contain 2 % OC by weight (Table 2). Excessively high % OC values determined for the H12 and B4 soils were due to the presence of coal in these samples.[4]

Texture analyses were performed using the pipette method.[10] Textural analyses is a measure of the size distribution of the individual particles in a soil sample. Particles in the size range < 2000 to 50 μm are defined as sand, 50 to 2 μm as silt, and < 2 μm as clay.

The iron contents of the soils were determined by X-ray fluorescence.[11] Typical soil Fe contents are 3 % (Table 2). The high Fe contents of the S5 and C1 soils resulted from the Fe-containing ores used at the smelter sites.

2. Spectroscopic Characterization of Soils

Spectroscopic analyses were conducted to characterize the soils used in this study. In addition, it was necessary to establish the feasibility of using spectroscopic techniques to characterize the soils. Spectroscopic techniques are ideal for the analyses and characterization of soils because they don not require disturbing the soil matrix. The soils were characterized by XRD, DRIFTS, and NMR. The results are presented herein.

a. XRD

XRD is one of the most useful methods for the analyses of the crystalline mineral components in soils and has contributed more to the mineralogical characterization of soils than any other single method of analysis.[12] XRD analyses of whole soils provides information on the major crystalline components present without the need to alter the soil matrix.

XRD analyses were performed on the BW, B4, H12, S5 and C1 soils. The powder patterns for the soils are presented in Figures 1 through 6. Identification of crystalline mineral phases was based on comparisons with standard powder patterns archived by the Joint Committee on Powder Diffraction Standards (JCPDS).[13] Evaluation of the soil XRD patterns revealed that quartz (SiO_2) was the major crystalline component in each soil. The powder pattern of each soil contained peaks at 20.9, 26.8, 36.7, 39.6, 40.4 and 42.5° 2θ (d-spacings 4.2, 3.3, 2.4, 2.3, 2.2, and 2.1 Å) indicative of the presence of quartz.

The B4 soil (Figure 3) also contained calcite ($CaCO_3$), as indicated by the peaks in the powder pattern at 23.0, 29.4, 36.0, 39.5, and 43.2° 2θ (d-spacings 3.86, 3.04, 2.50, 2.28, and 2.09 Å). The H12 and BW soils (Figures 1 and 2) contained mixtures of illite and montmorillonite clays, as indicated by peaks in the powder pattern at 19.75, 22.00, 25.39, 27.32, 27.80, and 34.9° 2θ (d-spacings- 4.49, 4.04, 3.51, 3.26, 3.21, and 2.57 Å).

Peaks indicative of iron-containing phases were identified in the powder patterns of soils with elevated concentrations of Fe, specifically, the C1 and S5 soils (Figures 4 and 5). The C1 soil powder pattern indicated the presence of magnetite (Fe_3O_4) and hematite (Fe_2O_3). The peaks ascribed to magnetite were located at 30.01, 35.49, and

42.42° 2θ (d-spacings 2.98, 2.53, and 2.13 Å), while those ascribed to hematite were at 24.20, 33.09, 35.49, and 40.85° 2θ (d-spacings 3.68, 2.71, 2.53, and 2.21 Å). XRD data also supported the identification of the sulfate containing phases, jarosite ($FeSO_4$) and gypsum ($CaSO_4 \bullet 2\ H_2O$), in the C1 soil. The peaks assigned to jarosite are at 14.83, 15.47, and 17.29° 2θ (d-spacings 5.97, 5.72, and 5.12 Å). The peaks assigned to gypsum are 28.50, 28.86, 31.42, and 42.23° 2θ (d-spacings 3.13, 3.09, 2.84, and 2.09 Å). The S5 soil contained magnetite (Fe_2O_3), as indicated by the peaks at 17.49, 30.23, 35.44, 37.21, and 43.21° 2θ (d-spacings 5.07, 2.95, 2.53, 2.41, 2.09 Å). The S5 soil also contained two sulfide minerals, pyrite (FeS) and manganese sulfide (MnS). The peaks at 29.10 and 34.79° 2θ (d-spacings 3.07 and 2.58 Å) were indicative of the presence of FeS; the peak at 27.48° 2θ (d-spacing 3.24 Å) is indicative of MnS.

b. DRIFTS

Infrared spectroscopy has been used extensively to identify soil constituents and to elucidate the structures of both the inorganic and organic components of soils.[14] The use of infrared spectroscopy to characterize the inorganic[15,16] and organic[17] components of soils has been reviewed. Unlike XRD methods that detect only the crystalline components, all of the solid and liquid components present in soil have a set of characteristic infrared vibrations.

While DRIFTS has been widely applied to the study of soil components, it is not often applied to the study whole soils. Nguyen has reported the only other application of DRIFTS to whole soils.[18] Although DRIFTS does have limitations in its use for the identification of soil components, comparison of the DRIFTS spectra of the soils reveals that it can be used as a "finger print" to differentiate the soils. DRIFTS is also useful for the rapid identification of organic matter and some mineral components in soils.[18] Tables 3 and 4 contain peak positions for some of the inorganic and organic constituents typically found in soils.[14]

Typical soil spectra include a multitude of bands due to the various organic and inorganic components present. Based on literature references for the assignments of the various organic and inorganic components of soils, the DRIFTS spectrum of a soil can be divided in to regions where bands associated with specific phases commonly occur.[14-18] Bands in the region from 3750 to 3550 cm^{-1} result from the stretching of isolated hydroxyl groups present in the bulk of the inorganic constituents present in soils. The broad hydroxyl stretching region from 3600 to 3300 cm^{-1} includes bands due to water molecules adsorbed onto the surfaces of the organic and inorganic components in soils. Bands due to the aliphatic organic components of soils are clearly visible in the 3100 – 2800 cm^{-1} range when present in soils. The region from 2700 to 1650 cm^{-1} includes the weak overtone and combination bands from the various mineral components in the soils, including carbonates, clays, and quartz. The region between 1700 and 1350 cm^{-1} contains the bands due to the various organic functional groups present in soils. Bands from C=O groups of carboxylates, amides and esters and bands from C=C of aromatic groups are present in this region. In addition, the band centered around 1440 cm^{-1} due to carbonates is also present in this region. The region from 1100 to 400 cm^{-1} includes the bands due to the vibrations of the metal oxygen bonds. The most intense of these bands are the Si-O-Si bands between 1100 and 1050 cm^{-1}. Characterization of phosphate and sulfate phases in soils are limited by the overlap of their most intense bands by the intense Si-O-Si band. Below 1000 cm^{-1} various weaker bands are present which result from O-(Al, Mg, Fe) interactions.

The DRIFTS spectra of the soils are presented in Figures 6 through 10. The spectrum for each soil is different, and verifies the DRIFTS can be used as a "finger print" for different soils. The information provided by DRIFTS data corroborates the presence of many of the minerals identified by XRD and provides additional evidence for the presence of organic matter in the soils, not obtained by XRD. For example, overtone bands at 2000, 1870, and 1790 cm^{-1}, characteristic of quartz, can be used to identify its presence in soils. These bands are observed in the spectra of all the soils, as predicted from the XRD data. Characteristic calcite bands at 2592, 2517, 1450, and 880 cm^{-1} are present in the spectra of the B4 and S5 soils (Figures 8 and 9). The chemical characterization data suggest that significant evidence of organic carbon should be evidenced in the spectra of the H12 and B4 soils (Figures 7 and 8). The bands at 2920 and 2860 cm^{-1}, resulting from aliphatic and aromatic C-H stretching, were prominent in the spectra of both soils. The high content of iron and sulfate phases in the C1 soil was also evident in the DRIFTS spectra. The intense bands at 3390 and 1210 cm^{-1} in the spectra of the C1 soil are a characteristic feature of iron sulfate phases containing hydroxyl groups or water such as, carphosiderite ($Fe_3(OH)_5H_2O(SO_4)_2H_2O$) or amaranite ($FeSO_4(OH)\ 3H_2O$).[19]

c. NMR

NMR is a valuable technique for probing the local environment of atoms in samples. Several reviews have been published on the application of NMR to soils.[20-22]

^{13}C, ^{31}P, ^{29}Si, and ^{27}Al NMR have been applied to characterize both whole soil and soil components.

i. ^{13}C NMR. The most widely used application of NMR in soil chemistry to date has been the use of ^{13}C NMR to characterize soil organic matter.[23] The chemical shift ranges for organic materials typically found in soils are summarized in Table 5.

^{13}C CP-MAS NMR experiments were conducted to characterize the organic matter in the BW, H12 and B4 soils. The ^{13}C NMR spectra for the B4 and H12 soils are presented in Figure 11. The spectra were collected using a quasi adiabatic pulse sequence with a 5 mm probe at spinning speeds of 4 KHz. A ^{1}H 90° pulse width of 4.25 µs , 0.5 ms contact time, and 1 s pulse delay were used; 18,000 acquisitions were collected. No signal was detected for the BW soil. This was attributed to the low carbon content of the BW soil (1.8%). Previous studies have demonstrated the detection limit for carbon in soils to be 3 % by weight.[20] The spectrum of the B4 soil showed only weak, indistinguishable resonances. The high organic carbon content of the B4 soil (10 %) suggested that ^{13}C experiments should have been successful with this soil. The minimal signal obtained with this soil was attributed to the significant contribution of coal to the % organic carbon. The H12 soil contained the highest organic carbon content (26 %) and resulted in the most resolved ^{13}C data. The spectrum of the H12 soil revealed multiple peaks. Comparison of the H12 spectrum with known chemical shifts for soil organic matter constituents provides evidence for the variety of organic functionality. Peaks at 18 and 29 ppm were assigned to the alkyl and aromatic components. The peak at 74 ppm was attributed to the C-O of alcohol, ester, and ether functional groups. The peak at 190 ppm was assigned to the carboxyl groups of carboxylic acids, esters, and amides.

ii. ^{31}P NMR. ^{31}P single pulse NMR experiments with 1H decoupling were conducted on the BW(b), H12(b), C1 and S5 soils. The data were collected using a 5 mm probe at spinning speeds of 5 KHz. The ^{31}P 90° pulse widths were 4 μs and 10 s pulse delays were used. No phosphorous resonances were observed for any of the soils after 1000 acquisitions. Theoretically, 10^{18} to 10^{19} nuclei are required for detection by NMR.[24] Based on this assumption, the detection limit for ^{31}P is as low as 0.05 % by weight. The ^{31}P NMR data for these soils suggest a very low P content. Because these soils had not been fertilized, a low P content would be expected based on the typical content observed in soils (Table 2).

iii. ^{1}H NMR. ^{1}H single pulse experiments were conducted on the BW(b), H12(b), S5, and C1 soils. The data were collected using a 5 mm probe at spinning speeds of 5 KHz. The ^{1}H 90° pulse length was 7 μs, 1 s pulse delays were used and 1000 to 6000 acquisitions were collected. The results of the ^{1}H NMR experiments are summarized in Table 6 and the spectra are presented in Figure 12. The spectra of all four soils revealed a peak centered between 4.6 and 5.4 ppm assigned to surface adsorbed water.[25]

Table 6. Summary of ^{1}H NMR data

Soil	Chemical Shift
BW(b)	4.6
H12(b)	4.9
S5	5.1
C1	5.4

iv. ^{113}Cd NMR. Attempts to collect ^{113} Cd were conducted using a single pulse experiment on the BW soil. No ^{113}Cd signal was observed after 16 hrs of data collection. This was attributed to the low Cd content of the soil sample. To date, only one study exists on the direct detection of metals in soils.[26] Ellis et al. used direct and cross polarization techniques to look at ^{113}Cd in soils contaminated with 2600 to 72,000 ppm Cd from a nickel-cadmium battery factory. The results of their study showed Cd signals were only detected in soils with Cd contents greater than 20,000 ppm and that factors other than Cd content contribute to the observed signal intensity.

C. Amendments

Six amendments were investigated in this study: three amendments containing organic and/or alkaline material (SS, LS, NV) and three phosphate amendments (RP, HA, CaP). These amendments were chosen based on previous which documented the ability of these substances to reduce metal solubility in contaminated soils through sequential extraction and plant growth/uptake studies.[4, 27]

1. Biosolids/Alkaline Amendments

Three biosolids amendments were investigated in this study, LS, NV, and SS. The chemical properties of the biosolids are presented in Table 7. The total metal content, organic carbon and pH were determined using the methods described in section B.[3,7,9] The calcium carbonate equivalent (CCE) was determined by reaction with HCl and back titration.[28] Biosolids are the solid material remaining after water sewage treatment facilities purify wastewater. Biosolids are a complex mixture of organic and inorganic components.[29] The application of biosolids to agricultural land has been practiced for decades.[30] The organic matter of biosolids is capable of immobilizing metals through chelation. In some cases, biosolids are treated to reduce microbial activity by raising the pH of the material. Both the LS and NV amendments were alkaline. The addition of alkaline biosolids to soils would raise the soil pH. Increasing the soil pH increases the soils negative charge and reduces the solubility and bioavailability of metals in soils, potentially increasing the precipitation of carbonates, oxides and hydroxides.[31]

a. Spectral Characterization

i. DRIFTS. Infrared studies on biosolids have been reported by Nelson.[32] The DRIFTS data for the biosolids amendments are presented in Figures 13 to 15. The spectra reveal that the samples are a mixture of organic and silicate components. The organic components have bands at 2935, 2857, 1655, and 1537 cm^{-1}. The silicate components have bands at 1040 and 600 to 400 cm^{-1} regions. The LS and NV amendments contain a significant carbonate content evidenced by the bands at 1445 and 875 cm^{-1}. Although the biosolids amendments are composed of similar components, the DRIFTS spectra are unique and may be used as a “finger print” to differentiate the materials.

ii. ^{13}C NMR. The ^{13}C NMR spectra of the LS, SS, and NV amendments are presented in Figure 16. The spectra were collected using a quasi adiabatic pulse sequence in a 7.5 mm probe at spinning speeds of 5 KHz. A 5.3 μs pulse width, 3 ms contact time and 1 s pulse delay were used and 18,000 acquisitions were collected. The ^{13}C NMR of the biosolids amendments reveal a variety of organic functionality in these samples and reflect the differences in organic carbon content between the amendments. The LS amendment contained the highest percentage of organic carbon and the NV amendment contains the lowest percentage organic carbon. Because cross polarization experiments were used to collect the data, one can not make predictions about the relative functional group content of the amendments. However, it can be ascertained that all three biosolids contain similar functional groups. The peaks between 20 and 28 ppm were assigned to alkyl carbon. The peaks at 71 and 103 ppm were assigned to C-O function groups. The peak at 125 ppm was attributed to the aromatic components of the biosolids. The peaks from 173 to 182 ppm were assigned to the C=O functional groups such as, carboxylic acids, esters, and amides.

2. Phosphate Amendments

Numerous studies have documented the ability of phosphates to remove Cd, Pb, and Zn ions from aqueous solution.[33-35] Past research efforts have shown that phosphate minerals are likely the controlling solids for Ca, Cd, Pb and Zn solubility in natural systems.[36] According to Nriagu, phosphate minerals appear to have the potential to immobilize Pb in contaminated soils due to the low solubility of Pb orthophosphates. Several studies have established the ability of phosphate to immobilize metals in soils.[35,37]

Three phosphate amendments were evaluated in this study, RP, HA, and CaP. Literature studies have suggested that the effectiveness of phosphate amendments is related to the solubility of the phosphate material.[35] The solubility of these phosphate materials decrease in the order CaP (-log K_{sp} = 19.09)[38] > HA (-log K_{sp} = 38.15)[38] > RP.[6]

a. Spectral Characterization

i. XRD. The XRD patterns of the RP, HA, and CaP amendments are presented in Figures 17 to 19. Comparison of the patterns with JCPDS reference patterns allowed identification of the samples.[13] The RP pattern matched the pattern for a carbonated apatite. The exact formula can not be determined from XRD alone, but it has the general formula $Ca_{10}(PO_4)_x(CO_3)_y(OH, F, Cl)_z$. The HA pattern verified that the material was hydroxyapatite ($Ca_5(PO_4)_3OH$). The CaP pattern matched with $CaHPO_4$.

ii. DRIFTS. The DRIFTS spectra of the RP, HA, and CaP amendments are presented in Figures 20 to 22. The identities of the amendments determined by XRD was further corroborated by the DRIFTS data. The spectrum of the CaP amendment matched published spectra of $CaHPO_4$.[19] Comparison of the RP and HA DRIFTS spectra reveal that both samples are apatites;[19] however, differences in their structures are evident. The HA has a sharp peak at 3600cm^{-1} resulting from isolated OH within the structure. This peak is absent in the RP sample. The RP sample has strong bands at 2500, 1450, and 875 cm^{-1} indicating this sample contains a significant amount of carbonate substitution. These bands are absent in the HA spectrum. This further refines the expected formula of the RP to $Ca_{10}(PO_4)_x(CO_3)_y(Cl, F)_z$.

iii. ^{31}P NMR. Many ^{31}P NMR studies have been conducted to examine the short range order in calcium phosphates.[39,40] The ^{31}P amendment spectra were collected using a single pule sequence with ^{1}H decoupling using a 5mm probe at spinning speeds of 5 KHz. A 2.1 μs pulse width and 10 s pulse delay were used over 1000 acquisitions. The ^{31}P NMR spectra of the CaP, HA, and RP samples all contain a single peak. The HA and RP samples had peaks at 2.9 ppm. This peaks corresponds to the isotropic chemical shift of PO_4^{3-} groups. The CaP amendment gave a peak at –1.5 ppm. This peak corresponds to the isotropic chemical shift of the HPO_4^{2-} group.

iv. ^{1}H NMR. Although many studies exist on the ^{31}P NMR of calcium phosphates, Eckert has published the only thorough ^{1}H study on calcium phosphates.[41] The ^{1}H NMR spectra were collected using a single pulse sequence with a 5 mm probe at spinning speeds of 5 KHz. A 7 μs pulse width and 1 s pulse delay were used over 1000 acquisitions. Figure 23 presents the ^{1}H spectra and Table 7 contains the peak positions and assignments for the phosphate amendments. The proton chemical shifts reported in this study agree with those previously published.[41] The ^{1}H NMR data also corroborates observations in the XRD and DRIFTS data. The RP amendment has a single ^{1}H peak at 4.9 ppm associated with surface adsorbed water. No peaks due to OH groups are present in this sample, corroborating the DRIFTS data. The HA amendment; however, revealed multiple ^{1}H resonances associated with surface adsorbed water and the OH groups present in the sample. The CaP amendment also had more than one peak.

The ^1H NMR for the phosphate amendments reveals very different surfaces would exist for each amendment. The RP surface would contain no hydroxyl groups and be relatively neutral. The HA amendment surface would contain hydroxyl groups and be more basic than the RP surface. The CaP surface would contain acidic protons.

Table 8. ^1H NMR results for phosphate amendments

Sample	**^1H Chemical Shift**	**Assignment**
RP	4.9	Surface adsorbed water
HA	5.3	Surface adsorbed water
	3.4	Surface OH
	1.0	Defect OH
	-0.3	Structural OH
CaP	15.7	Acidic proton most strongly H-bonded
	12.6	3 acidic proton environments, unresolved

D. Conclusions

These spectroscopic studies demonstrate that it is possible to characterize the soils and amendments using these techniques. The spectra of the soils and amendments are unique and provide a spectral "finger print" which may be used to identify the material. These results establish the feasibility of using these techniques to study soil-amendment interactions.

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Table 1. Soil Properties

	Total Metal, ppm			pH	EC	OC	Texture, wt %			Fe
Soil	**Cd**	**Pb**	**Zn**		dSm^{-1}	Wt %	**Clay**	**Silt**	**Sand**	Wt %
BW	296	497	12740	6.4	2.9	1.8	24	45	31	1.46
B4	112	1200	8960	6.6	0.28	10.0	24	46	30	nd
H12	81	2648	19505	6.8	0.82	26.0	14	34	52	nd
S5	179*	11526	3399	7.4	nd	3.22	7.5	45.6	46.9	18.33
C1	20*	11072	1599	2.6	nd	0.36	5.7	51.6	42.7	29.66

nd = not determined
* = sum of sequential extracts

Table 2. The average content of various elements in soils.

Element	Concentration (ppm)
Si	320,000
O	490,000
Al	71,000
Fe	38,000
C	20,000
Ca	13,700
K	8,300
N	1,400
P	600
Cd	0.6
Pb	10
Zn	50

Table 3. Characteristic Infrared Bands for Soil Inorganic Components

Component	cm^{-1}
CO_3^{2-} Vibrations	
Combination	2592, 2517 (Calcite)
Asymmetric stretch	1490-1410
Symmetric Stretch	1085-1050
Out of plane bend	876-860
In plane bend	750-700
	676 ($Pb(CO_3)_2$)
SO_4^{2-} Vibrations	
Stretching	1180-1100
Bending	680-650
PO_4^{3-}Vibrations	
Antisymmetric stretch	1100-1000
Bending	500-635
Sorbed Water	
OH Stretch	3600-3300
OH Bend	1650-1620
Clay Minerals and Oxides	
OH Stretch	3750-3300
OH Bend	950-820
Si-O-Si	1200-970
Quartz overtones	2000, 1870, 1790

Table 4. Characteristic Infrared Bands for Soil Organic Components.	
Assignment	**Frequency (cm^{-1})**
O-H and N-H stretching	3400-3300
Aliphatic C-H stretch	2940-2900
C=O stretch of COOH	1725-1700
C=O stretch of amides (amideI band)	1660-1630
COO^- symmetric stretch, N-H + C-N stretch (amideII band)	1590-1517
Aliphatic C-H bend	1460-1450
C-O stretch of polysaccharides	1170-950

Table 5. Chemical Shifts for Common Organic Functional Groups in Soils.	
Functional Group	**Chemical Shift (ppm)**
Alkyl	10-50
O-alkyl (alcohol, ester, ether)	50-100
Acetal	100-107
Alkene and Aromatic	110-160
Carboxyl (carboxy, ester, amide)	160-200
Carbonyl (aldehyde, ketone)	200-220

Table 7. Amendment properties						
	Total Metal, ppm					
	Cd	**Pb**	**Zn**	**pH**	**OC, %**	**CCE, %**
LS	8	63	415	12.3	30.2	21.4
NV	11	<1	254	7.9	5.7	46.7
SS	41	274	1675	7.1	22.3	21.4
RP	15	2.8	159	7.0	nd	<2

nd = not determined

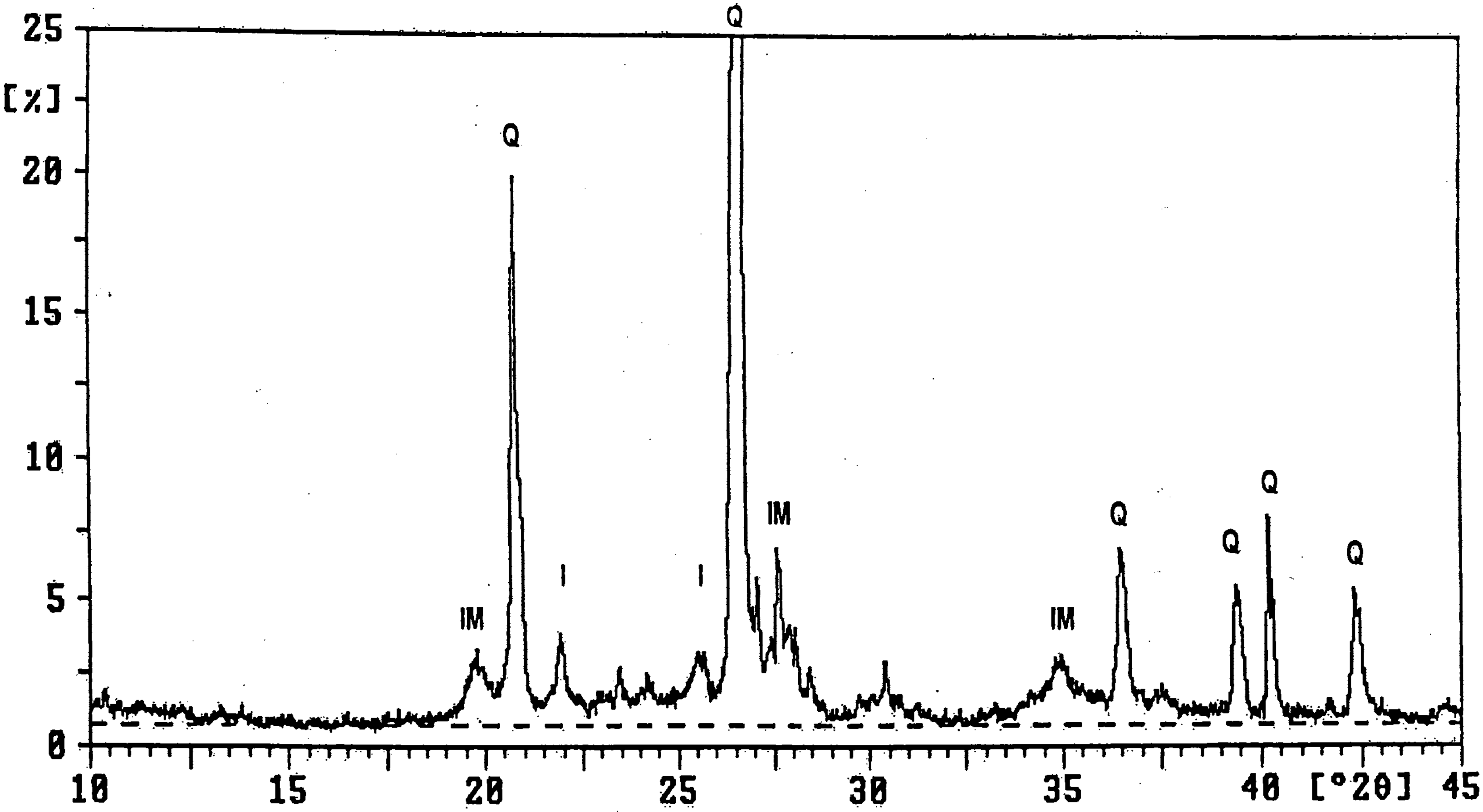

Figure 1. Blackwell soil XRD pattern. Q = quartz, I = illite, IM = illite/montmorillonite

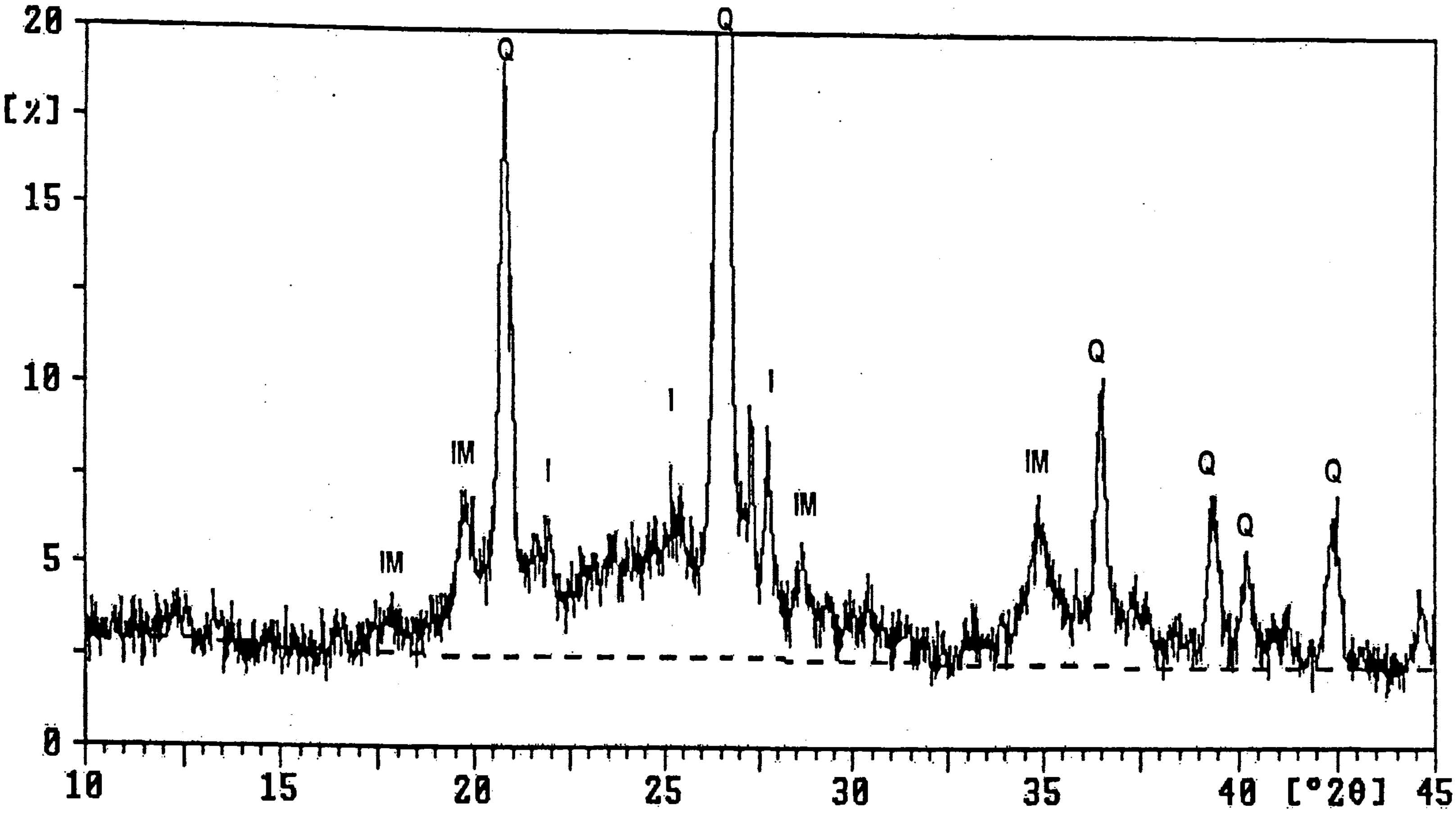

Figure 2. Henryetta soil XRD pattern. Q = quartz, I = illite, IM = illite/montmorilllonite.

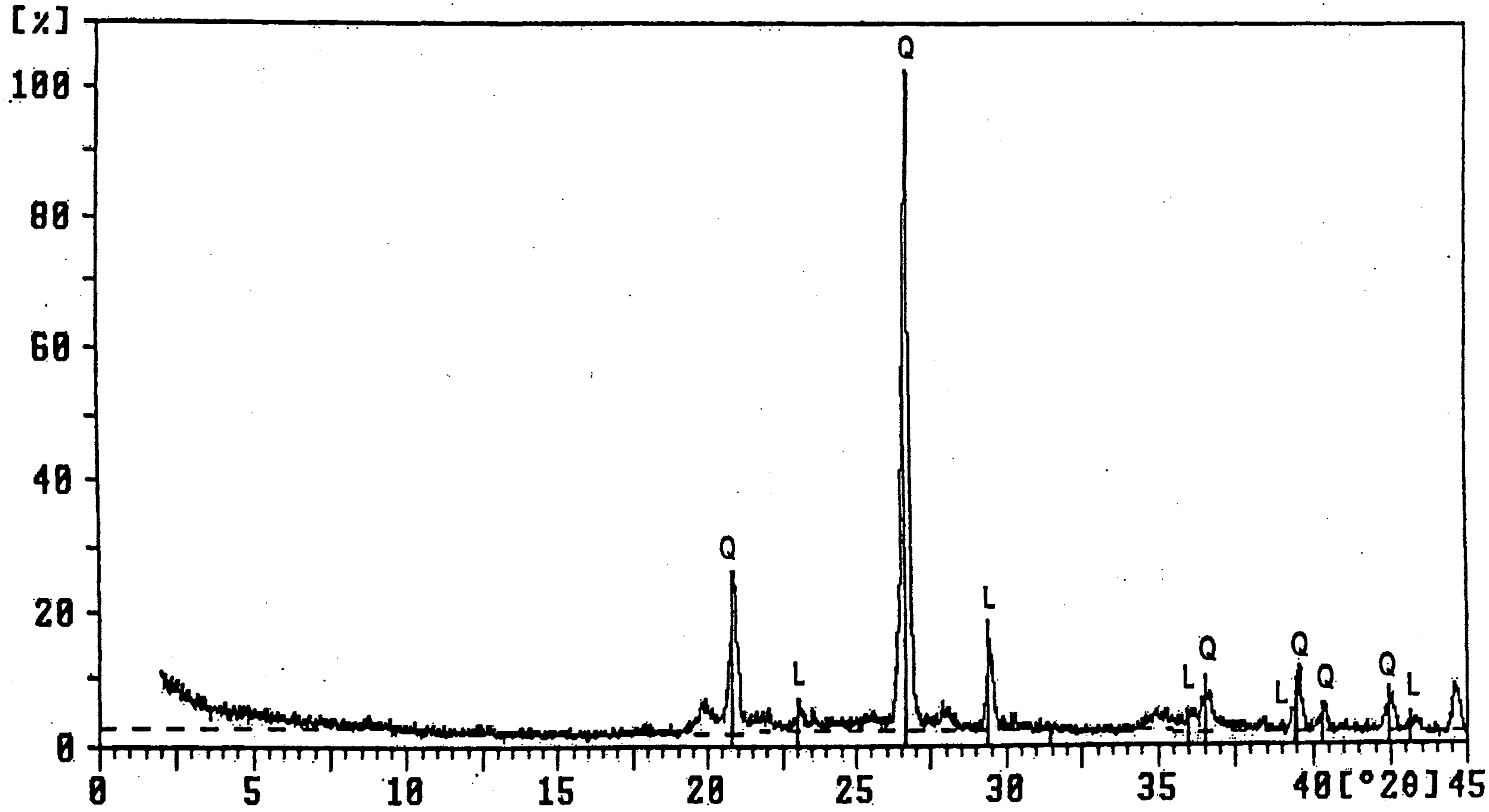

Figure 3. Bartlesville soil XRD patter. Q = quartz, L = calcite.

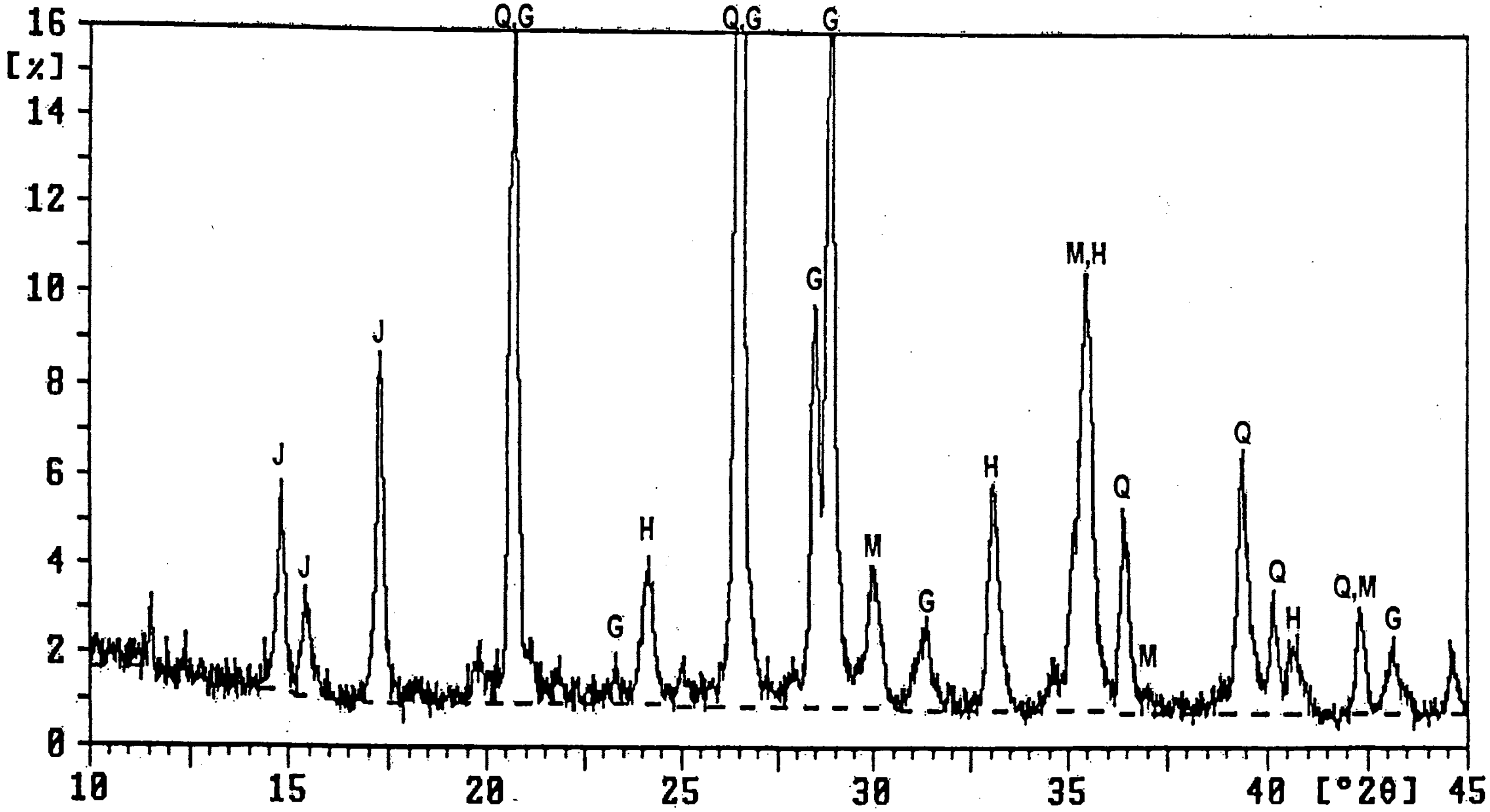

Figure 4. C1 soil XRD pattern. Q = quartz, H = hematite, J = jarosite, G = gypsum, M = magnetite.

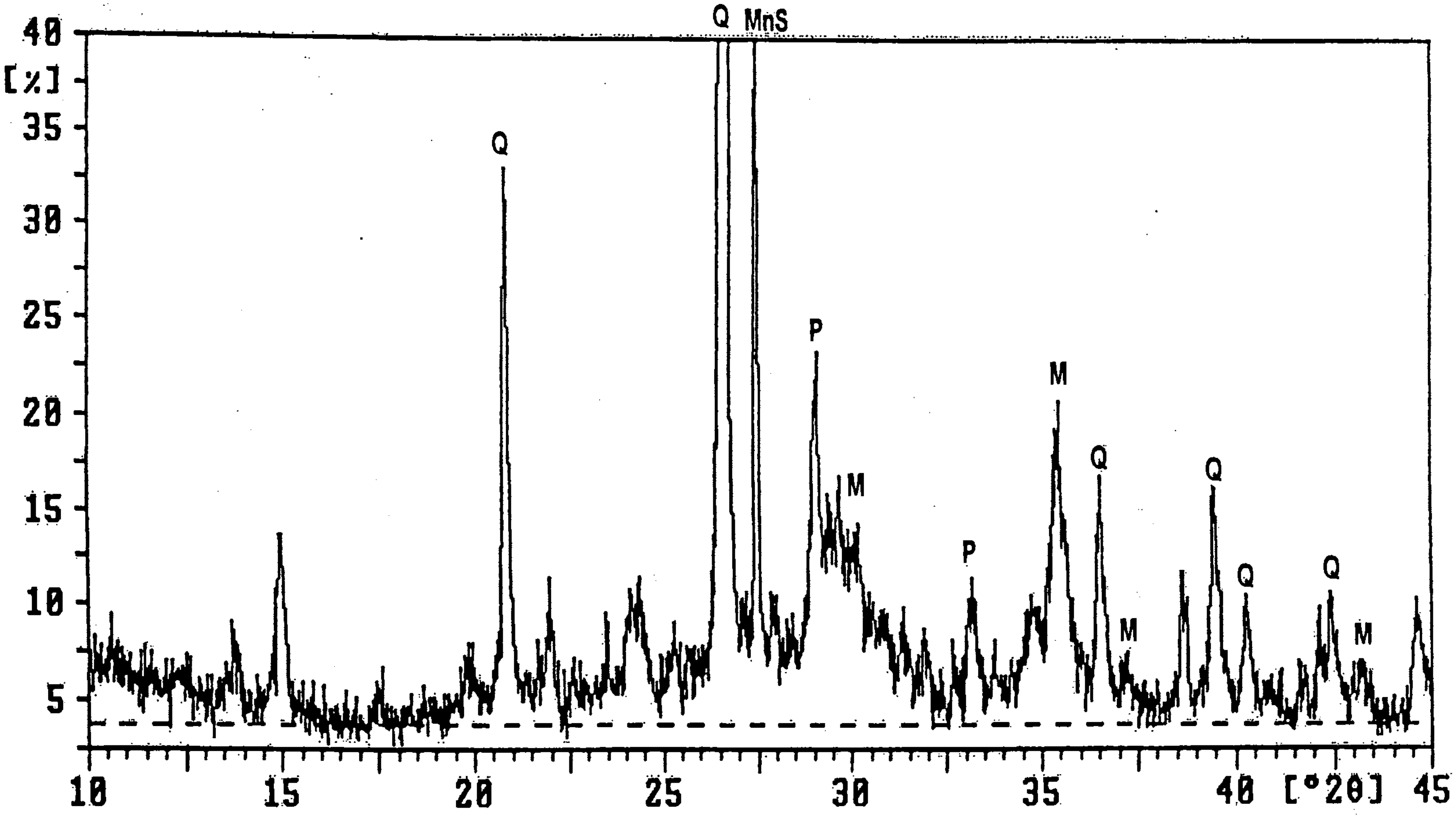

Figure 5. S5 soil XRD pattern. P = pyrite, M = magnetite, Q = quartz, MnS = manganese sulfide.

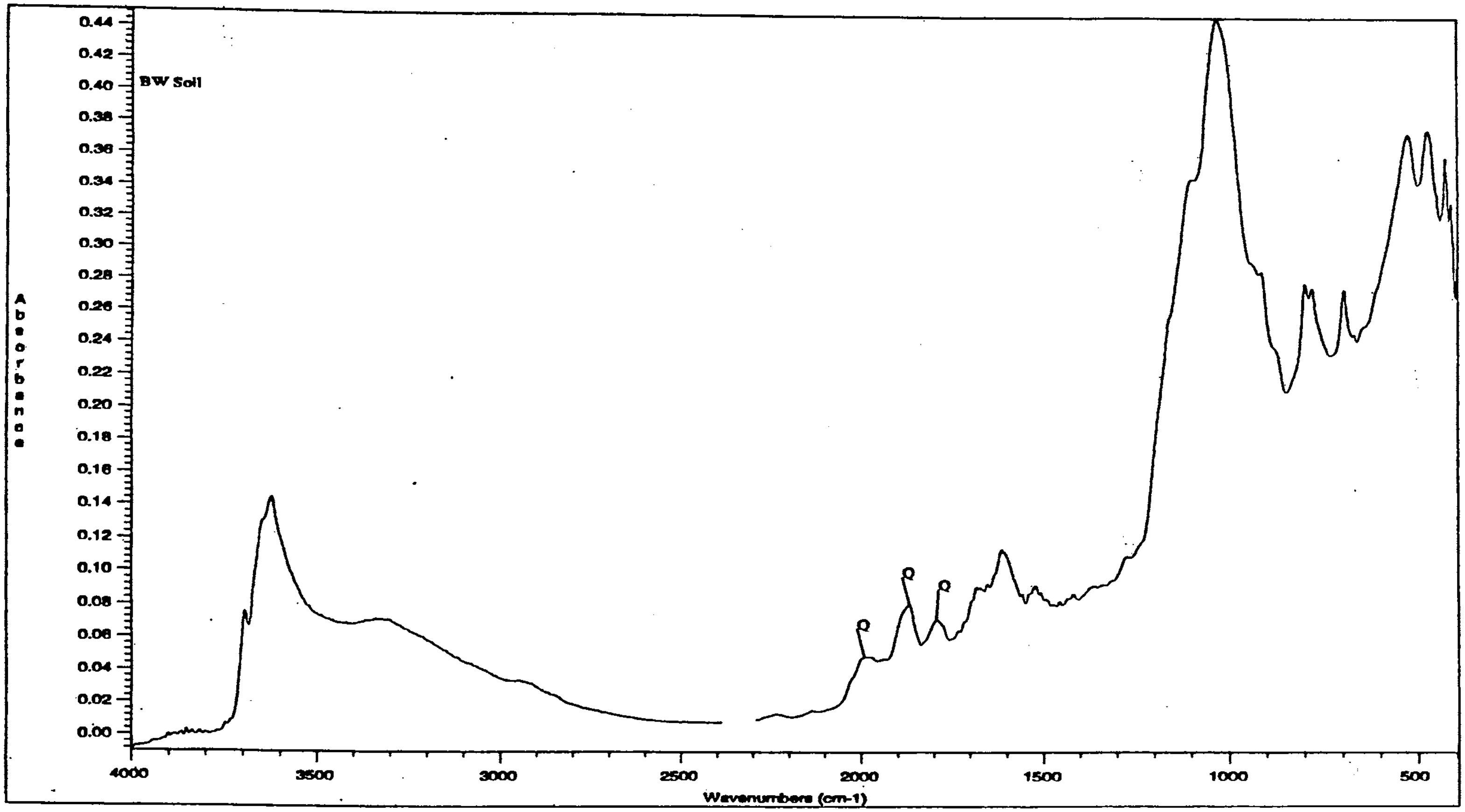

Figure 6. Blackwell soil DRIFTS spectrum. Q = quartz.

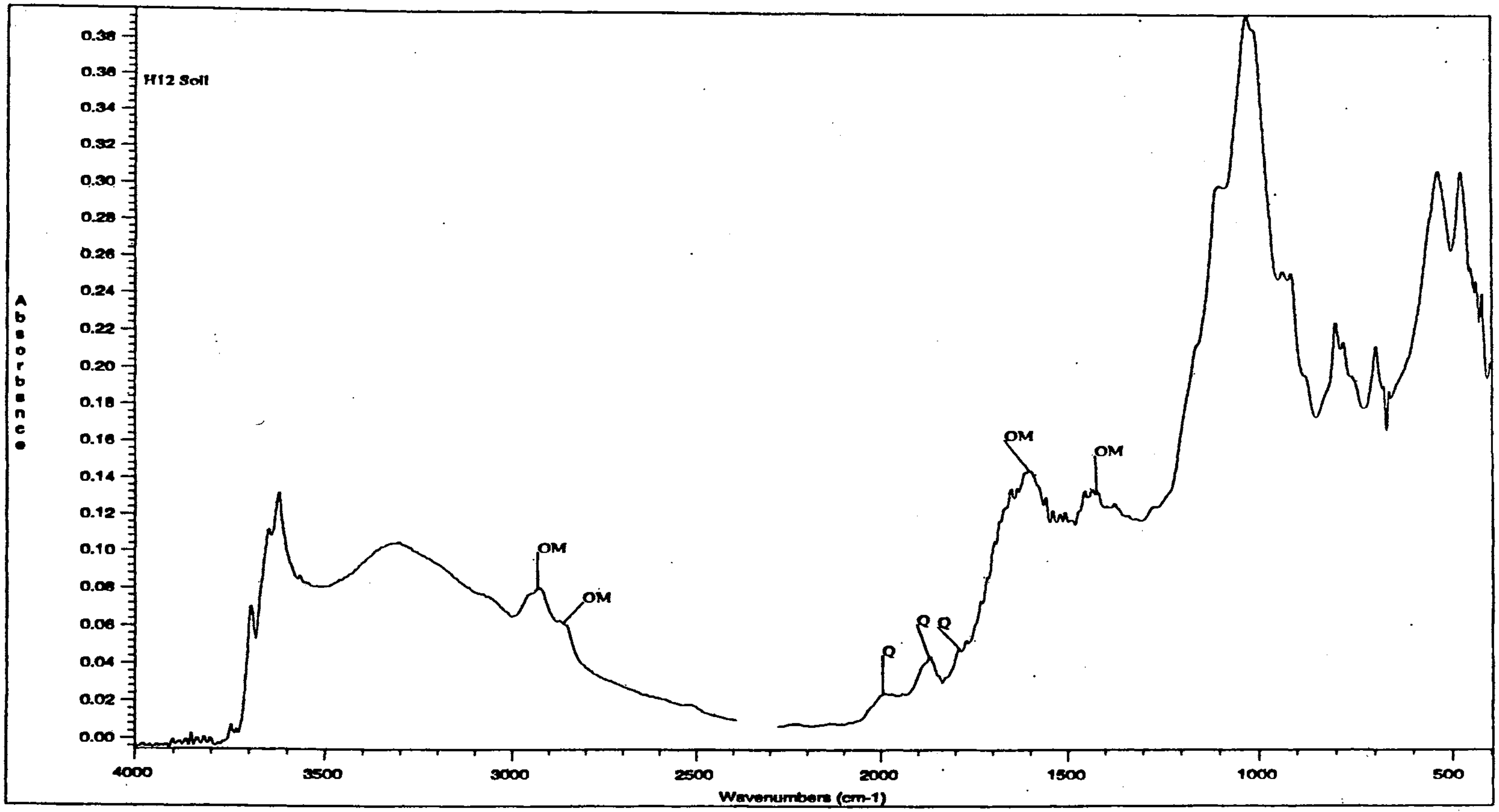

Figure 7. Henryetta soil DRIFTS spectrum. Q = quartz, OM = organic matter.

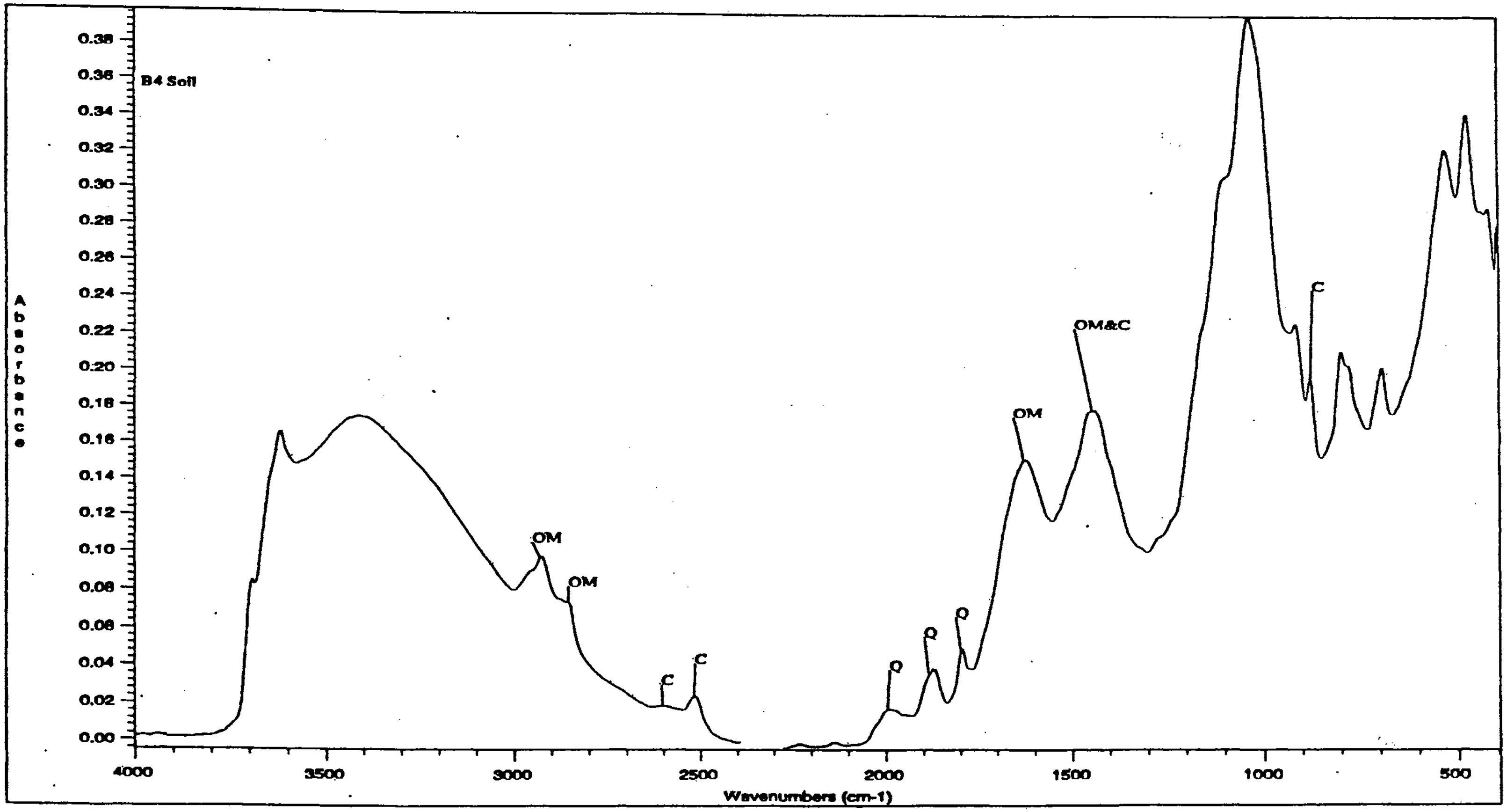

Figure 8. Bartlesville soil DRIFTS spectrum. C = calcite, Q = quartz, OM = organic matter, OM&C = organic matter and calcite.

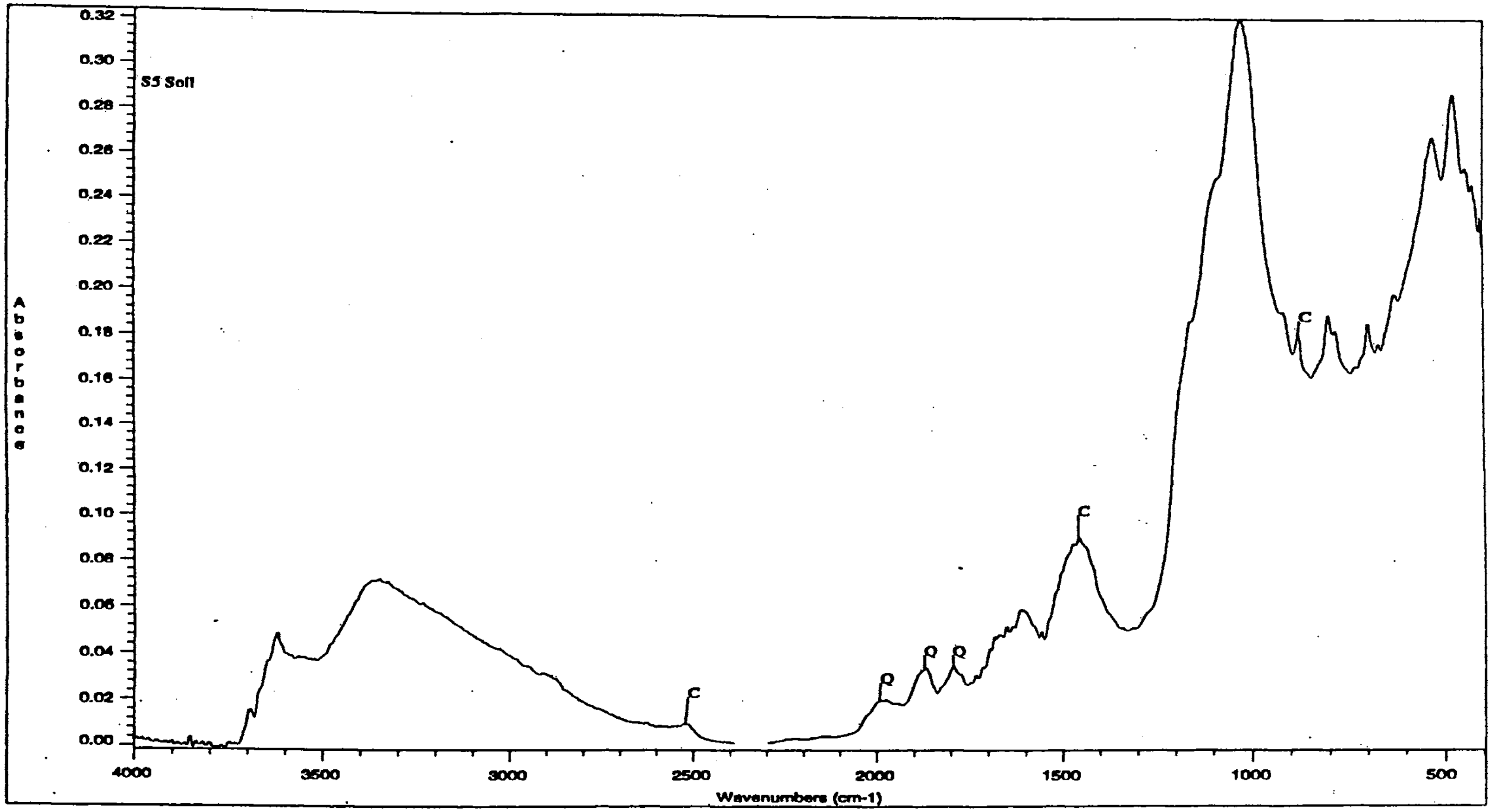

Figure 9. S5 soil DRIFTS spectrum. C = calcite, Q = quartz.

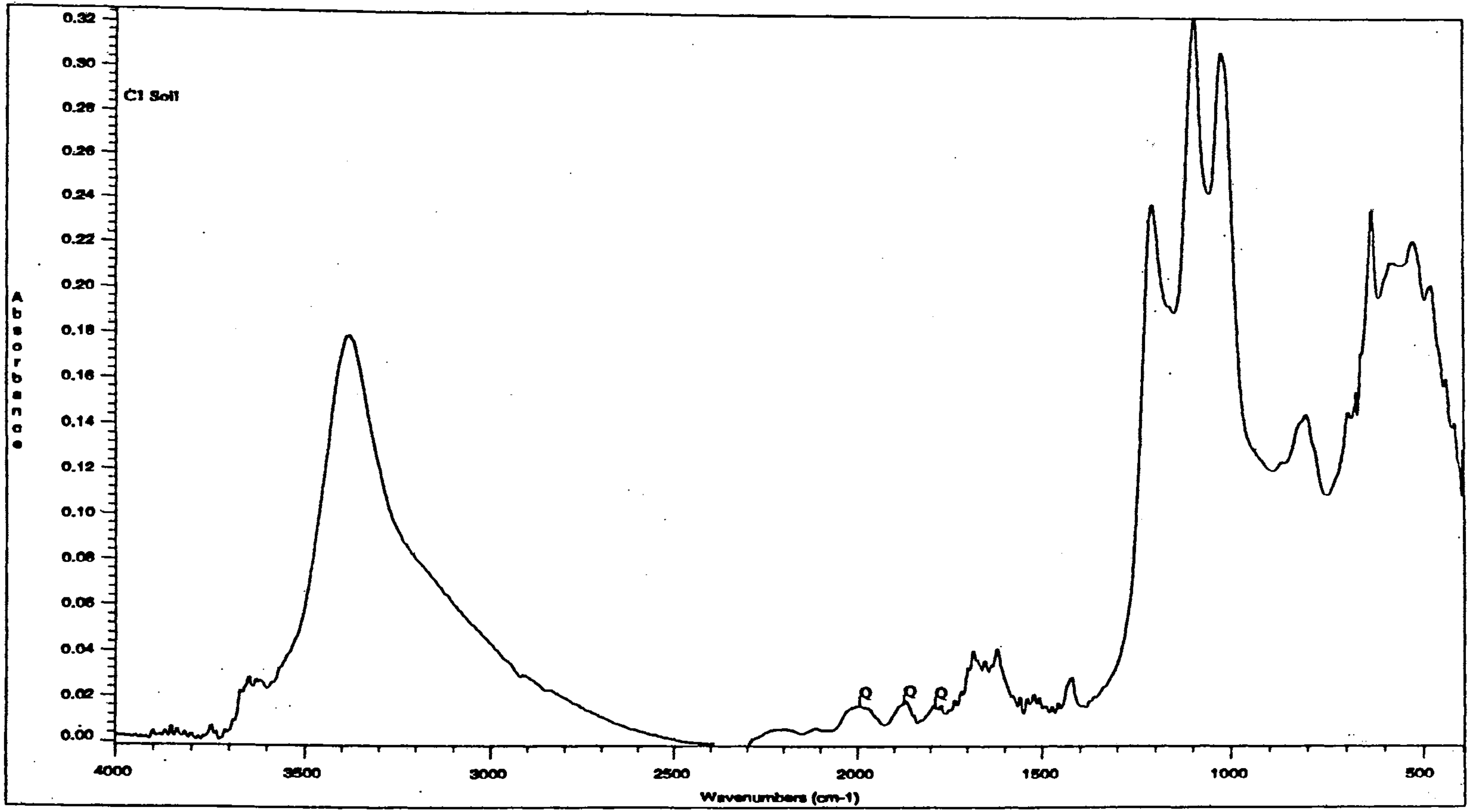

Figure 10. C1 soil DRIFTS spectrum. Q = quartz.

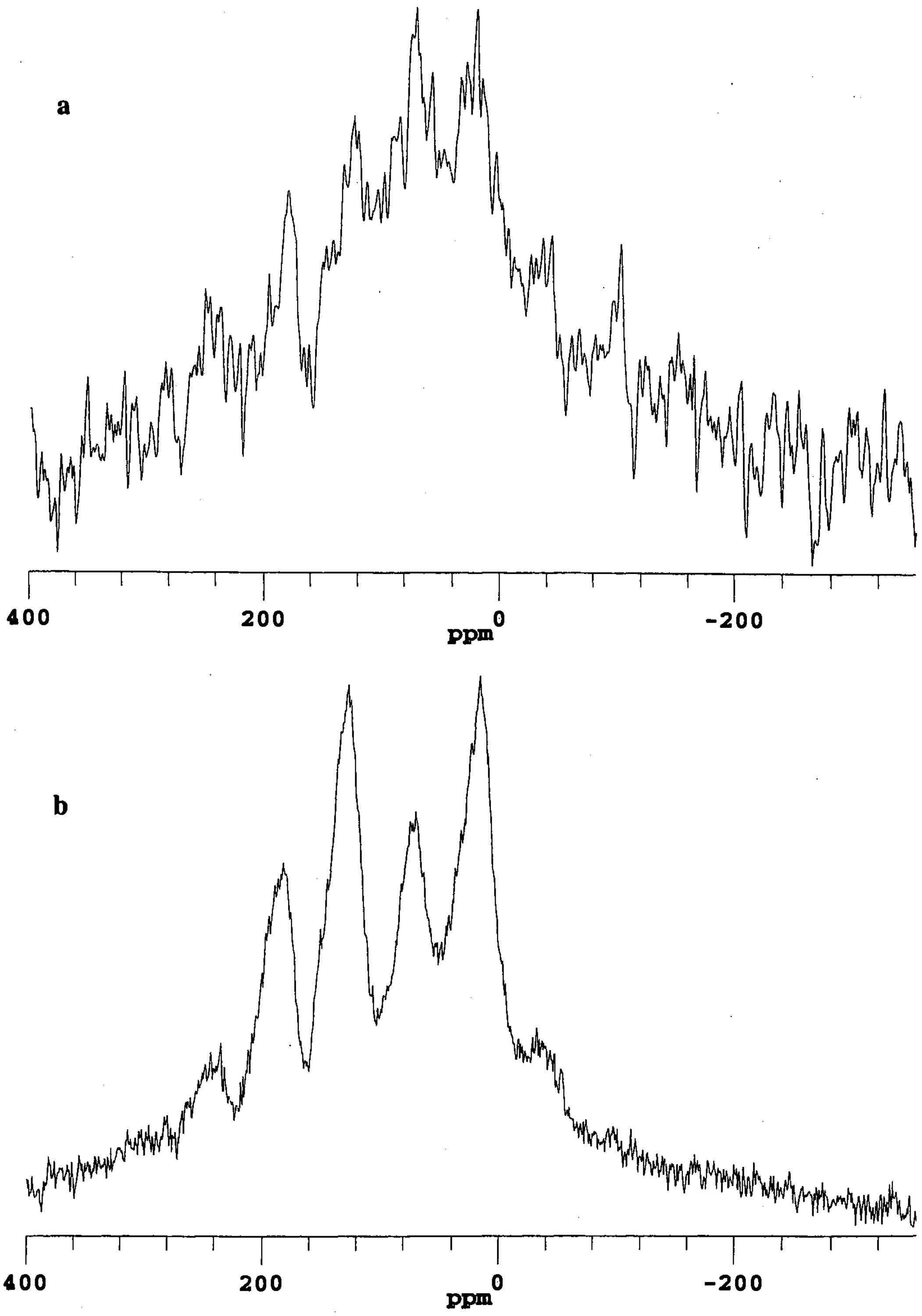

Figure 11. ^{13}C CP-MAS spectra of soil samples (a) B4, 200 Hz line broadening and (b) H12, 50 Hz line broadening.

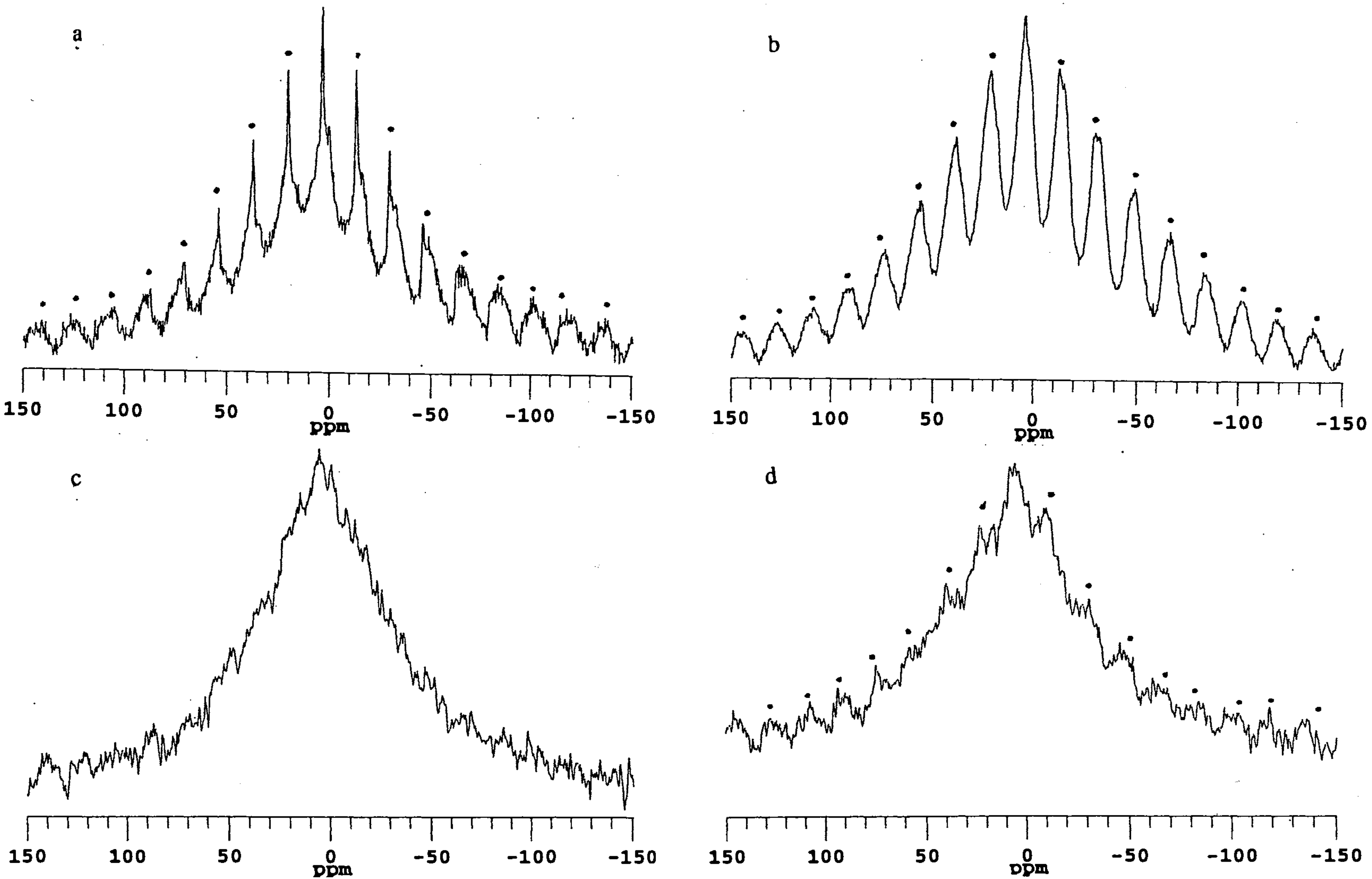

Figure 12. ^{1}H single pulse MAS NMR spectra of soils (a) BW(b); (b) H12(b); (c) S5; 200 Hz line broadening; and (d) C1, 200 Hz line broadening. • denote spinning side bands.

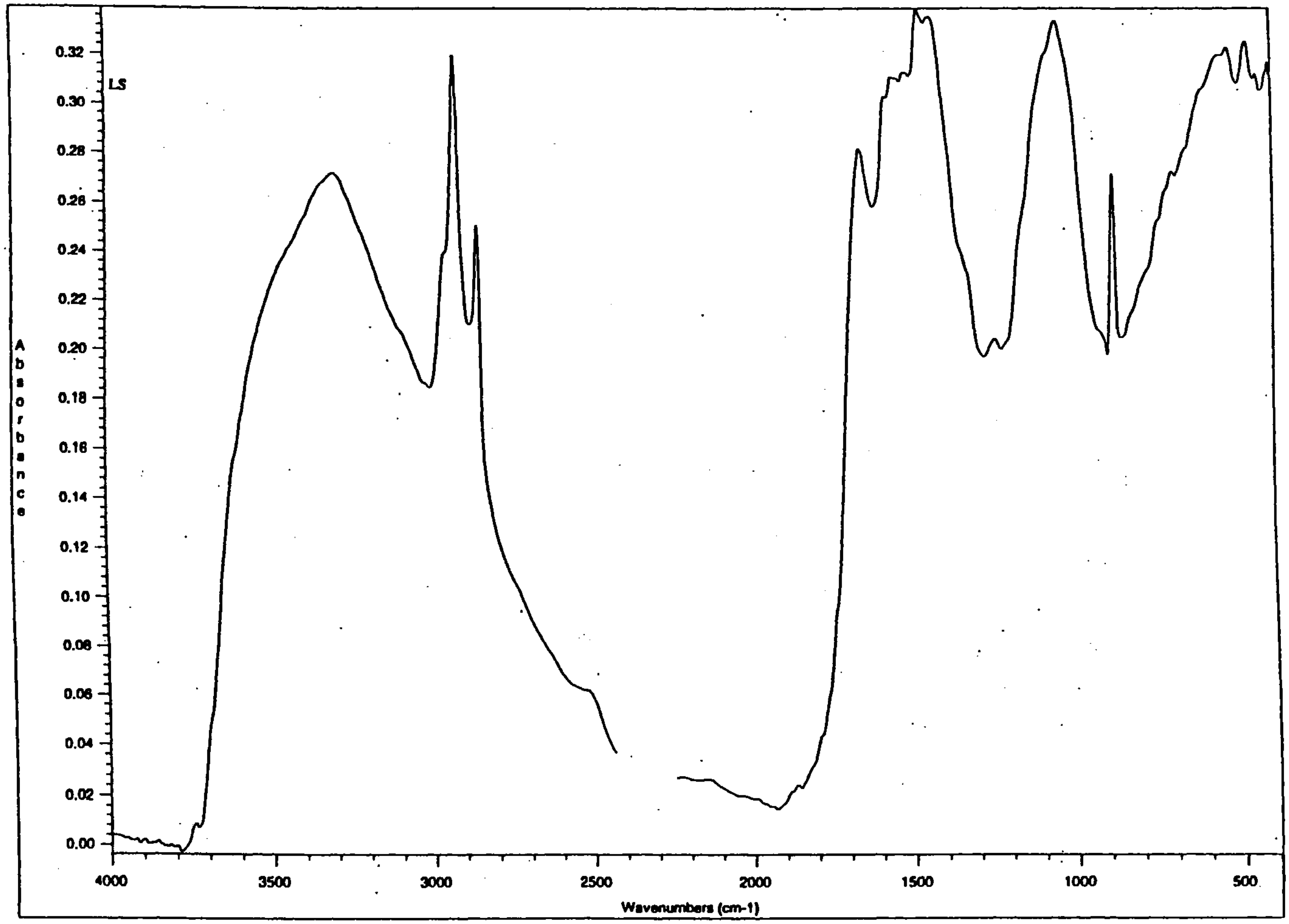

Figure 13. Oklahoma City Biosolids (LS) amendment DRIFTS spectrum.

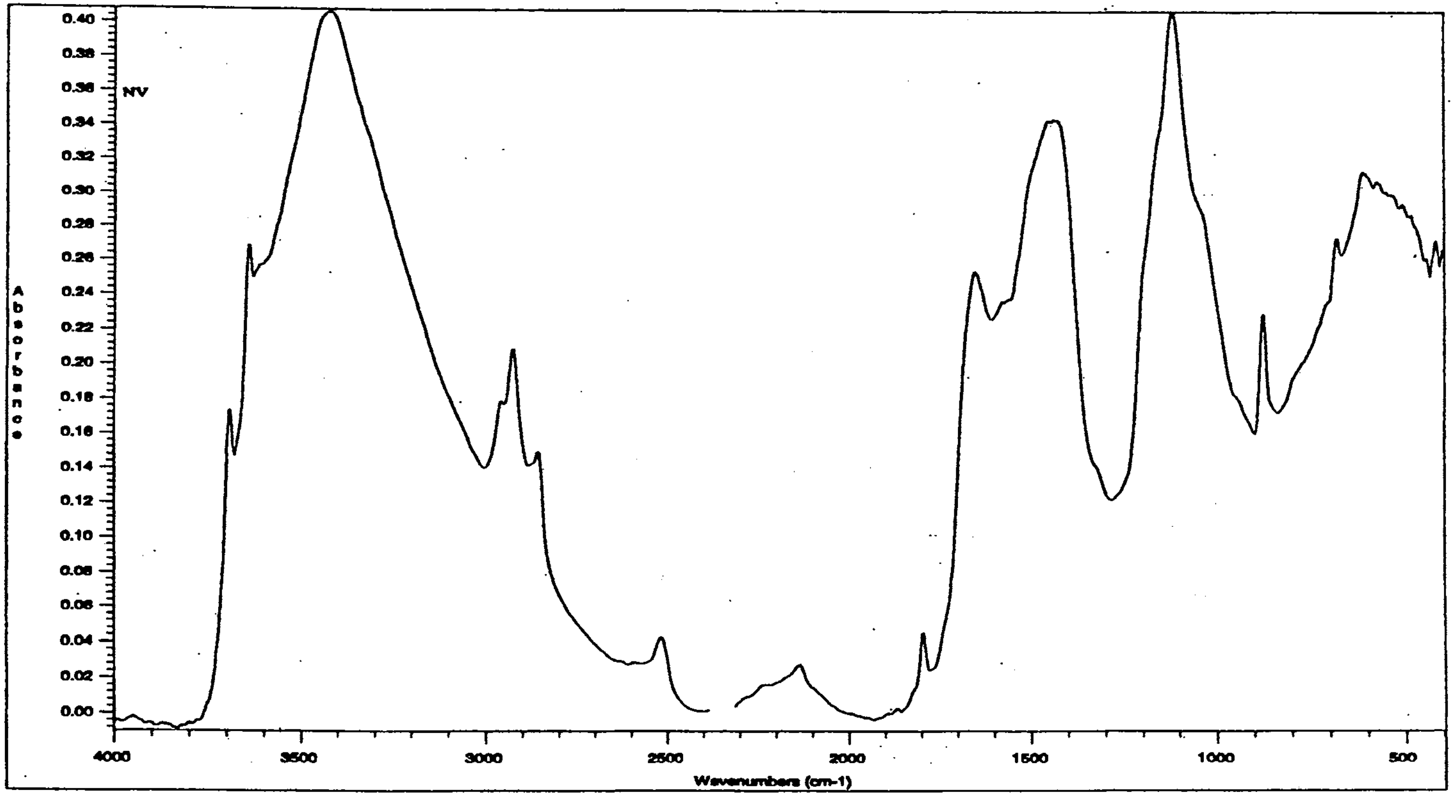

Figure 14. N-Viro (NV) amendment DRIFTS spectrum.

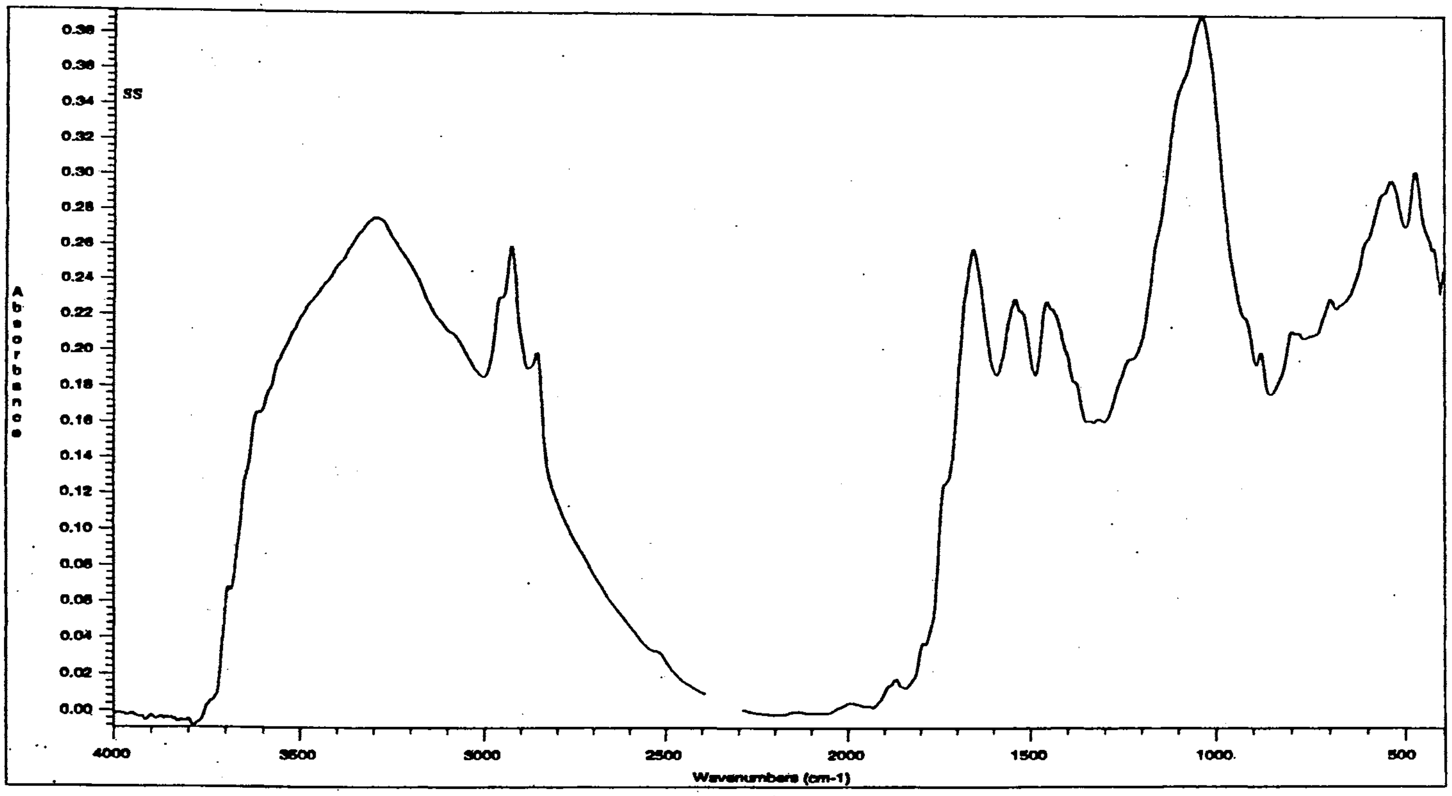

Figure 15. Tulsa biosolids (SS) amendment DRIFTS spectrum.

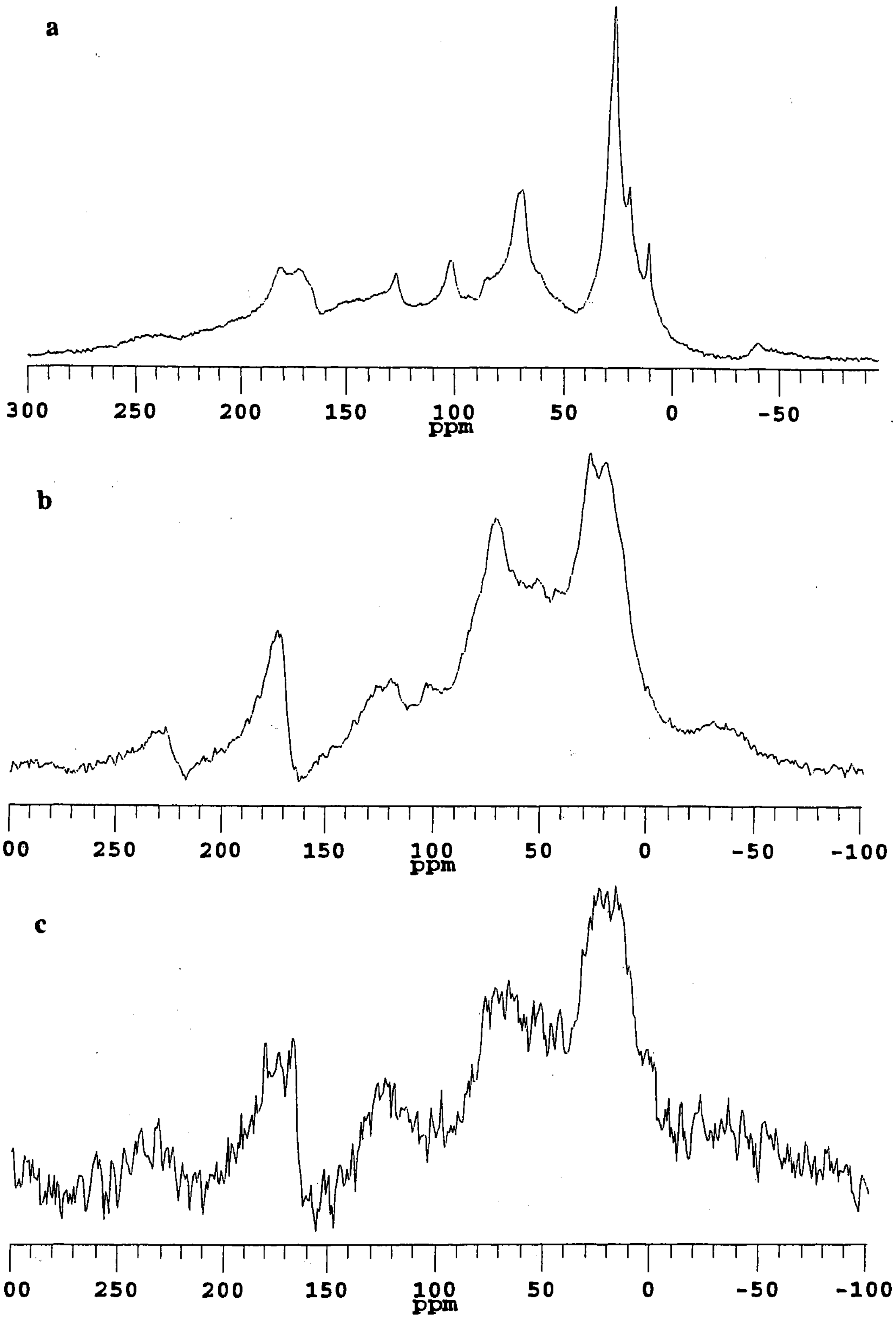

Figure 16. ^{13}C CP-MAS NMR spectra of biosolids amendments (a) LS, 25 Hz line broadening; (b) SS, 50 Hz line broadening; and (c) NV, 50 Hz line broadening.

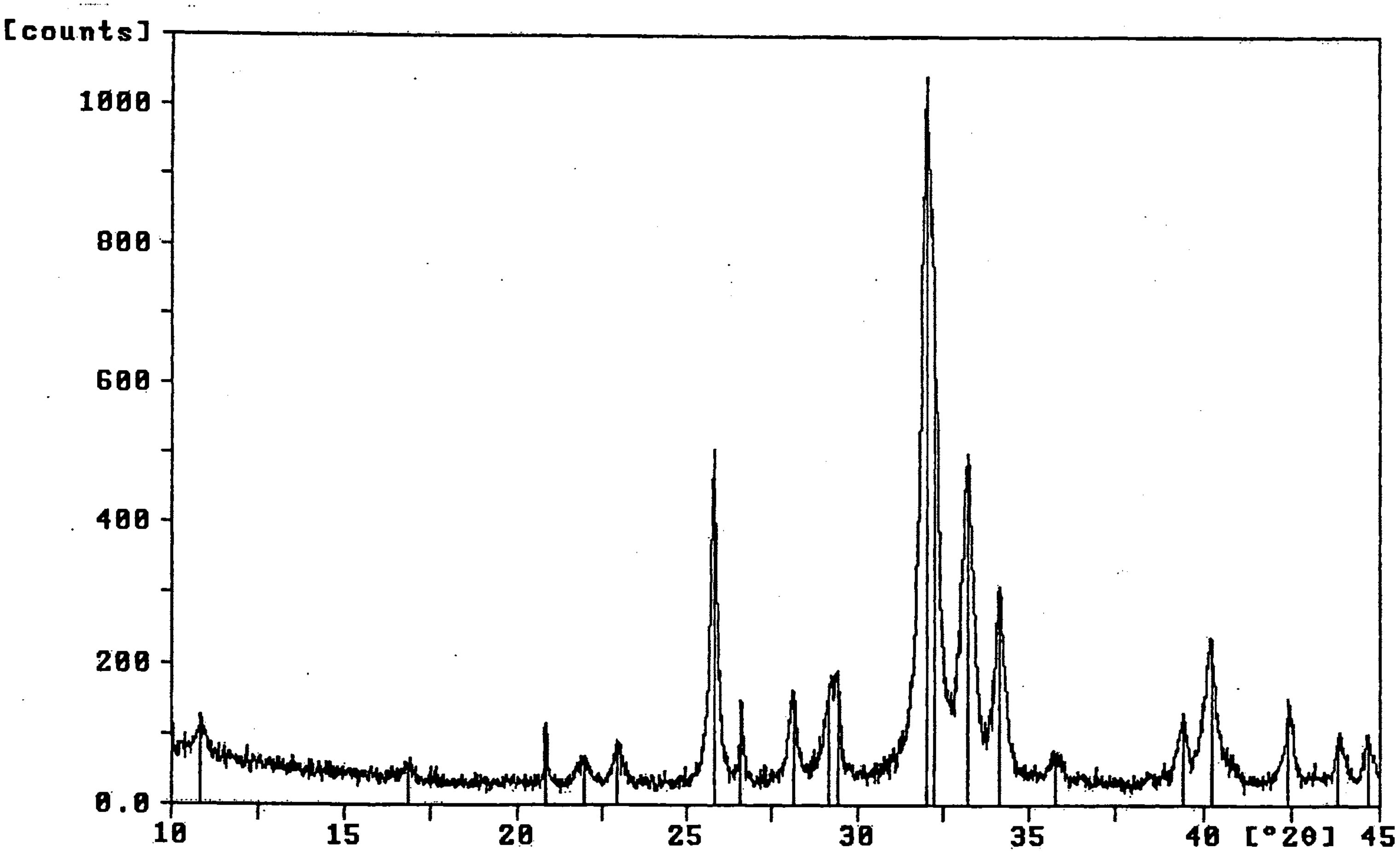

Figure 17. Rock phosphate (RP) amendment XRD pattern.

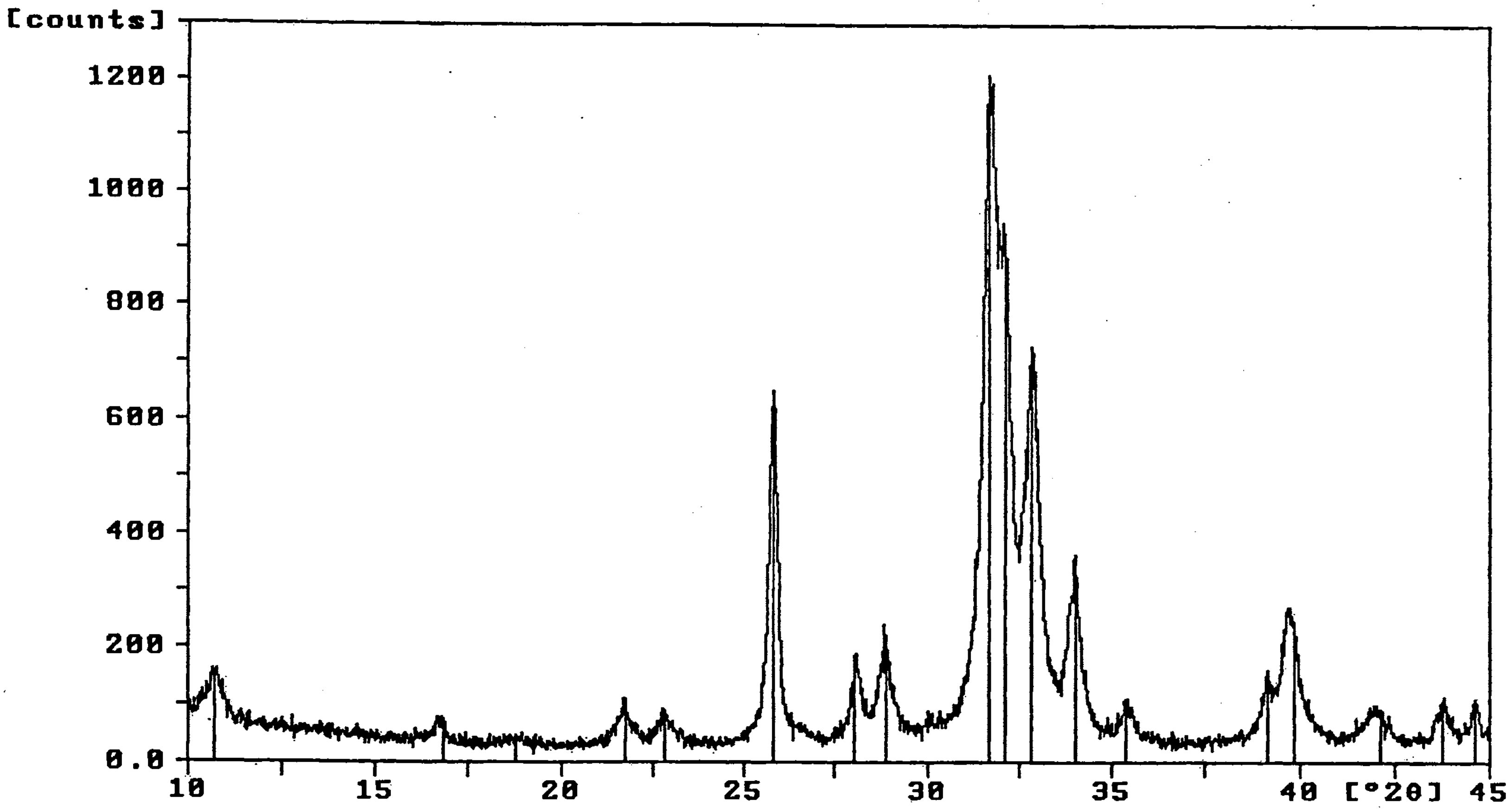

Figure 18. Hydroxyapatite (HA) amendment XRD pattern.

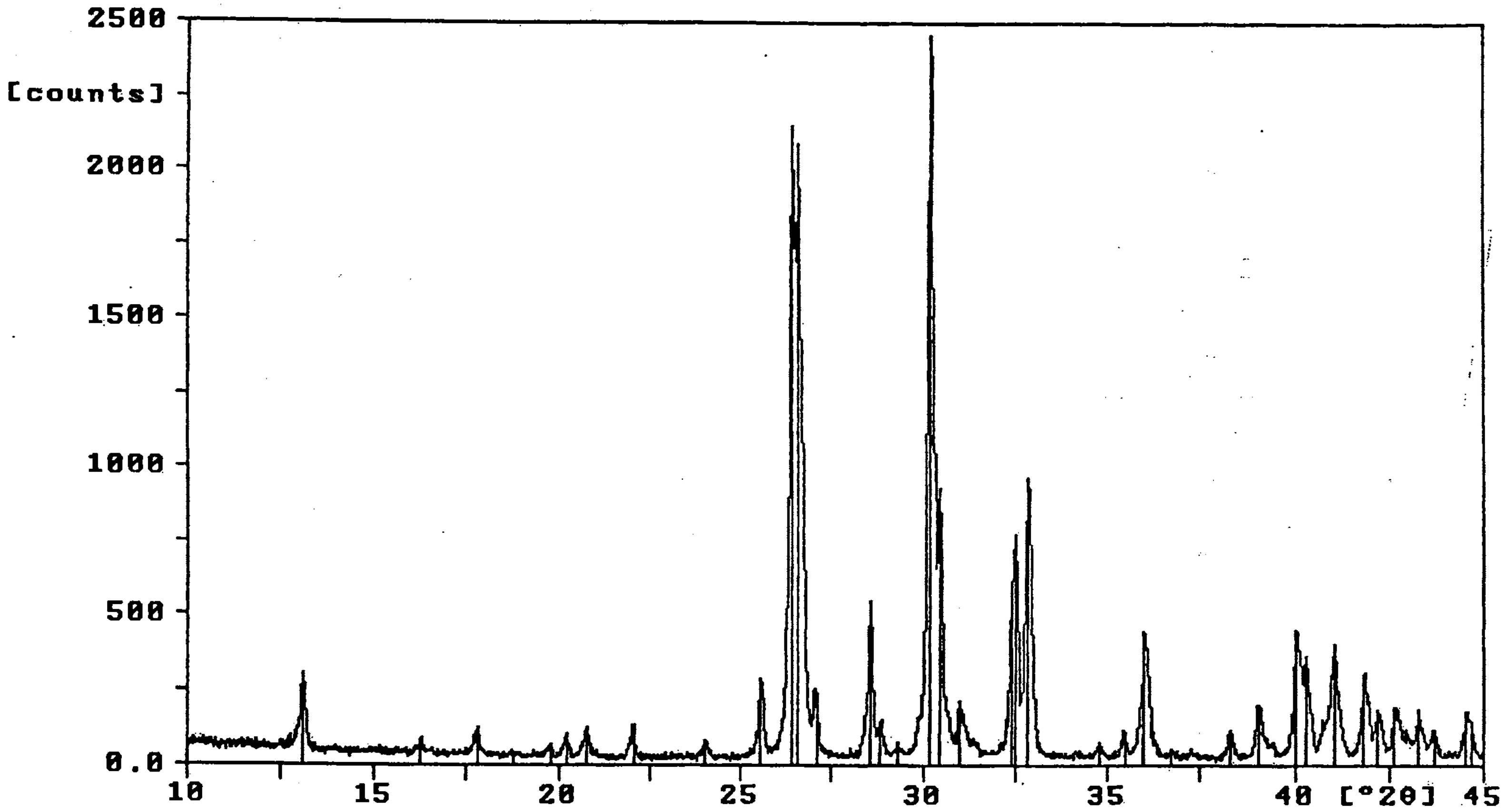

Figure 19. $CaHPO_4$ (CaP) amendment pattern

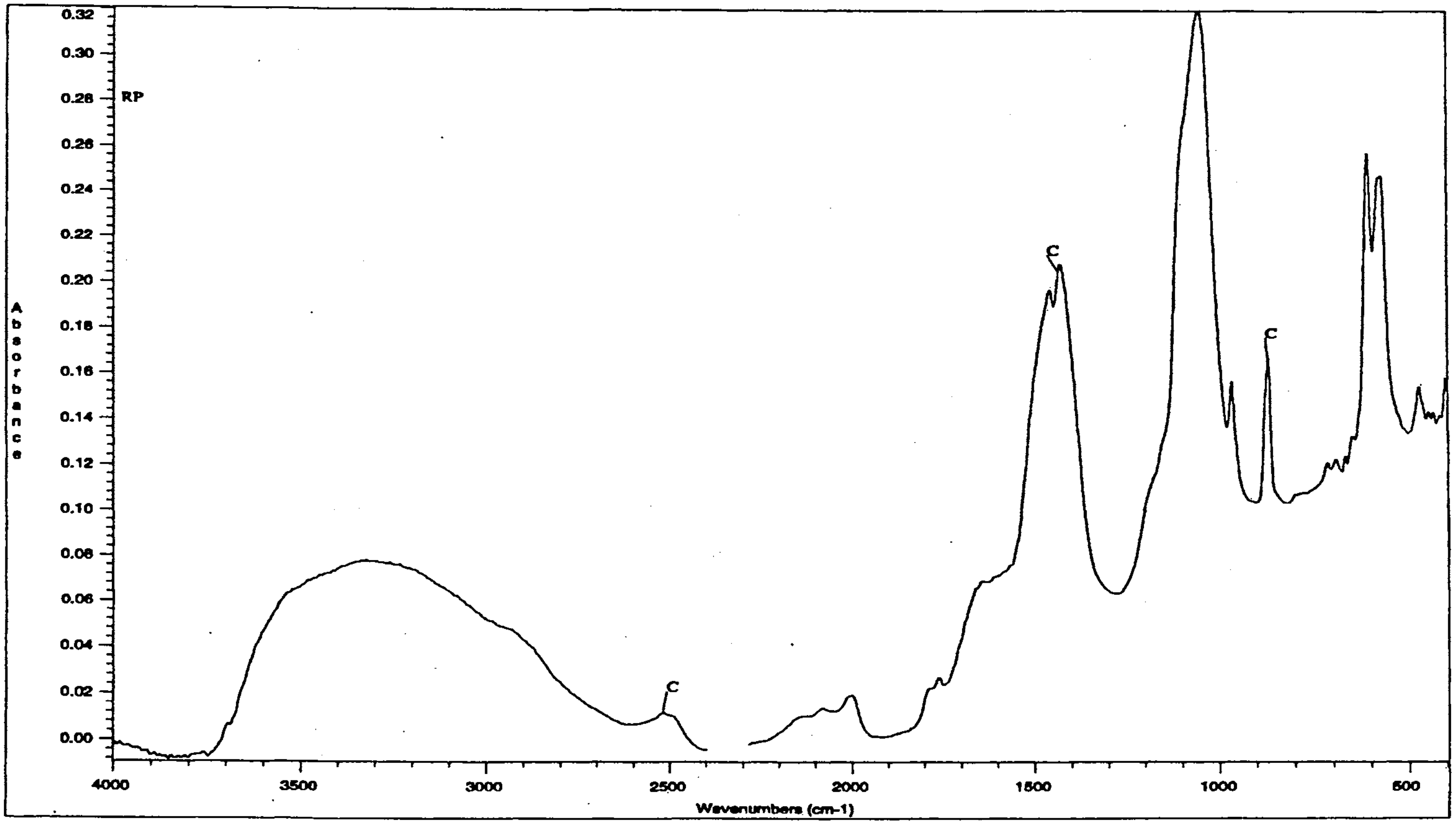

Figure 20. Rock phosphate (RP) amendment DRIFTS spectrum. C = carbonate

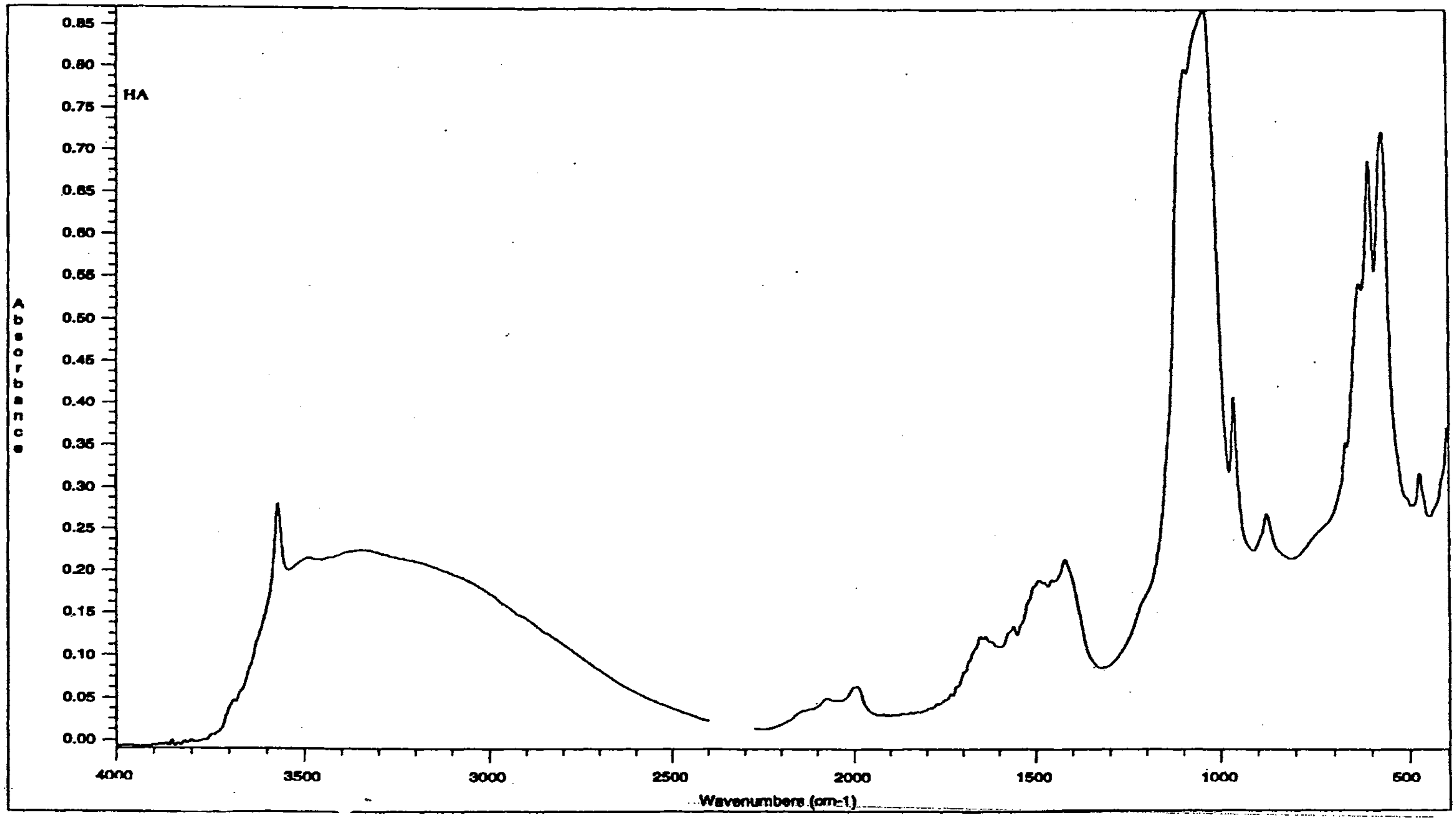

Figure 21. Hydroxyapatite (HA) amendment DRIFTS spectrum.

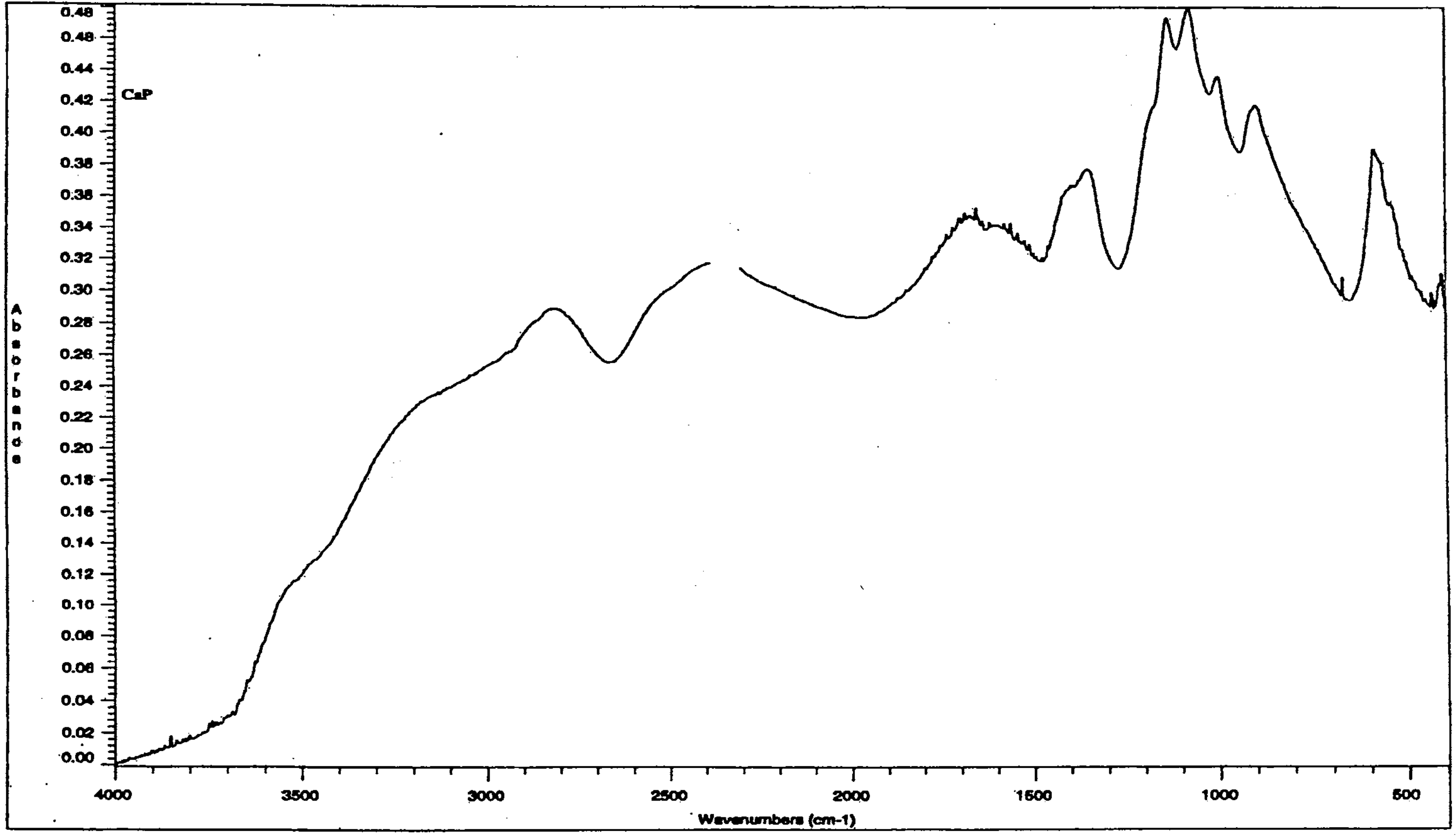

Figure 22. CaHPO$_4$ (CaP) amendment DRIFTS spectrum.

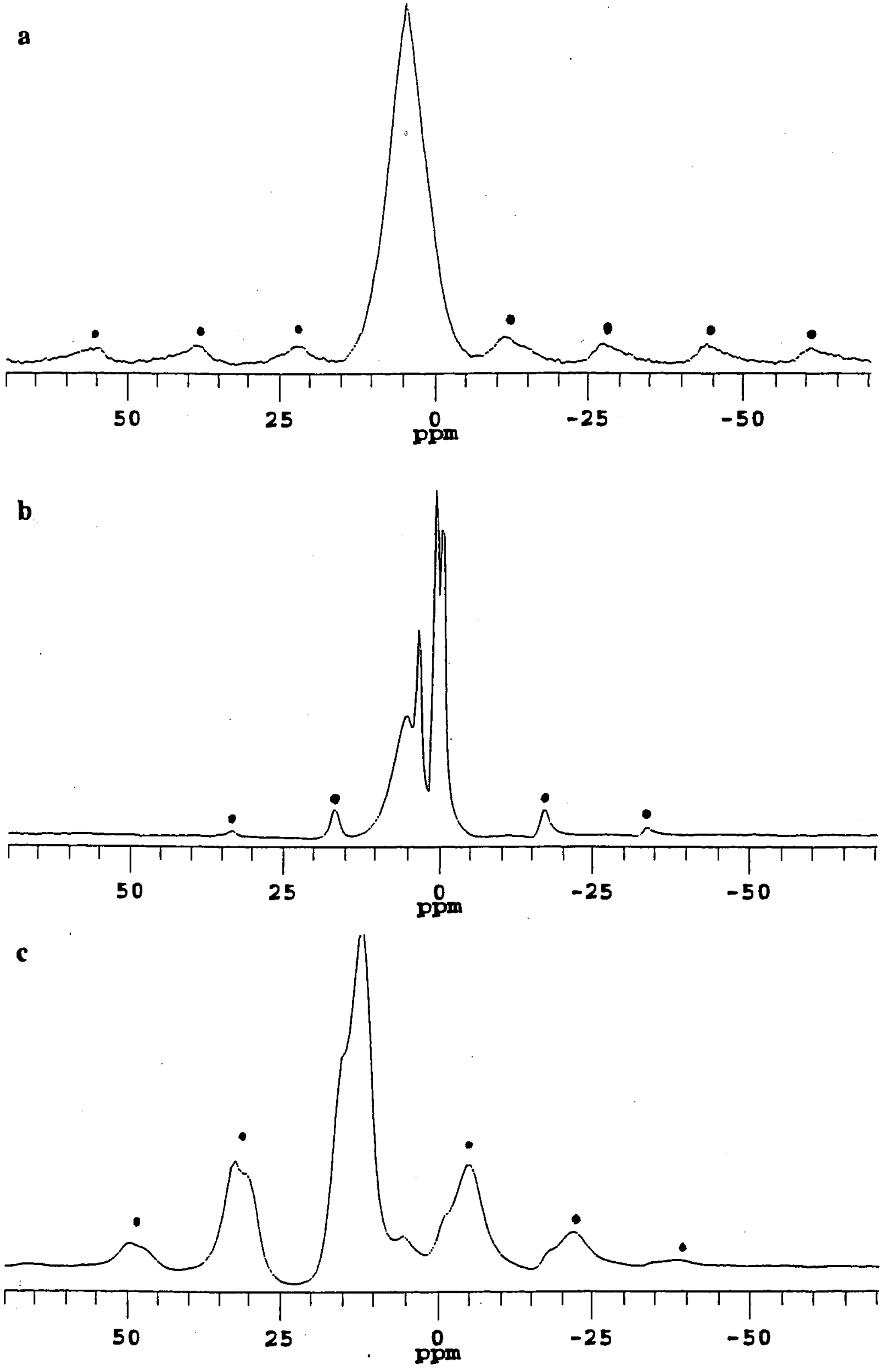

Figure 23. ^{1}H single pulse MAS NMR spectra of phosphate amendments (a) RP, (b) HA, and (c) CaP. • denotes spinning side bands.

CHAPTER IV

SEQUENTIAL EXTRATION SCHEME

A. Background

Soil is a complex, heterogeneous medium consisting of phases including mineral fragments, inorganic materials of differing degrees of stoichiometery and crystallinity and organic materials of poorly defined nature, and aqueous and gaseous components. These phases can exist separately, but are usually associated with one another as aggregates or coatings (i.e organic material coating the surface of mineral fragments). The total concentration of any elemental species can be dispersed between many components and bonded in a variety of different ways. In soils, metals are dissolved in the soil solution, held on inorganic constituents through sorption or exchange reactions, complexed with soil organic matter, or precipitated as pure or mixed phases.[1] Some of these phases may make the element "available", i.e. releasable to plants growing in the soil or to mobile ground water. The magnitude of this available fraction is of interest to agronomists and environmental scientists.

Much effort has been devoted to developing procedures which distinguish between the total heavy metal content of a soil and the fractions present in different forms.[2] Precise separation and identification of heavy metals in soils into all specific chemical forms is not possible with current analytical procedures. However, attempts have been made to partition solid phases into chemically similar forms through the use of sequential extractions with selective chemical reagents. There are no agreed divisions and the approaches have ranged from simple systems, which attempt to distinguish between residual and non-residual elements, to complex procedures with up to nine categories.[3] The most widely applied sequential extraction scheme is the five step scheme developed by Tessier.[4] The scheme uses 1 M $MgCl_2$, 1 M NaOAc (pH 5), 0.3 M $Na_2S_2O_4$ + 0.175 M Na-citrate, 0.02 M HNO_3 + 30 % H_2O_2, and HF + $HClO_4$. The scheme was designed to separate metals into five operationally defined fractions; exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual.[5]

The primary criticism of sequential extraction is the non-selectivity of the extractants.[6] The use of chemical reagents to extract a specific form of metal is not exact. It is probably more appropriate to say these reagents extract chemically similar forms. Redistribution of the metal between the variety of soil phases present may also occur during the extraction.[4]

A procedure of sequential extraction by specific reagents, though not exact, can provide useful qualitative estimates of the chemical forms of heavy metals in soils. Sequential extraction is currently the standard method used by soil scientists to characterize metals in soils and sediments.[4] In addition, sequential extractions conducted in conjunction with plant uptake studies have been used to estimate metal mobility and bioavailability.[7,8] Hence, sequential extraction can provide more useful information about heavy metals in soil than analyses of the total metal content.

B. Sequential Extraction Scheme

The sequential extraction scheme used is this study was developed by Basta, et al.[9] The solutions and conditions used for the sequential extraction are shown in Table 1.

The scheme consists of four successive extractions: an inert, weak electrolyte ($Ca(NO_3)_2$);, a weak acid (NaOAc); a complexing agent (Na_2EDTA); and a strong acid (HNO_3). Each extraction removes an increasingly less soluble species of metal from the soil. This scheme was developed based on extractability of metal soil phases. No efforts were made to select reagents to extract a specific geochemical pool and the extraction scheme does not significantly alter soil components until the fourth step. For example, many schemes employ a hydrogen peroxide step which destroys the organic matter present in soil though oxidation, or a citrate-dithionate step which solubilizes Fe and Mn containing hydrous oxides.[5] The designated chemical forms extracted by specific reagents listed in Table 1 are not meant to imply specific chemical forms of the metal, but are listed to designate the phases commonly suggested in the literature to be extracted in each step. Plant uptake studies conducted in conjunction with sequential extraction by Gradwohl have revealed that the metal extracted in the first step of this extraction scheme is correlated with plant uptake.[8]

The first extractant, $Ca(NO_3)_2$ was chosen for several reasons. It closely resembles salt inputs that can occur in natural systems and should cause the dissolution of sparingly soluble components.[2] Since $Ca(NO_3)_2$ has no buffering capacity, soil pH should be unaffected. Divalent Ca^{2+} containing salt was chosen because it should be effective at removing exchangeable divalent ions such as Pb, Cd, and Zn.[10] The nitrate salt was chosen because these ions do not normally interact with metal ions to form stable metal complexes. The 1 M NaOAc (pH 5) was chosen because it is commonly used as a single extractant to evaluate available concentrations of metals in soils. Reagents to evaluate contamination effects or available concentrations should ensure the release of all species of interest from secondary components without causing decomposition of any of the mineral fragments. Dilute acids have been shown to meet these requirements.[11] EDTA has the ability to form very stable water soluble complexes with a wide range of cations. In addition, EDTA has been shown to effectively complex ions bound to insoluble organic or inorganic surfaces.[10] The final step of the extraction uses 4 M HNO_3. This reagent is expected to extract metal occluded in the structure of non-silicate minerals and insoluble precipitates. Nitric acid will not solubilize metal occluded in the structure of silicate minerals, HF is necessary to release these metals.

C. Sequential Extraction of Model Compounds

Various Pb and Cd containing phases expected to occur in the soil-amendment system were prepared and processed through the sequential extraction scheme. The purpose of conducting these experiments was to determine if the scheme could differentiate between metals based on solubility and to get an idea of which step of the scheme would solubilize various metal phases. Preparation of the phases and experimental details of the extraction procedures are described in Chapter II. The correlations between extraction step and metal compound solubility are presented in Table 2. The complete sequential extraction data are presented in the Appendix, Tables A1 and A2. The model study demonstrated that more soluble model compounds are extracted early in the extraction scheme (steps 1 and 2), while less soluble compounds are extracted later (steps 3 and 4). This verifies that sequential extraction can be used to estimate the relative solubility of metal containing phases. For example, metals on clay surfaces would be readily exchangeable and extract in the first step; however, metal sulfides or metals coprecipitated with mineral phases would not be extracted until the fourth step. In addition, extraction data indicated different metals in similar phases do not always behave the same. For example, Cd associated with organic matter was extracted in the first and second steps, while Pb associated with organic matter was extracted in the third and forth steps. Finally, the data also verified what had been predicted by many researchers, the extractant solutions are not phase selective. Since a variety of phases can be extracted in a single step, the scheme is not phase selective. In addition, no single phase was completely extracted in any one step. Partial extraction of a metal from a discrete compound was observed in every analysis. Although the majority of a particular material was extracted in one step of the scheme, a certain portion of material was also solubilized in other steps

The results of this study verify that the sequential extraction scheme can be used to differentiate between metal phases based on differences in solubility. Because the goal of in situ chemical immobilization is to remediate a contaminated soil by reducing the solubility of the metals in the soil, sequential extraction is an ideal technique to evaluate the effectiveness of the amendments.

D. References

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Table 1. Experimental conditions and chemical forms of heavy metal determined by sequential extraction.[12]

Extraction Sequence	Chemical Extractant	Extraction Conditions	Chemical Form of Metal Extracted	Plant Availability
1	0.5 M $Ca(NO_3)_2$	shake 16 h	Soluble, Exchangeable	readily
2	1.0 M NaOAc, pH 5	shake 5 h	weakly complexed carbonate precipitates "acid-labile"	potential
3	0.1 M Na_2EDTA, pH7	shake 6 h	complexed/surface precipitaes with oxides/ organic matter	unavailable
4	4 M HNO_3	shake 16 h, 80° C	occluded insoluble precipitates	highly unavailable

Table 2. Summary of major extraction step for model compounds.

Metal Form	Major Extraction Step	Solubility and Mobility
Mineral:		
Clay-exchange(pH4)	1	High
Clay-surface precipitate(pH10)	2	High
Hydrous Oxide-exchange	3&4	Low
Hydrous Oxide-coprecipitate	4	Low
Organic:		
Cd Phthalate	2	High
Humic Acid-Cd	1&2	High
Humic Acid-Pb	3&4	Low
Inorganic:		
Phosphate	3	Low
Carbonate	3	Low
Sulfide	4	Low

CHAPTER V

AMENDMENT EVALUATION

A. Background

In recent years, sequential extraction techniques have become the standard method to characterize metal phases in soils and sediments. In Chapter IV, it was shown that sequential extraction allows an estimation of soluble metal phases in soils and can be correlated with metal mobility and bioavailability. In-situ chemical immobilization treatments attempt to remediate metal contaminated soils by reducing the solubility of metals in soils. Since sequential extraction provides a method to quantify and differentiate between metals in soil based on solublity, it is an ideal tool to evaluate the effectiveness of amendments. Both single[1-5] and sequential[5-9] extraction schemes have been widely applied to evaluate the effectiveness of in situ chemical immobilization treatments. In a comparative study, a change in the distribution of metal among the fractions of the sequential extraction scheme in a control versus an amended soil provides evidence for a chemical transformation resulting in a reduced solubility of the metal. An ideal amendment would eliminate the metal extracted in the early steps of the extraction scheme and convert it to a form which is not extracted until the later steps of the extraction scheme.

Metals extracted by salt solutions, such as $Ca(NO_3)_2$, are highly soluble and therefore very mobile and bioavailable. Plant uptake studies conducted by Gradwohl verified that the metal extracted in the first step of the extraction scheme used in this study is correlated with plant uptake.[10] The metals extracted by weak acid solutions, such as acetic acid, are less soluble than those extracted by neutral salt solutions; however, still have a high potential to be solubilized as the more soluble metals are leached or taken up by plants. The U.S. EPA Toxicity Characteristic leaching Procedure (TCLP), which involves extraction with dilute acetic acid, is used to predict the potential hazard or toxicity associated with a metal contaminated material.[11] Both neutral salt solutions and dilute acids extractions have been used to evaluate amendment effectiveness.[4,5]

For the purpose of this study, amendment effectiveness was defined based on a reduction in the metal extracted in the first and second steps of the sequential extraction scheme. The sum of the metal extracted in the first and second steps was termed "bioavailable metal". The sum of the first and second steps was chosen because these two fractions represent the most readily extractable metal forms and are expected to present the greatest threat to the surrounding environment. The most effective amendments caused the greatest reduction in bioavailable metal. Acceptable amendments reduced the amount of metal extracted in the first step and transformed it to a form extracted in the second step. Ineffective amendments did not reduce the available metal. It is possible that the reduction in the bioavailable metal could be attributed to the attenuation of the metal concentration by dilution of the soil with the amendment. In situations where the reduction in bioavailable metal approached that expected based on dilution, amendments were still considered effective, if the decrease in metal content of one of the steps was greater than that which could be explained by dilution or an increase in metal extracted in steps three or four was observed.

This remediaiton study was divided into two parts. The first part, described in section B, compared the effectiveness of phosphate, organic, and/or alkaline amendments for the remediation of Cd, Pb, and Zn in smelter contaminated soils. The second part, described in section C, compared the effectiveness of three phosphate amendments of varying solubility for the remediation of Cd, Pb, and Zn in smelter contaminated soils.

B. Evaluation of Phosphate, Organic, and/or Alkaline Amendments

1. Background

In the first remediation study, the effectiveness of four amendments (LS, NV, RP, SS) on three soils (BW, H12, and B4) was investigated. The soils and amendments were mixed and stored at field moisture capacity for twelve weeks. The experimental details of the remediation process were described in Chapter II. Detailed descriptions of the soils and amendments were presented in Chapter III.

2. Metal Distribution in Control Soils

The results of the sequential extraction experiments for the BW, H12, and B4 control soils are presented in Figure 1. The sequential extraction results revealed that the Cd, Pb, and Zn were more soluble in the BW soil than in the H12 and B4 soils. This was evidenced by the greater fraction of metal solubilized in steps one and two (bioavailable metal) for the BW soil. The sequential extraction results for the BW soil reveal that greater than 65 % of the Pb and Zn, and greater than 90 % of the Cd were extracted in steps one and two (bioavailable metal). The sequential extraction results for the H12 and B4 soils reveal that the metals are less soluble in these soils than in the BW soil. The majority of the Cd, greater than 70 %, was extracted by steps one and two; however, only 25 % of the Pb and 40 to 45 % of the Zn were extracted by steps one and two.

The sequential extraction studies support the assertion that the total metal content of a soil does not necessarily reflect the risk associated with the soil. For Cd, the BW soil contains the highest level of total contamination and the highest level of soluble Cd. However, for Pb and Zn, the situation is not the same. Although the B4 soil contains 2.5 times the total Pb of the BW soil, both soils have similar contents of soluble metal. A similar situation occurs for Zn. Although the H12 soil contains twice the total Zn of the B4 soil the amount of Zn extracted in step one is essentially the same for both soils. Even more dramatic, the BW soil contains 40 % less total Zn than the H12 soil, but over twice the amount of soluble Zn.

The sequential extraction studies revealed that all three soils were candidates for in-situ immobilization due to the presence of soluble forms of metal in these soils. The BW soil is the most promising candidate due to the greater fraction of soluble metal present in this soil.

3. Sequential Extraction Results for Remediation Study

The results of the sequential extraction analyses for Cd, Pb, and Zn extracted in steps one and two are presented in Tables 1 to 3. The complete sequential extraction data are presented in the Appendix, Tables A3 to A5. The results observed for each metal will now be discussed.

a. Cadmium

For Cd, the amendment effectiveness follows the order SS = RP > LS = NV. The results of the sequential extraction analyses for Cd in steps one and two for the control soils are presented in Table 1.

Table 1. Sequential extraction results for Cd in steps one and two.

	Cd (mg/kg soil)								
	BW			H12			B4		
	Step1	Step2	Step1+2	Step1	Step2	Step1+2	Step1	Step2	Step1+2
Con	186	83	269	23	42	65	24	52	76
LS	33	206	239	7	50	57	7	63	70
NV	20	215	235	5	53	56	5	65	70
SS	93	104	197	20	36	56	21	45	66
RP	98	83	181	19	36	55	20	53	73

The LS and NV amendments were most effective in reducing soluble metal (step one). Reductions of up to 90 % were observed for each soil. However, this decrease was accompanied by an increase in potentially available metal (step two), which reduced the overall effectiveness of these amendments for reducing the bioavailable Cd. An increase in the Cd extracted in steps two and three was observed for all three soils with each amendment.

The SS amendment was effective in reducing bioavailable Cd for each soil. Reductions of 27, 14 and 12 % were observed for the BW, H12, and B4 soils, respectively. An increase in the Cd extracted in step three was observed for all three soils.

The effectiveness of the RP amendment varied from soil to soil. For the BW soil, the RP amendment was most effective, resulting in a 33 % reduction in bioavailable Cd. This reduction was accompanied by an increase in the Cd extracted in both steps three and four of the extraction scheme. For the H12 soil, the RP amendment reduced the bioavailable metal by 14 %. This reduction was accompanied by an increase in the metal extracted in step three. Although the reduction in available metal due to the RP amendment was low for the B4 soil, the amendment was still considered to be effective because an increase in the metal extracted in step three was observed.

b. Lead

For Pb, the amendment effectiveness was generally, SS > LS > RP > NV. The amount of soluble Pb (step one) present in all three soils was low, therefore, reductions in bioavailable metal resulted mainly from reductions in potentially available Pb (step two). The results for the sequential extraction analyses for Pb in steps one and two for the control and amended soils are presented in Table 2.

Table 2. Sequential extraction results for Pb in steps one and two.

	Pb (mg/kg soil)								
	BW			H12			B4		
	Step1	Step2	Step1+2	Step1	Step2	Step1+2	Step1	Step2	Step1+2
Con	5.4	253	258.4	5.1	653	658.1	1.3	226	227.3
LS	0.6	158	158.6	0.8	461	461.8	0.7	171	171.7
NV	0.1	232	232.1	0.4	577	577.4	0.8	211	211.8
SS	3.4	137	140.4	5.4	388	393.4	1.6	150	151.6
RP	3.7	184	187.7	4.3	564	568.3	1.4	235	236.4

The SS amendment was the most effective in reducing the bioavailable Pb, reductions in bioavailable Pb of 45, 40, and 35 % were observed for the BW, H12, and B4 soils, respectively. The LS amendment was also effective in reducing the bioavailable Pb. Reductions in bioavailable Pb of 38, 40, and 24 % were observed for the BW, H12, and B4 soils, respectively. The LS amendment was more effective in reducing the soluble Pb, and the SS amendment was more effective in reducing the potentially available Pb. Both the LS and SS amendment converted the bioavailable metal to a form which was not extracted until step three of the sequential extraction scheme for all three soils.

The RP amendment was effective for BW and H12 soils. The bioavailable Pb was reduced by 27 and 14 % for the BW and H12 soils, respectively. The RP amendment was not effective for the B4 soil, as no reduction in bioavailable Pb was observed. For the BW soil, the RP amendment resulted in an increase in the metal extracted in step three. This was not observed for the H12 soil.

The NV amendment was not effective for any soil. The observed decrease in the Pb extracted in steps one and two approached that expected based on dilution of the soil with the amendment, and no increases in the metal extracted in the third or forth step of the extraction were observed.

c. Zinc

For Zn, the amendment effectiveness followed the order, LS = NV > RP, SS. The results for the sequential extraction analyses of Zn in steps one and two for the control and amended soils are presented in Table 3.

Table 3. Sequential extraction results for Zn in steps one and two.

	Zn (mg/kg soil)								
	BW			H12			B4		
	Step1	Step2	Step1+2	Step1	Step2	Step1+2	Step1	Step2	Step1+2
Con	1090	6781	7871	472	9176	9648	492	2663	3155
LS	84	6754	6838	86	7906	7992	64	2564	2628
NV	20	6666	6686	27	7977	8004	23	2605	2628
SS	1200	5930	7130	757	7224	7981	543	2195	2738
RP	740	6247	6987	407	8368	8775	434	2595	3029

The LS and NV amendments reduced bioavailable Zn for all three soils by 15 to 17 %. The LS and NV amendments were most effective at reducing the soluble Zn extracted in step one. Reductions of up to 90 % in soluble Zn were observed for each soil. For the H12 soil, reductions in the potentially available Zn were also observed for the LS and NV amendments. In the case of the BW soil, an increase in the Zn extracted in step three was observed for both the LS and NV amendments. No increase in the Zn extracted in the third or forth steps was observed for the H12 or B4 soils. A possible explanation for this observation was related to the relative increase expected in these fractions for the different soils. For the BW soil the decrease in metal from steps one and two would result in a 25 % increase in the amount of metal extracted in steps three or four. However, for the H12 and B4 soils only a 10 % increase in the metal extracted in steps three or four would be expected.

The SS amendment was effective in reducing bioavailable Zn. However, for the SS amendment, the soluble Zn (step one) was increased while the potentially available Zn (step two) was reduced. The SS amendment was most effective at reducing potentially available Zn. The reduction in Zn extracted in step two was 13, 21, and 18 % for the BW, H12, and B4 soils, respectively. An increase in the Zn extracted in step three of the sequential extraction scheme was observed for all three soils.

The effectiveness of the RP amendment varied from soil to soil. When comparing the three soils, the RP amendment was most effective for the BW soil. A 32 % reduction in metal extracted in step one was observed for the BW soil. In addition, an increase in the Zn extracted in step three of the sequential extraction scheme was observed for the BW soil. For the H12 soil, the apparent effectiveness of the RP amendment approaches that which could be explained by dilution; however, an increase in the amount of metal extracted in step three was observed indicating an immobilization reaction did occur. The RP amendment was not effective for the B4 soil. The decrease in available Pb approached that expected based on dilution, and no increase in Pb extracted in steps three or four was observed.

4. Conclusions of Greenhouse Study

The sequential extraction study revealed that the concept of remediating smelter contaminated soils using in-situ chemical immobilization is valid. In general, when amendments were added to the soils, the amount of metal extracted in steps one or two decreased and the amount of metal extracted in steps three or four increased. Similar observations have been reported in the lieterature.[5-7] These results indicate that the amendments react with the metals present in the soils to form phases that are less soluble. However, the data also revealed that complex reaction chemistry was occurring when amendments were added to the soils. This was evidenced by the fact that each metal responded differently to a particular amendment, and each soil was effected differently by each amendment.

a. Amendment effectiveness by soil

Overall, the amendments were most effective on the BW soil. The order of effectiveness was BW > H12 > B4. This could be correlated with the relative solubilities of the metals in the control soils. The BW soils contained a greater percentage of Cd, Pb, and Zn in the available fractions to begin with. Additionally, other soil properties may be related to the effectiveness of the amendments.

The soil pH at the completion of the twelve week remediation process for the control and amended soils are summarized in Table 4. Soil pH is one of the most important variables controlling metal solubility on soils.[12] The BW soil has a lower initial pH (6.8) than the H12 or B4 soils (7.1). In addition, at the completion of the incubation reactions, the pH of the BW (8.2/8.3) soil treated with limed amendments was higher than the H12 (7.5/7.9) or B4 (7.9/8.2) soil pH. Since the pH of the BW soil was lower initially and higher after amendments had been added to the soil, the effects of pH on the mobility of metals in the BW soil amended with LS and NV would be greater than those for the H12 and B4 soils and may explain the increased effectiveness of the amendments with the BW soil.

Another possible explanation for the increased effectiveness of the amendments for the BW soil is related to the organic matter content of the soils. As presented in Chapter III, the BW soil also has a much lower organic matter content than the H12 or B4 soils. With this in mind, the addition of an amendment containing organic material (LS, NV, SS) would be expected to be more effective on a soil with a lower organic matter content.

b. Amendment effectiveness by metal

The most significant changes in metal distribution were observed for Cd and Zn. The metal distributions determined by sequential extraction for the control soils showed that Cd and Zn were more soluble than Pb in the soil initially. For Cd and Zn, up to 185 and 1090 mg/kg soil are extracted in step one, respectively. However, for Pb, the maximum amount of Pb extracted in step one was only 5 mg/kg soil. The increased effectiveness of the amendments for Zn and Cd may be attributed to the fact that these metals were more soluble in the soil initially. Amendments designed to reduce metal solubility would be expected to have the greatest impact on the soluble metal in the soil (metal extracted in step one). The lower solubility of Pb in the soil initially would make reductions in its solubility less dramatic.

For Zn and Cd, alkaline amendments, such as LS and NV, had similar effectiveness on metal solubility. For Pb, the LS and NV amendments did not behave similarly; however, the LS and SS amendments were equally effective at reducing Pb solubility. As discussed in Chapter III, the common feature of the LS and NV amendments was their high carbonate content; the common feature of the LS and SS amendments was their organic matter contents. These results indicate that for Pb, the organic matter content of the amendments seemed to have a greater impact on the effectiveness than the liming capacity. This trend is supported by literature studies which have demonstrated that Pb forms more stable metal-organic complexes than Cd or Zn.[13,14] The alkaline amendments provide the most straight forward evidence of changes in metal distribution for Cd, the metal extracted in step one was reduced concurrent with an increase in the metal extracted in step two for all three soils.

c. Amendment evaluation by amendment

Although all of the amendments were effective in reducing metal solubility, the effectiveness of the amendments varied and the mechanisms of immobilization were probably different. The LS and NV amendments were most effective in reducing bioavailable Cd and Zn. The reason could be related to the fact that these amendments combine two in-situ immobilizers, alkaline and organic materials. The alkaline components of the amendment raise the soil pH leading to decreased metal solubility through metal adsorption and precipitation. The organic material decreases metal solubility by binding metals through cation exchange or the formation of metal-organic complexes.[15] The LS and NV amendments produced Cd phases that are extracted in steps two and three, as opposed to step one, and in step three as opposed to steps one and two. A similar trend was reported by Mench, et al., who observed a decrease in the

$Ca(NO_3)_2$ extractable Cd, but no decrease in the NaOAc extractable Cd when alkaline amendments were used.[5] Alkaline amendments raise the soil pH and were more effective than the non-alkaline amendments at reducing the soluble metal for each metal in each soil. In general, alkaline amendments transfer metal solubility for Cd from the $CaNO_3$ to the NaOAc step of the extraction scheme. The LS and NV amendments effectiveness was due to the increase in soil pH that resulted upon their addition to the soil.

The SS amendment was more effective at reducing the metal extracted in step two than step one. The addition of the SS amendment to the soils resulted in the formation of Cd, Pb, and Zn phases that were extracted in step three instead of step two. Pierzynski reported a similar trend when amending soils with manure.[7] In that study, alkaline amendments were more effective at reducing the metal extracted by neutral salt solutions, but the manure amendments were more effective at reducing the metal extracted in the later steps of the extraction scheme. For Zn, an increase in the metal extracted in step one was observed for each soil upon addition of the SS amendment. The increase in soluble Zn observed for the SS amendment may be explained by the slight decrease in soil pH (Table 4) or an increase in the soluble organic matter in the soil resulting from the addition of the amendment to the soil.

The RP amendment produces Cd, Pb, and Zn phases that are extractable in steps three and four, as opposed to steps one and two. Ma also reported a transformation of metal solubility from the $Ca(NO_3)_2$ and NaOAc extractable forms to the EDTA extractable form.[4] The RP amendment did not effect soil pH (Table 4). This observation indicates that the effectiveness of the RP amendment was not due to pH effects

4. Soil Acidification

Acid rain and natural soil weathering processes result in a lowering of soil pH with time. For an amendment to be effective over the long term in the field, the metal immobilized by the treatments must remain immobilized when the pH of the soil lowers. Acidification studies of the amended soils conducted by Gradwohl were designed to evaluate the long term effectiveness of the amendments.[10]

During the acidification study, soil pH was lowered to 6, 5.5, and 4 by the addition of 1 M HNO_3 to a 1:2 soil to water slurry. Subsequently, the soils were processed through the sequential extraction procedure to determine the effects of lowering the soil pH on the distribution of the metals in the soils. These soil acidification studies revealed that metal immobilized by the LS, NV, and SS amendments was re-solubilized and extracted in the first step of the sequential extraction scheme. However, the species formed on reaction with the RP amendment resist conversion of the immobilized metal to more soluble species.

The results of the soil acidification study are supported by Chen, et al., who showed that HA was very effective in retaining Pb and moderately effective at retaining Cd and Zn at pH 4 to 5.[16] Their desorption experiments showed that 100 % of the Pb was retained as the pH was lowered and only 14-23 % and 7-14 % of the Cd and Zn were mobilized as the pH was lowered. In a six month study conducted by Chlopecka,[8] the effectiveness of lime for reducing soluble Zn in artificially contaminated soils decreased with time to a greater extent than RP amended soils.

These studies suggest that, under field conditions, the RP amendment would be the most effective because it is stable to changes in soil pH. These results may have been predicted based on the final pH of the amended soils. The LS and NV amendments often resulted in the greatest decrease in bioavailable metal; however, they also resulted in the greatest increase in soil pH. The RP amendment was effective in reducing metal solubility; however, this was not accompanied by an increase in soil pH for this amendment.

Due to the inability of the biosolids and alkaline amendments to retain their immobilization efficiencies as soil pH was lowered, these substances were abandoned as potential amendments. The focus of the study turned to phosphate amendments. The acidification study further corroborates the necessity of understanding the chemistry occurring during in incubations.

C. Evaluation of Phosphate Amendments

1. Background

For the second remediation study, the effectiveness of three phosphate amendments (RP, HA, CaP) on four soils (BW(b), H12(b), S5, C1) were investigated. A two week slurry experimental approach was selected to evaluate the amendments. The experimental details were presented in Chapter II. Detailed descriptions of the soils and amendments were presented in Chapter III.

A slurry remediation process was chosen to facilitate the evaluation of the amendments in a shorter period of time. The immobilization reactions that are proposed to occur during in situ immobilization by phosphates, precipitation, ion exchange and surface adsorption, occur in solution, between soluble metal contaminants and solubilized amendment, or at the solid-solution interface, between a soluble metal contaminant and a solid amendment.[17] The increased soil solution volume increases the possibility of both of these reactions and may decrease mass transport limitations.[18]

Literature references have indicated that the solubility of phosphate amendments determine their effectiveness for in situ immobilization. Ma showed that hydroxyapatite was six times more effective at reducing aqueous Pb concentrations than rock phosphate.[2] In a separate study, Ma showed that $CaHPO_4$ was even more efficient than HA at removing aqueous Pb from solution, in both cases the XRD of the solid residues revealed the presence of pyromorphite, ($Pb_5(PO_4)_3OH$).[19] Based on these studies it has been predicted that more soluble phosphate amendments would be more effective at reducing metal mobility in soils. However, no studies have been published which directly compare the effectiveness of these three phosphate amendments at reducing metal solubility on the same soil. This study represents the direct comparison the effectiveness of RP, HA, and CaP for reducing metal solubility in contaminated soils.

2. Metal Distribution in Control Soils

The results of the sequential extraction analyses for the BW(b), H12(b), S5, and C1 soils are presented in Figure 2. For the BW(b) soil, the percentage of bioavailable metal was much greater than that of the other soils. The percentage of bioavailable metal is 72 % for Cd and 45 % for Pb and Zn. Due to the large portion of metal present in the bioavailable fractions, the BW(b) soil is an ideal candidate for in-situ chemical immobilization. For the H12(b) soil, the available fraction of the metals were similar to those for the BW(b) soil, except, the bioavailable Pb was much lower, accounting for only 24 %. For the S5 soil, the metal contaminants were only slightly available. The bioavailable Cd, Pb, and Zn account for 22, 8.7, and 9.3 % of the total metal respectively. Although the bioavailable Pb only accounted for 8.7 % of the total metal, the extremely high total Pb content of the soil still makes it a candidate for in-situ immobilization. The initial distribution of the metals in the C1 soil demonstrated that the metals in the soil are not soluble. Approximately 90 % of the Cd and Zn, and 99 % of the Pb remain insoluble until the fourth step of the extraction scheme. The C1 soil would not be a candidate for in-situ chemical immobilization.

These data show that total metal content is not a good measure of metal availability.[12] These results bear out the importance of determining the solubility of metal contaminants before choosing a remediation strategy

3. Sequential Extraction Results of Remediation Study

The results of the sequential extraction analyses of Cd, Pb, and Zn for steps one and two of the control and amended soils are presented in Tables 5 to 7. The complete sequential extraction data are presented in the Appendix, Tables A6 to A8. The results observed for each metal will now be discussed.

a. Cadmium

Table 5. Sequential extraction results for Cd in steps one and two.

	Cd (mg/kg soil)											
	BW(b)			H12(b)			S5			C1		
	Step1	Step2	Step1+2	Step1	Step2	Step1+2	Step1	Step2	Step1+2	Step1	Step2	Step1+2
Con	225	88	313	23	57	80	4.1	35.3	39	1.5	0.7	2.2
RP	57	85	142	14	48	62	3.7	30.3	34	0.3	0.9	1.2
HA	44	111	156	7	50	57	2.3	37.7	40	0	0.5	0.5
CaP	55	121	177	17	51	68	3.6	28.6	32	0.2	0.6	0.8

For Cd, the phosphate amendments were clearly effective when there was a substantial amount of soluble Cd, as evidenced for the BW(b) soil. For the BW(b) soil, the RP amendment was the most effective, reducing bioavailable Cd by 55 %. The HA and CaP amendments were effective at reducing the metal extracted in step one; however, this decrease was accompanied by an increase in the amount of metal extracted in step two which reduced the overall effectiveness of these amendments. All three treatments resulted in an increase in the amount of Cd extracted in step three. For the H12(b) and S5 control soils, the amount of Cd extracted in steps one and two was much lower than that of the BW(b) control soil and the differences in amendment effectiveness were minimal. Based on a reduction in bioavailable Cd, the HA amendment was the most effective for the H12(b) soil and the CaP amendment in the most effective for the S5 soil. For the C1 soil, essentially no Cd was present in the available fraction, therefore amendment effectiveness could not be evaluated for this soil.

b. Lead

Table 6. Sequential extraction results for Pb in steps one and two.

	Pb (mg/kg soil)											
	BW(b)			H12(b)			S5			C1		
	Step1	Step2	Step1+2	Step1	Step2	Step1+2	Step1	Step2	Step1+2	Step1	Step2	Step1+2
Con	27.6	643	670.6	4.5	740	745.5	2.5	1344	1347	0.1	5.1	5.2
RP	3.9	335	338.9	1.9	509	510.9	1.6	860	861.6	0	3.1	3.1
HA	1.4	85	86.4	0.1	169	169.1	0.5	340	340.5	0	2.4	2.4
CaP	4.0	310	315	3.4	519	522.4	0.9	671	671.9	0	4.7	4.7

The HA amendment was the most effective at reducing the bioavailable Pb. Reductions of 87, 77, and 74 % of the available Pb were observed for the BW(b), H12(b), and S5 soils. An increase in the amount of Pb extracted in the third and fourth steps of the extraction scheme was observed for all three soils. The RP and CaP amendments resulted in similar reductions of bioavailable Pb for the BW(b) and H12(b) soils, 50 and 30 % respectively. However, for the S5 soil, the CaP amendment was more effective than the RP amendment, decreasing the bioavailable Pb by 50 versus 36 %. For the BW(b) soil amended with RP and CaP, an increase in the amount of Pb extracted in step three was observed. For the H12(b) soil and increase in the Pb extracted in step four was observed for the CaP amendment. No increase in Pb extracted in the third or fourth steps is observed for the S5 soil amended with HA or CaP. This could be attributed to the high concentration of Pb already present in the third and fourth fractions for the S5 soil. Based on the reduction of Pb from steps one and two with the S5 soil, only a 3 % increase in metal extracted in the third and fourth steps would be expected. For the C1 soil, the amount of Pb extracted in steps one and two was very low. Evaluation of the relative effectiveness of the amendment for immobilizing Pb was not possible for this soil.

c. Zinc

Table 7. Sequential extraction results for Zn in steps one and two.

	Zn (mg/kg soil)											
	BW(b)			H12(b)			S5			C1		
	Step1	Step2	Step1+2	Step1	Step2	Step1+2	Step1	Step2	Step1+2	Step1	Step2	Step1+2
Con	4899	11883	16782	495	9674	10169	7.1	457	464	89	17.3	106
RP	640	10507	11147	300	8465	8765	6.4	383	389	8.6	18.4	27
HA	938	14021	14959	182	8197	8379	2.4	321	324	3.3	5.4	9
CaP	481	9530	10011	367	8562	8929	7.7	341	349	14	17.2	31

The HA amendment was the most effective in reducing the soluble Zn for the H12(b), S5, and C1 soils. Reductions of 18, 30, and 92 % were observed for the H12(b), S5, and C1 soils, respectively. In each case, an increase in the amount of Zn extracted in the third step of the extraction scheme was observed. For the BW(b) soil, the HA amendment was the least effective, reducing bioavailable Zn by only 11 %. The HA amendment was effective in reducing soluble Zn, however, an increase in the amount of Zn extracted in step two, reduced the overall effectiveness of the HA amendment for the BW(b) soil. The Zn was reduced only in the first step of the extraction scheme and an increase in the Zn extracted in the second and third steps was observed.

For the BW(b) soil, the CaP amendment was most effective, reducing bioavailable Zn by 40 % and increasing the Zn extracted in step three. The RP amendment reduced available Zn by 34, 14, 36, and 39 % for the BW(b), H12(b), S5, and C1 soils, respectively.

4. Summary of Slurry Incubation Study

The first study conducted to investigate the ability of phosphate amendments to reduce metal solubility in soils was conducted by Ma in 1993.[1] In that study, reductions of 90 to 98 % in the water soluble Pb were observed when a soil contaminated by lead acid battery processing/recycling (2100 mg/kg Pb) was amended with HA at 8 to 33 % by weight. In another study[2], reductions of 73 to 96 % in the water soluble Pb were observed when a soil contaminated by $PbHAsO_4$ insecticide (2560 mg/kg Pb) was amended with RP at 10 to 40 % by weight. In a third study,[3] a soil contaminated due to a paint spill was separated by density to obtain the fraction enriched with the heavy metal containing phases (82,000 mg/kg Pb). The enriched fraction of this soil was amended with HA at 20 to 40 % by weight. After 9 days, the water soluble Pb was reduced by 13 %. The differences in the effectiveness of immobilization of Pb by phosphate in these soils could be attributed to the amendment (HA vs. RP) or initial form of the metal in the soil.

More recently, Ma published two studies on in-situ immobilization of Pb in soils contaminated from a variety of activities including; smelters, $PbHAsO_4$ insecticide, battery acid, and building demolition.[4,9] In one study[4], the soils were amended with RP at 10 % by weight and incubated under greenhouse conditions for 8 weeks. Three different single extractants were used to evaluate the amendment effectiveness: 0.1 M $CaNO_3$, 0.43 M HOAc, and 0.02 M EDTA/0.025M NH_4OAc. These extractant solutions were similar to the extractant solutions used in the first three steps of the sequential extraction scheme used in this study and were expected to extract similar metal phases. The study revealed that the $Ca(NO_3)_2$ extractable Pb was reduced by 16 to 52 % and the HOAc extractable Pb was reduced by 12 to 100 %. No reductions were observed in the EDTA extractable Pb. In a second study,[9] using soils contaminated due to similar activities, the soils were amended with 12.5 to 25 % by weight RP which had been ground to a fine powder and incubated as a 1:15 soil to water slurry for 2 hr. The effectiveness of the amendments was evaluated using a five step sequential extraction scheme. The amendments were very effective in this study, the Pb extracted in the first four steps of the sequential extraction scheme was reduced for each soil, and an increase in the metal extracted in step five was observed. The RP amendments in the second study were much more effective than in the first study or the studies conducted for this research. There were two differences between the first and second study. In the first study the RP was used as is, in the second study it was ground to a fine powder. In the first study the incubations were conducted under greenhouse conditions, in the second study, the incubations were conducted as a 1:15 soil to water slurry. These results indicate that surface reactions may be an important variable in amendment effectiveness.

The sequential extraction results for this study were similar to the extraction results reported in the literature with the exception of the study by Ma using finely ground RP.[5] The amount of metal extracted in the first and second steps were reduced, and the metal was converted into forms extracted in the third and fourth steps. For the slurry incubation study, it was assumed that a more soluble phosphate amendment would be more effective at immobilizing the metal. In general, this was not the case. The results of the slurry incubation study indicate that the solubility of the phosphate amendment does not determine the effectiveness of the amendment. For Pb, the HA amendment was the most effective for all four soils. For Zn, the HA amendment was most effective for the H12, S5, and C1 soils. For Cd, the RP amendment was the most effective with the BW soil. In only one case, Zn for the BW(b) soil, was the most soluble amendment, CaP, clearly the most effective. In general, HA was more effective than RP, as expected based on the increased solubility of HA; however, the CaP was the most soluble phosphate of the three and in most cases it was the least effective. This indicates that solubility of the phosphate source is not the only factor determining amendment effectiveness. With the exception of the C1 soil, no differences in soil pH were observed between the soil pH with the phosphate amendments. These results indicate that the solubility of phosphate amendments and differences in soil pH can not be used to explain the variations in amendment effectiveness. Reactions other than precipitation of insoluble phosphate phases from solution must be contributing to the reduced solubilites of the metals. As discussed in Chapter III, the phosphate amendments have different surface functionality. The variation in surface reactivity may be a factor in determining amendment effectiveness. This hypothesis is supported by the study conducted by Ma using finally ground RP.[5] The increased amendment effectiveness observed with the increased surface area of the amendment indicates that surface reaction may contribute to the immobilization of the metals.

D. Conclusions

The sequential extraction data show that the idea of remediating smelter contaminated soils using in-situ chemical immobilization is valid, but to select or develop remediation strategies requires information beyond the total metal content of the soil. The differences in behavior of the individual metals reveal that one amendment may not be suitable for all the metal contaminates. The differences in effectiveness of the amendment from soil to soil show that the form of the metal in the soil and the characteristic of the soil matrix also effect the effectiveness of the amendments. The effectiveness of the phosphate amendments may not be attributed to the solubility of the amendments. The results of these sequential extraction studies indicate that complex chemical reactions are occurring in these soils and traditional techniques such as total metal content, metal distributions and sequential extraction do not adequately explain the reactions occurring.

Metals that are no longer soluble must have participated in a chemical reaction which transformed the metal to a less soluble phase. Depending on the amendment added a variety of reactions may occur. These include sorption of the metal to solid surfaces and precipitation of the metal as phosphates, carbonates, oxides or hydroxides.

To evaluate the amendment effectiveness, identification of these new phases would be helpful. Identification of the metal phases formed during the remediation process may provide information which can be used to determine the mechanism of immobilization and the long term stability of the treatments. The final objective of the project involved applying spectroscopy to study the soil-amendment interactions. The results of the spectroscopic studies will presented in Chapter VI.

E. References

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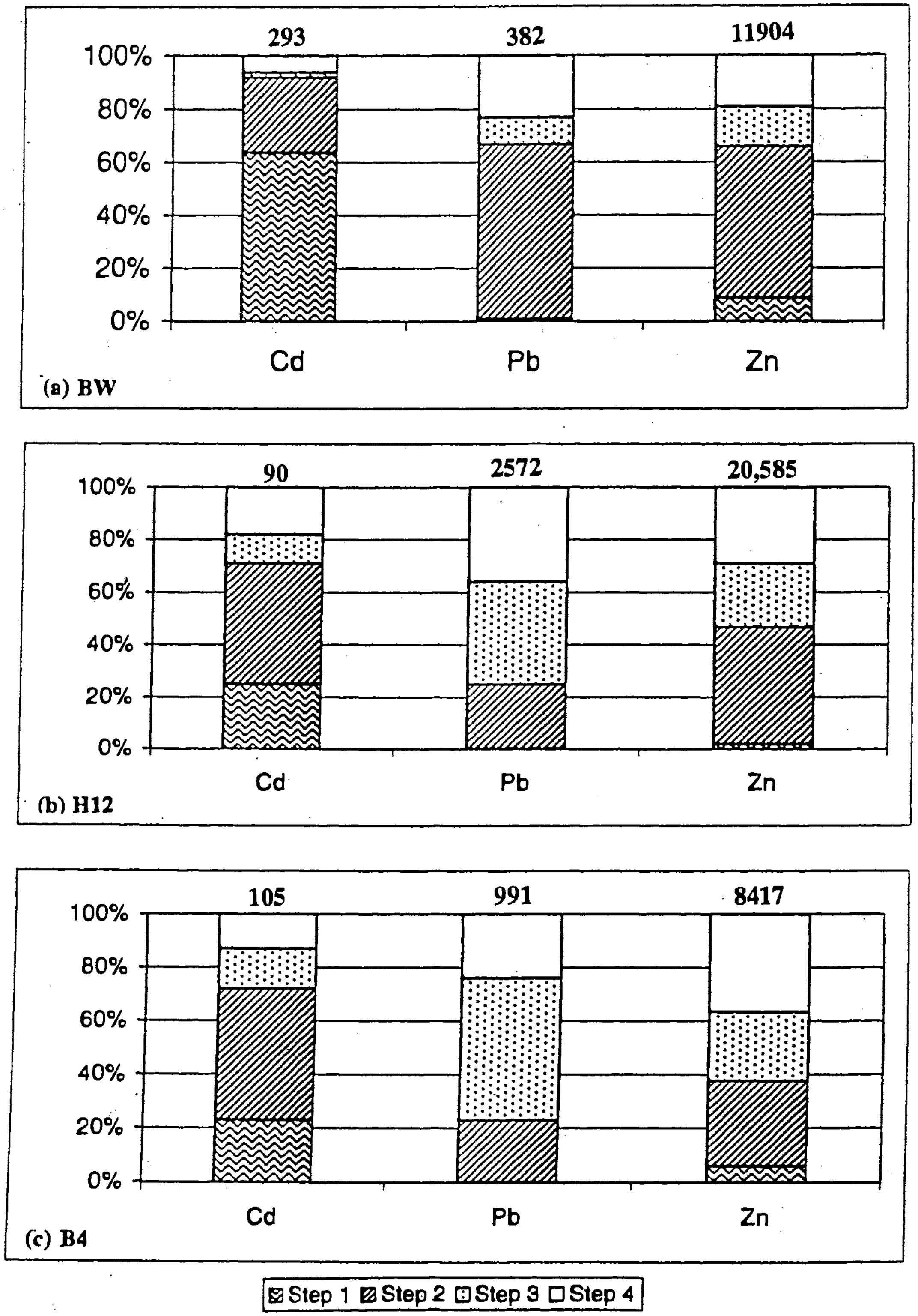

Figure 1. Distributions of Cd, Pb, and Zn in the sequential extracts of the 2 mm fractions for the (a) BW, (b), H12, and (c) B4 control soils expressed as a percentage of the summed total. The summed total of the sequential extracts are expressed (mg kg^{-1} soil) over the respective columns.

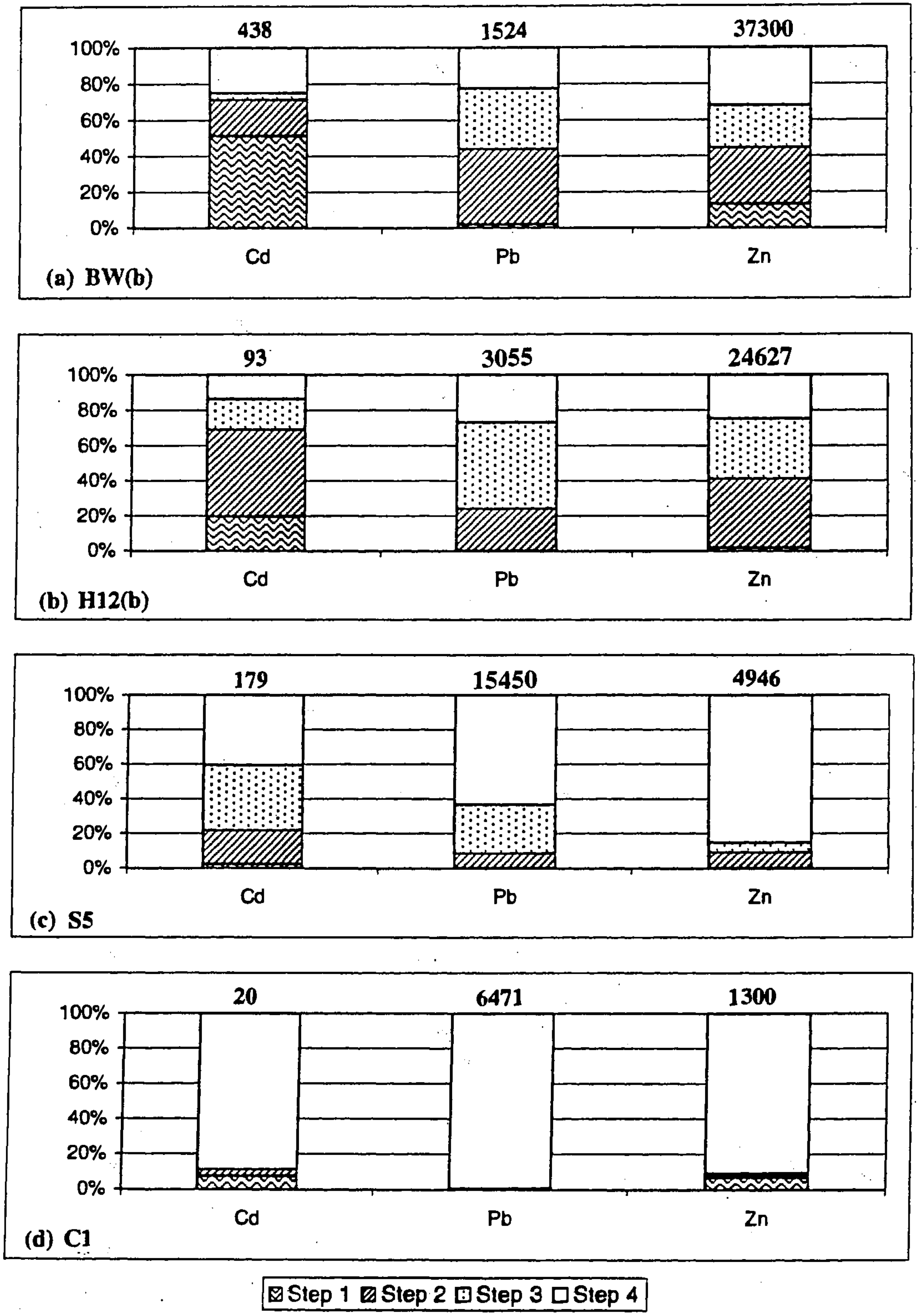

Figure 2. Distributions of Cd, Pb, and Zn in the sequential extracts of the 250 μm fractions for the (a) BW(b), (b), H12(b), (c) S5, and (d) C1 control soils expressed as a percentage of the summed total. The summed total of the sequential extracts are expressed (mg kg^{-1} soil) over the respective columns.

Table 4. Soil pH at completion field moisture capacity remediation process.

	pH		
	BW	**H12**	**B4**
Con	6.8	7.1	7.1
LS	8.2	7.5	7.9
NV	8.3	7.9	8.2
SS	6.6	6.6	6.7
RP	6.9	7.3	7.1

Table 8. Soil pH at completion of slurry remediation process.

	pH			
	BW(b)	**H12(b)**	**S5**	**C1**
Con	6.1	6.8	7.4	2.4
RP	6.6	6.8	7.4	5.7
HA	6.7	6.9	7.5	5.6
CaP	6.5	6.8	7.4	4.6

CHAPTER VI

SPECTROSCOPY

A. Introduction

Although XRD analyses has been applied to the study of soil-amendment interactions[1-3], this study is the first published application of DRIFTS and solid state NMR to the study of soil-amendment interactions. DRIFTS, XRD, and NMR were used to detect the formation of new metal containing phases in the amended soils which lead to the reduced metal solubilities observed in the sequential extraction study, Chapter V. The instrumentation and protocols used to collect the data were described in Chapter II. The spectral characteristics of the soils and amendments were presented in Chapter III. The results from the spectroscopic analysis of the whole soils are presented herein.

B. DRIFTS

1. Background

As demonstrated in Chapter III, infrared spectroscopy is a powerful tool which can be used to characterize soils and amendments. Spectra of soils and amendments contain bands which are unique and can be used for their identification. This study represents the first published example of the application of DRIFTS to investigate soil-amendment interactions.

DRIFTS spectra were collected for the control and amended soils at the conclusion of the twelve week field capacity and two week slurry remediation studies. The spectra of the amended soils were compared to the spectra of the control soils to identify new metal containing phases. Ideally, the formation of these phases could be used to explain the reduced metal solubility observed in the sequential extraction study, Chapter V.

Comparison of the spectra of amended and control soils revealed new features in the spectra of the amended soils. The spectra for the BW soils amended with biosolids (LS, NV, SS) and the BW(b) soils amended with phosphates (RP, HA, CaP) are presented in Figures 1 and 2, respectively. In each case, all of the new features observed in the spectra were attributed to the addition of the amendment to the soil. For example, in the spectra of the BW soils amended with biosolids, LS, NV, SS (Figure 1), increases in the hydroxyl stretching (3380 cm^{-1}) and aliphatic C-H stretching (3000 – 2800 cm^{-1}) regions were due to the organic matter contained in the amendments. In the spectra for the BW soils amended with LS and NV (Figure 1), additional bands at 1435 and 875 cm^{-1}, due to the carbonates present in these amendments, were observed. The spectra of the BW(b)RP sample (Figure 2) also revealed new peaks at 1435 and 875 cm^{-1}, due to the carbonate present in the RP. None of the bands characteristic of phosphates were observed, due to their overlap with the bands due to the silicate phases present in the soil. For the BW soil amended with HA (Figure 2), several new bands were observed: an isolated OH peak at 3571 cm^{-1}, an increase in the shoulder of the silicate band at 1094 cm^{-1}, and two new bands at 606 and 569 cm^{-1}. All of these features were attributed to the HA amendment. The band at 3571 cm^{-1} was attributed to the structural hydroxyl groups of HA. The band at 1094 cm^{-1} was attributed to the PO_4^{3-} stretching mode and the bands at 606 and 569 cm^{-1} to the PO_4^{3-} bending modes. An elevated baseline extending from the hydroxyl stretching region up to 2000 cm^{-1} was a characteristic feature in the spectra of the CaP amendment. For the BW soil amended with CaP (Figure 2), an elevation of the baseline in this region was observed. Similar features were observed in the spectra of the B4, H12, S5, and C1 amended soils.

The observation that the new bands in the spectra of the amended soils were attributed to the amendments was not entirely surprising. The soil-amendment DRIFTS spectra contain many intense, overlapping spectral features. The new phases that may have formed in the soil during the incubation would be present in small quantities. In addition, the new phases are expected to form through surface absorption or co-precipitation reactions. In these cases, the spectral features of the new metal phases would resemble those of the amendment and have spectral features which overlap with those of the soil and amendment. These factors hinder the direct observation of new phases in the soil-amendment mixture spectra. However, detection limits for impurities in infrared spectra as low as 0.01 % by weight (100 ppm) have been reported.[4] Therefore, the detection of small quantities of new phases should be possible using DRIFTS. In order to observe these new phases it would be necessary to simplify the spectra. To uncover dilute or overlapping spectral features, spectral subtraction was used.

2. Spectral Subtraction

Spectral subtraction is a technique commonly used by spectroscopists to analyze multi-component systems.[5] Spectral subtraction removes the spectral features of one component from a mixture. Persson, et al. have used spectral subtraction to study the interaction of phosphate ions with goethite and hematite surfaces.[6] The authors used spectral subtraction to remove the goethite and hematite spectral features from the mixture and observed only those bands due to the phosphate ions. Baenziger, et al., have used spectral subtraction techniques to remove water vapor contributions from the infrared spectra of proteins.[7]

In this research, spectral subtraction was used to remove the soil spectrum from the soil-amendment spectrum. The resulting subtraction spectrum should be representative of the amendment, changes in the amendment, and/or new phases that had formed during the incubation. To subtract an unwanted component from the spectrum of a mixture it is necessary to multiply the unwanted component by a subtraction factor. The subtraction factor for the soil-amendment spectral subtractions was determined based on the ratio of soil to amendment in the mixture. For example, in the slurry incubation study the soil-amendment mixture for RP was 15:85 RP to soil. For subtractions with the RP amended soils, a subtraction factor of 0.85 was used for the control soil

Once the subtraction spectra were obtained, the next step was to compare the subtraction spectra with the amendment spectra. Bands present in the subtraction spectra, which can not be attributed to the amendment, may be attributed to the formation of a new phase in the soil. To identify the new phases, comparisons of the new bands observed in the subtraction spectra with the bands of phases expected to form during the soil-amendment incubation must be made.

3. Spectral Characteristic of New Phases

In the soils amended with phosphates, the new phases formed would most likely be phosphate phases.[8] In general phosphates have two sets of intense bands at 940 to

1120 and 540 to 650 cm^{-1}, characteristic of PO_4^{3-} stretching and bending, respectively.[9] The band positions for selected metal phosphates are presented in Table 1. From this information, it can be seen that the spectra of Cd, Pb and Zn phosphates all have features which differentiate them from Ca phosphates. The spectra of Cd, Pb, and Zn phosphates all have PO_4^{3-} stretching and bending bands at lower wavenumbers than the Ca phosphates. These differences would make observation of the presence of Cd, Pb, or Zn phosphate possible in a mixed phosphate system.

Table 1. Characteristic infrared bands for various metal phosphates (cm^{-1}).

	PO_4^{3-}	
Sample	**Stretch**	**Bend**
RP	1053	608, 572
HA	1090, 1037	632, 606, 569
$Ca_3(PO_4)_2$	1053	609, 576
$Cd_3(PO_4)_2$	1140, 1071, 1017, 926	585, 529
$Pb_5(PO_4)_3Cl$	1030, 970	572, 542
$Pb_3(PO_4)_2$	979	652, 621, 595, 554, 459, 445
$Zn_3(PO_4)_2$	1114, 1000, 1003, 942	585, 529

In the soils that had been treated with amendments containing carbonate, such as the LS, NV, and RP amendments, the formation of new carbonate phases would be possible. Carbonates tend to have three characteristic bands, one stretching and two bending modes.[9] Table 2 presents the positions of these carbonate bands for various carbonate minerals. Similar to the spectra of phosphates, there are variations in the positions of the bands in the spectra of metal carbonates which would make the identification of their presence in a mixed carbonate system possible.

Table 2. Characteristic infrared bands for various metal carbonates (cm^{-1}).

		CO_3^{2-}	
	Stretch	**Bend**	**Bend**
$CaCO_3$	1435	876	712
$CdCO_3$	1462	862	724
$PbCO_3$	1410	837	677
$ZnCO_3$	1440	870	743

When alkaline amendments, such as LS or NV are added to soils, the soil pH is raised. In addition to the carbonate phases which may form upon addition of alkaline amendments, other phases, such as oxides and hydroxides may form. The spectral features associated with metal-oxygen interactions appear between 800 and 200 cm^{-1}.[9] The presence of new oxide phases in the soil would be indicated by new bands in the 800 to 400 cm^{-1} range. New hydroxide phases could be identified by the presence of an isolated hydroxyl band in the 3700 to 3500 cm^{-1} range in addition to the metal-oxygen bands.

When amendments containing biosolids were added to soils, interactions of metals with the organic matter through complexation reactions would be expected. Previous infrared studies conducted on biosolid[10] and soil organic matter[11] have shown evidence for metal-organic matter interactions in these systems. In the study conducted using the biosolid organic matter, a shift in the position of the C=O band at 1655 cm^{-1} to 1644 cm^{-1}, was observed upon extraction of the metal cations with EDTA and subsequent saturation with Cu^{2+} ions. In the study conducted using soil organic matter, a reduction in the COOH band at 1730 cm^{-1} combined with a shift of the 1630 cm^{-1} band to

1600 cm^{-1} (C=O of acids and amides) were observed when these materials were saturated with Ca^{2+}, Co^{2+}, or Cu^{2+}.

4. DRIFTS Results of Remediation Study

The results of the spectral subtractions are presented in Table 3. In general, the subtraction spectra resembled the spectra of the amendments. In most cases, the bands in the subtraction spectra were consistent with the amendments and no new bands were observed. For example, the subtraction spectra for the S5RP and S5HA soils are presented in Figure 3. Both subtraction spectra resemble the amendment and no evidence for the formation of new phases was observed. These results were not unexpected. Since an excess of amendment had been added to the soils, only a portion of the amendment would be required to immobilize the metal. These results don't necessarily indicate that new phases weren't forming in the soil-amendment mixture, only that new phases could not be observed.

In four cases, BWRP, BW(b)RP, BW(b)CaP, and S5CaP, the subtraction spectra revealed evidence for the formation of new phases. In most cases the bands due to new phases were not observed after subtraction. In the spectra of the C1 soils, no new phases were observed. The sequential extraction data for this system did not indicate changes in the metal solubility and the formation of new phases would not be expected. In the soils amended with organic materials (LS, NV, SS), evidence for the formation of new phases was not observed. This may be attributed to the fact that the reductions in metal solubility were expected to occur due to chelation of the metals by organic matter. The organic amendments already contained Cd, Pb, and Zn (Chapter III, Table 7); therefore, changes in the spectra due to chelation of additional metal by these materials would have been minor.

Table 3. Summary of DRIFTS spectral subtraction results.

	Field Capacity		
Soil/Amendment	**BW**	**H12**	**B4**
LS	-	-	-
NV	-	-	-
SS	-	-	-
RP	PO_4/CO_3	-	-

Soil/Amendment	Slurry			
	BW(b)	**H12(b)**	**S5**	**C1**
RP	$PO_4/CO_3/OH$	-	-	-
HA	-	-	-	-
CaP	PO_4/OH	-	PO_4/OH	-

(-) = No new phases detected

The subtraction spectra for the BW(b) soil amended with RP are presented in Figure 4. In general, the spectrum resembles the RP amendment; however, some changes in the spectrum have occurred and are summarized in Table 4. The new bands observed in the subtraction spectra were compared with the bands for the phosphate, carbonate, oxide and hydroxide phases expected to occur in this soil. Two pieces of evidence exist for the formation of Cd, Pb, and Zn phosphates. The first is the shift and broadening of the 1053 cm^{-1} phosphate stretching band to 1039 cm^{-1}. The data in Table 1 show that Cd, Pb and Zn phosphates all exhibit bands at lower wavenumbers than 1052 cm^{-1}. The formation of these phases would cause a shift and broadening of the 1052 cm^{-1} band. Second, the new bands at 530 to 422 cm^{-1} support the formation of new phosphate phases. The DRIFTS spectra of calcium phosphates do not have any bands in this region; however, the spectra of Cd, Pb, and Zn phosphates all exhibit bands in this region. The band at 671 cm^{-1} could be evidence for $PbCO_3$, as the band for $PbCO_3$ is significantly shifted from other types of carbonates. The additional new bands at 3625, 913, 801, 778, and 696 cm^{-1} may indicate the formation of new oxide and/or hydroxide phases.

Table 4. New peaks identified from BW soil amended with RP.

Peak Position (cm^{-1})	Possible Identity
3625	Hydroxide
1039 (shifted from 1052)	Pb, Cd, and Zn phosphates
913	Oxide
801/778	Oxide
696	Oxide
671	$PbCO_3$
520, 531, 474, 438, 422	Pb, Cd, and Zn phosphates

Figures 5 and 6 show the subtraction spectra for the BW(b) and S5 soils amended with CaP. Comparison of the subtraction spectra with the spectra of the CaP amendment showed changes in the region below 1300 cm^{-1}. This region now resembled the phosphate region for PO_4^{3-} phases. Two intense, broad bands were observed one centered at 1040 cm^{-1} and one from 590 to 450 cm^{-1}. Both of these changes were consistent with the stretching and bending bands of PO_4^{3-}. For CaP, the most intense band is centered at 1075 cm^{-1}; while, in the subtraction spectra this band is centered at 1040 cm^{-1}. The breadth of the band is indicative of a mixed phosphate phase; therefore, the identification of any one particular phosphate is not possible. The bands in the region from 590 to 450 cm^{-1} are consistent with the formation of Cd, Pb, and/or Zn phosphates.

Differences between the BW(b)CaP and S5CaP subtraction spectra were apparent. The increased intensity of the bands at 1075 and 900 cm^{-1} in the S5CaP subtraction spectra compared with the BW(b)CaP subtraction spectra may indicate that the amendment has reacted to a greater extent in the BW(b)CaP soil as these bands are associated with the CaP amendment and are less intense in that spectrum. Additionally, for the BW(b)CaP soil new bands are observed at 953, 442, and 429 cm^{-1} which are not observed in the S5CaP subtraction spectra. Differences also exist in the hydroxyl stretching region for these samples. In the BW(b)CaP subtraction spectra, the 3215 cm^{-1} band has increased in intensity relative to the CaP amendment. For the S5CaP subtraction spectra, the 3215 cm^{-1} band was reduced and a new bands at 3357 and 3622 cm^{-1} were observed. These results could indicate the interaction of metal ions in the soil with the acidic protons of the CaP amendment.

5. Conclusions

In conclusion, this study has shown that a combination of DRIFTS and spectral subtraction can be useful for investigating soil-amendments interactions. The first examples of identification of new phases in soil-amendments mixtures by DRIFTS were presented. In addition to evidence for the formation of new phases, changes observed in the hydroxyl regions of the subtraction spectra (3700 to 2000 cm^{-1}) indicate interactions of the metals with the amendment surfaces may occur. The fact that new phases were not observed in the soil-amendment system by DRIFTS does not mean new phases were not forming.

C. XRD

1. Background

In Chapter III, it was established that XRD could be used to characterize soils and amendments. Differences exist between the powder patterns of the soils and amendments which can be used for their identification. Recently, XRD has been used to investigate soil-amendment interactions in phosphate amended soils.[1-3] In a soil contaminated by a paint spill, Laperche observed the formation of hydroxypyromorphite ($Pb_5(PO_4)_3OH$) in the enriched fraction of the soil and in the soil associated with the roots of sudax grass.[1,3] In a soil contaminated by mine waste, Cotter-Howells observes the formation of a Ca rich pyromorphite after treatment of the soil with Na_2HPO_4.[2]

XRD powder patterns were collected for the control and amended soils at the conclusion of the incubations. Due to limited instrument access, XRD data were collected for selected samples. Samples were chosen based on the sequential extraction and DRIFTS data. For the greenhouse incubation study, powder patterns for the BW and H12 soils amended with RP were collected. Powder patterns for the biosolids amended soils were not collected for two reasons. First, the DRIFTS data did not reveal the presence of any new phases during the incubation. Second, the phases expected to form would not be crystalline. For the slurry incubation study, powder patterns for the BW(b) and S5 soils amended with RP, HA, and CaP were collected. The DRIFTS and sequential extraction data for these soils indicated the formation of new phases.

Because the concentration of the new phases in the soil-amendment mixtures are low (generally ppm), the presence of the most intense XRD peak for a phase was considered evidence for the formation of that phase. This criterion has been used by others working in this area.[1-3,12] Eighmy has reported the detection of phases in a mixture as low as 0.33 % by weight using a three peak match.[13] These results suggest that the detection of the most intense peak for a new phase in the soil-amendment system may be possible at concentrations lower than 0.33 %. The detection of new phases by XRD may be limited because the accuracy of the peak positions is diminished by low sample concentrations and variations in the composition, phase, and crystallinity of the component.[14]

2. XRD Results of Remediation Study

The first step in the analysis of the XRD data was comparison of the powder patterns of the control and amended soils. The powder patterns for the BW(b) and S5 soils amended with RP, HA, and CaP are presented in Figures 7 to 12. As with the DRIFTS data, evidence for the presence of the amendment in the soil-amendment mixture was observed. The most intense peaks associated with the phosphate amendments occur between 25 and 35° 2θ. In the powder patterns for the BW(b) and S5 amended soils, evidence for the presence of the amendment exists. For example, in the RP amended soils (Figures 7 and 10) peaks at 25.78, 32.06, and 33.23° 2θ (d-spacings 3.54, 2.79, and 2.69 Å) in the powder patterns were attributed to RP. In the S5RP soil powder pattern, an additional peak at 34.14° 2θ (d-spacing 2.62 Å) was observed which was also attributed to RP. For the HA amended soils (Figures 8 and 11), peaks in the powder patterns at 25.82, 31.74, 32.12, 32.84, and 33.96° 2θ (d-spacings 3.44, 2.82, 2.78, 2.27, and 2.64 Å) were attributed to the amendment. For the CaP amended soils (Figures 9 and 12), peaks in the powder patterns at 30.14, 30.47, 32.4, and 32.86° 2θ (d-spacings

2.96, 2.93, 2.76, and 2.72 Å) were attributed to the amendment. An additional peak at 28.85° 2θ (d-spacing 3.12 Å), attributed to CaP, was observed in the S5CaP soil powder pattern.

In addition to the amendment peaks, new peaks not associated with the amendments were observed in the powder patterns of the soil-amendment mixtures. The results are summarized in Table 5. The presence of a peak or peaks in the powder patterns of the amended soils, which are absent in the powder pattern of the control soil and can not be attributed to the amendment, suggests the formation of a new crystalline phase or phases in the soils. Identification of the new peaks was accomplished by comparison with JCPDS powder patterns.[15] Probable new phases were defined as those most likely to form on interaction of the amendments with Cd, Zn, or Pb as described in the DRIFTS section.

Table 5. Summary of XRD results for amended soils.

	Field Capacity	
	BW	**H12**
RP	PO_4/CO_3	-
	Slurry	
	BW(b)	**S5**
RP	PO_4	PO_4
HA	-	OH/HPO_4
CaP	PO_4	PO_4

(-) = no new phases detected

New peaks were observed in the powder pattern of the BWRP soil at 3.44, 3.23, 2.97, 2.61, and 2.03 Å. The peak at 2.97 Å indicates the formation of hydroxypyromorphite ($Pb_{10}(PO_4)_6OH$). The peak at 2.61 Å indicates the formation of hydrocerussite, ($PbCO_3OH$). The peaks at 3.44, 3.23, and 2.03 Å were not consistent with the formation of any phosphate, carbonate, oxide or hydroxide phase considered in this study and could not be unambiguously identified.

New peaks were observed in the H12RP powder pattern at 3.04 and 1.91 Å. These peaks were not consistent with the formation of any phosphate, carbonate, oxide or hydroxide phase and could not be unambiguously identified.

New peaks were observed in the powder pattern of the BW(b)RP soil at 3.71, 3.70, 3.02, 3.01 and 2.99 Å. The peak at 2.99 Å is consistent with the formation of pyromorphite ($Pb_5(PO_4)_3Cl$). The peak at 3.01 Å is consistent with cadmium phosphate hydroxide ($Cd_5(PO_4)_3OH$). No new peaks were identified in the powder pattern of the BW(b)HA soil. New peaks at 3.76, 3.66, 3.22, 3.19, 3.18, and 2.99 Å were observed in the powder pattern of the BW(b)CaP soil. The peak at 2.99 Å is evidence for the formation of pyromorphite ($Pb_5(PO_4)_3Cl$).

The identity of three peaks in the BW(b)RP powder pattern, 3.71, 3.70, and 3.02 Å, and five peaks in the BW(b)CaP powder pattern, 3.76, 3.66, 3.22, 3.19, 3.18 Å, could not be determined. These peaks did not correspond with any of the phosphate, carbonate, oxide or hydroxide phases expected to form in the soil upon addition of the amendment.

New peaks were observed in the powder pattern of the S5RP soil at 3.01, 2.85, 2.84, 2.43, 2.05, and 2.04 Å. The peaks at 3.01 and 2.85 Å are consistent with the formation of cadmium phosphate hydroxide ($Cd_5(PO_4)_3OH$) and hopeite ($Zn_3(PO_4)_2 \bullet 4 H_2O$), respectively. For the S5HA soil, new peaks in the powder pattern at 3.30, 2.54, and 2.13 Å were observed. The peaks at 3.30 and 2.54 Å are consistent with the formation of lead hydrogen phosphate ($PbHPO_4$) and cadmium hydroxide ($Cd(OH)_2$), respectively. For the S5CaP soil, new peaks in the powder pattern were identified at 3.17, 2.88, and 2.83 Å. The peak at 2.88 is consistent with the formation of Ca-Pb phosphate phase ($Pb_{5-x}Ca_x(PO_4)_3OH$).

For the S5 soils, two peaks at in the RP amended soil, 2.43 and 2.05 Å, and one peak in the HA amended soil, 3.30 Å, and two peaks in the CaP, 3.17 and 2.83 Å, amended soils were not identified. These peaks were not consistent with any of the carbonate, oxide or hydroxide phases expected to form in the soil upon addition of the amendment.

In the soil-amendment powder patterns, new peaks that could not be assigned to any of the new phases expected to form were observed. These peaks may be attributed to two factors. These peaks may be due to new phases formed in the soil that have not been considered. These peaks may also be attributed to phases present in the soil that were not observed in the powder pattern of the control soil. Soil is a complex mixture of many components and it is possible that peaks from all the soil components may not have been observed each time the powder patterns were collected. For example, Figure 13 contains three powder patterns obtained for the S5 control soil. Each pattern is slightly different. Pattern (a) contains a peak at 27.45° 2θ which is absent in patterns (b) and (c). Pattern (b) contains peaks at 25.56, 27.66, and 27.87 ° 2θ which are absent in patterns (a) and (c). Pattern (c) contains peaks at 28.45, and 30.55 ° 2θ which are absent in patterns (a) and (b). Based upon these results, the absence of a peak in the soil-amendment mixture was attributed to variability of the soil, rather than the loss of that peak due to reaction with the amendment.

3. Conclusions

Three studies have been published applying XRD to phosphate amended soils to test for the formation of metal phosphate phases.[1-3] In the first study,[1] HA was applied to the enriched fraction of a paint spill contaminated soil. At ambient pH (7.7) no pyromorphite formation was observed. However, if the soil pH was lowered to 5.5, the formation of hydroxypyromorphite was observed after 9 days. In the second study,[2] 10 % by weight Na_2HPO_4 was applied to two soils contaminated by mine waste and the soils were incubated under greenhouse conditions for three months. The amended soils were then separated to obtain the high density fraction. The XRD data showed the presence of Pb phosphate in one of the soils. In the most recent study,[3] a soil contaminated by a paint spill was amended with 0.58 to 3.1 % by weight HA and RP under greenhouse conditions. After 9 to 12 weeks of incubations, the formation of hydroxypyromorphite was observed in the soil associated with the roots of sudax grass grown in the amended soils. These studies suggest that the detection of Pb phosphate phases formed during the remediation of soils with phosphate amendments may be possible, but does not always occur.

Similar to previous studies, Pb phosphate phases were observed in the BW and S5 soils amended with RP and HA amendments. In addition, the fact that Pb phosphate phases were not observed in each of the amended soils is also supported in the literature. Just because new phases were not detected does not mean new phases did not form. In addition to Pb phosphate phases, other phosphate, carbonate and hydroxide phases were observed. The formation of phases other than Pb phosphates upon the interactions of metals with the phosphate amendments has been reported in the literature.[12,16] Ma reported the formation of both pyromorphite and hydrocerussite upon the interaction of RP with a Pb nitrate solution.[12] Chen also reported the formation of pyromorphite and hydrocerussite when RP was reacted with a Pb nitrate solution.[16] In addition, Chen reported the formation of $CdCO_3$, ZnO and $Zn_3(PO_4)_2 \bullet 4\ H_2O$ when RP was reacted with Cd or Zn nitrate solutions. The variety of phases identified by XRD suggests that more complex reactions than the precipitation of insoluble metal phosphate phases are occurring during the remediation process.

D. NMR

1. ^{31}P NMR

a. Background

^{31}P NMR experiments were conducted to characterize the soil-amendment interactions. The absence of a ^{31}P resonance in the control soils indicated that ^{31}P signals observed in an amended soil would be due to amendment, or new phases which had formed in the soil.

Phosphates have a chemical shift range spanning over 70 ppm.[17] ^{31}P experiments conducted during this project indicate that the PO_4^{3-} chemical shift is sensitive to the metal cation in the structure. The ^{31}P chemical shifts for Cd, Pb, and Zn phosphate are presented in Table 6. Cadmium, zinc and lead phosphates have distinct chemical shifts and their presence in amended soils may be detected by ^{31}P NMR.

Table 6. ^{31}P NMR results for various metal phosphates.

Sample	^{31}P Chemical Shift (ppm)
$Cd_3(PO_4)_2$	8.0, 3.8
$Pb_3(PO_4)_2$	1.9, -1.2
$Zn_3(PO_4)_2$	8.1, 4.9

b. ^{31}P NMR results of field capacity remediation study

Single pulse ^{31}P NMR experiments were conducted on the BW, H12, and B4 soils treated with RP on the first day of the remediation process, and for the BW and B4 soils at 4 weeks and 12 weeks. A standard set of experimental conditions including a ^{31}P 3.8 μs pulse width and a 10 s pulse delay were used; 64 to 1000 scans were acquired. For the BWRP and B4RP four week samples, a cross polarization experiment was used with a 5 μs ^{1}H pulse width, 1 ms contact time and a 10 s pulse delay; 900 scans were acquired. A single ^{31}P resonance was observed in each sample. The ^{31}P chemical shifts for the samples are summarized in Table 7. The ^{31}P chemical shifts observed for the BWRP and H12RP amended soils at the start of the incubation (1 day) were 3.1 and 3.0 ppm, respectively. These chemical shifts are similar to that of the RP amendment, 2.9 ppm. For the B4RP soil, the observed ^{31}P chemical shift at the start of the incubation (1 day) was 4.3 ppm. The linewidth for the ^{31}P peak in the B4RP soil, 385 Hz, was much broader than those observed for the BWRP and H12RP soils, 280 and 290 Hz, respectively. The results of these experiments reveal that the soil can affect the chemical shift of the amendment. Because these experiments were conducted at the beginning of the incubation, no reaction between the amendments and soils was expected. The shift and broadening of the peak for the B4RP soil was attributed to presence of paramagnetic Fe or Mn containing phases in the soil. Generally, the presence of paramagnetics in a sample can have three effects on a peak.[18] The intensity may be lowered, the peak width may broaden, and the chemical shift may change. In certain cases, the linewidths may be broadened to such an extent that the peak is no longer observed.

^{31}P NMR experiments were conducted for the BWRP and B4RP amended soils after four and twelve weeks of incubation. For the BWRP soils, the chemical shifts were 3.1, 3.0, and 3.1 ppm at one day, four weeks, and twelve weeks, respectively. For the B4RP soils, the ^{31}P chemical shifts were 4.3, 4.4, and 4.2 ppm at one day, four weeks, and twelve weeks, respectively. No new ^{31}P peaks were observed in either soil. These experiments revealed that the ^{31}P chemical shift did not change significantly during the incubation indicating that the RP remains essentially unchanged over the course of the incubation.

Table 7. ^{31}P NMR results for field moisture capacity remediation study.

Sample	^{31}P Chemical Shift (ppm)
RP	2.9
BWRP (1day)	3.1
BWRP (4wk)	3.0
BWRP (12wk)	3.1
H12RP (1day)	3.2
B4RP (1day)	4.3
B4RP (4wk)	4.4
B4RP (12wk)	4.2

c. ^{31}P NMR results of slurry remediation study

Single pulse ^{31}P NMR experiments were conducted on the BW(b), H12(b), S5, and C1 soils amended with RP, HA, and CaP at the completion of the two week incubation. A standard set of conditions using a ^{31}P pulse width of 2.1 μs, a 10 s pulse delay and 1000 acquisitions were used. The results of the ^{31}P NMR study, summarized in Table 8, were similar to those obtained from the greenhouse incubation. In general, the phosphate amendment remains essentially unchanged during the incubation. No evidence for the formation of new phosphate phases exists as each ^{31}P spectra contained a single peak attributed to the amendment. Changes in the chemical shift of the ^{31}P resonance were observed in the spectra of the S5HA, S5CaP, C1RP and C1CaP soils. Because the initial ^{31}P resonance for the amendment is not present, even though DRIFTS and XRD data indicate the presence of the amendment in the soil, it is believed that the peak shifts observed in the spectra of these samples were the result of paramagnetic phases in the soil since both soils have high Fe contents.

d. Conclusions

^{31}P NMR did not provide any insight into the phases formed during the immobilization reactions. This does not mean new phosphate phases were not forming, only that they were not detected. As discussed in Chapter III, the detection limit for ^{31}P should be low; however, many factors contribute to the detection of phases by NMR including the concentration, number of different environments of the nuclei, and the association of the nuclei with paramagnetic components.

2. ^{1}H NMR

a. Background

^{1}H NMR experiments were conducted on the phosphate amended soils from the slurry study. The control soils all exhibited a peak between 4.6 and 5.4 ppm due to surface adsorbed water. In the ^{1}H spectra of the RP amendment a single peak at a 4.9

ppm was observed; however, the ^{1}H spectra of the HA and CaP amendments both have features in their ^{1}H spectra which differentiate them from the soil spectra. The HA amendment has peaks for hydroxyl groups and 3.4, 1.0, and -0.3 ppm in addition to a surface adsorbed water peak at 5.3 ppm. The CaP amendment has peaks for acidic protons at 15.7 and 12.6 ppm. ^{1}H NMR experiments were conducted to determine if any changes in these isolated hydroxyl groups or acidic protons could be observed in the ^{1}H NMR spectra. Changes in these peaks may indicate the interaction of metals present in the soils with the functional groups associated with the protons.

b. ^{1}H NMR results of remediation study

Single pulse ^{1}H NMR experiments were conducted for the BW(b), H12(b), S5, and C1 control soils and these soils amended with RP, HA and CaP. The ^{1}H 90° pulse width was 7 μs, a pulse delay of 1 s was used, and 1000 to 6000 scans were acquired. The results of these experiments are summarized in Table 9. Figure 14 presents the ^{1}H NMR spectra for the BW(b) phosphate amended soils.

The surface adsorbed water peak between 4.6 and 5.4 ppm in the spectra of the control soils occurs at a position similar to the chemical shift for surface adsorbed water in the RP amendment spectra (4.9 ppm). For the BW(b), H12(b), and S5 soils, no change in the ^{1}H spectra occurs upon addition of the amendment to the soil. The chemical shift of the peak in the C1RP soil spectra has shifted to 2.5 ppm. The shift of the peak to 2.3 ppm may indicate a change in the surface adsorbed water in the soil upon addition of the amendment. The shift of the peak from 5.4 to 2.5 ppm indicates the water is chemisorbed to the soil surface after addition of the amendment. A second explanation for the shift of the peak may be attributed to the presence of paramagnetic phases in this sample. A peak shift was also observed in the ^{31}P spectra of this sample.

For the HA amended soils, the presence of new features in the spectra were observed in all four soil samples. In addition to the surface adsorbed water peak, additional peaks were observed at -0.3, 1.0, -0.7, and -0.3 ppm for the BW(b), H12(b), S5, and C1 soils amended with HA, respectively. The new features were all associated with the structural hydroxyl groups of the HA amendment. For all four soils, the peak at 3.4 ppm associated with surface hydroxyl groups was not observed. This was attributed to overlap of this peak by the surface adsorbed water peak of the soil. For the BW(b), S5, and C1 soils, the peak at 1.0 ppm, associated with OH defect sites, was not observed. This could be attributed to the interaction of these hydroxyl groups with metals from the soil solution. For the H12(b) soil, the peak at -0.3 ppm associated with bulk hydroxyl groups was no longer visible. This could indicate that the HA amendment has reacted differently in the H12(b) soil. The loss of the -0.3 ppm peak indicates that the OH groups in the bulk of the HA structure have changed. This could be attributed to a dissolution of the HA amendment which would expose the bulk hydroxyl groups or ion exchange into the structure of the HA amendment.

For the CaP amended soils new features were observed in the spectra of the amended soils. For the BW(b) and H12 soils, the surface adsorbed water peak was still observed in the ^1H spectra. In addition, acidic proton peaks at 16.2/13.8 and 16.6/13.9 ppm were observed in the spectra for the BW(b) and H12 samples. These peaks were shifted downfield from their initial position in the amendment. This shift is indicative of stronger hydrogen bonding for the protons in the amended soils. Two possible explanations are proposed: CaP has adsorbed onto the surface of another soil component or Ca has been exchanged by another metal ion. The S5 and C1 amended soil spectra reveal no evidence for the acidic protons from the CaP amendment. This could be attributed to the interaction of the CaP amendment with the paramagnetic phases in the soil. If the CaP amendment has interacted with the paramagnetic phases in the soil, either through surface adsorption, ion exchange or coprecipitation, the acidic proton peaks may be broadened or shifted to such an extent that they are no longer visible in the spectrum. In addition, the surface adsorbed water peak in the C1 spectra was shifted upfield to 2.3 ppm. The same explanations that were proposed for the shift in the C1RP peak are proposed here.

c. Conclusions

Evidence for the interactions of metals in the soils with the functional groups associated with the protons in the HA and CaP amendments was observed. A possible explanation for the observation of changes in the ^1H and not ^{31}P spectra may be the increased sensitivity of the proton. The proton is fifteen times more sensitive than phosphorous for detection by NMR.[17] In addition, direct interactions between the metal and protons are expected; however, interactions between the metal and phosphorous would occur indirectly through the P-O bonds.

E. Conclusions

Spectroscopy has provided evidence for the formation of new phases and surface reactions in the soil-amendment systems. In most cases, the formation of new phases upon addition of the amendment to the soil was not observed spectroscopically, even though the sequential extraction data revealed that the metal solubility had been reduced. Based on this study, it does not appear that predictions can be made regarding whether spectroscopic analyses will be useful for a particular soil-amendment system. The ability to detect phases has several variables and just because phases were not detected does not mean new phases were not formed.

Several possible explanations exist for why new phases were not observed. The content of the phases could have been too low to detect. For XRD, non-crystalline phases would not be detected. For NMR, the detection of phases associated with paramagnetic ions may have been limited. Also, the metal could have been immobilized in a form other than the phosphate, carbonate and oxide/hydroxide phases considered in this study. For example, the immobilized phases could have been formed with other phases in the soil such as Fe or Al containing phases. The phases could have spectral features very similar to the added amendments. For example, the chelation of metals by the organic matter in the biosolids amended soils or the adsorption of metals to the amendment surfaces.

The results of the spectroscopic studies conducted in this research establish that a variety of techniques must be employed to understand soil-amendment interactions. Generally, the spectroscopic techniques used in this study were complementary. It is difficult to assign a preference as each technique, with the exception of ^{31}P NMR, provided useful information. The ^{1}H NMR spectra provided evidence for the interactions of metal ions from the soil with the functional groups associated with protons in the amendments. The XRD powder patterns provided evidence for the formation of new crystalline precipitates in the soil-amendment systems. The DRIFTS subtraction spectra provided evidence for both surface reactions and the formation of new precipitates.

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Table 8. ^{31}P NMR results for slurry remediation study.

Sample	^{31}P Chemical Shift (ppm)
BW(b)Con	-
H12(b)Con	-
S5Con	-
C1Con	-
RP	2.9
BW(b)RP	2.9
H12(b)RP	2.7
S5RP	2.7
C1RP	-2.5
HA	2.9
BW(b)HA	2.9
H12(b)HA	2.7
S5HA	3.3
C1HA	2.6
CaP	-1.5
BW(b)CaP	-1.5
H12(b)CaP	-1.5
S5CaP	11.0
C1CaP	-12.6

(-) = No ^{31}P resonance observed

Table 9. ^{1}H NMR results for slurry remediation study.

Sample	^{1}H Chemical Shift (ppm)
BW(b)Con	4.6
H12(b)Con	4.9
S5Con	5.1
C1Con	5.4
RP	4.9
BW(b)RP	4.9
H12(b)RP	4.9
S5RP	5.4
C1RP	2.5
HA	5.3, 3.4, 1.0, -0.3
BW(b)HA	4.6, -0.3
H12(b)HA	4.9, 1.0
S5HA	5.1, -0.6
C1HA	5.1, -0.3
CaP	15.7, 12.6
BW(b)CaP	16.3, 13.8, 4.3
H12(b)CaP	16.6, 13.9, 4.3
S5CaP	5.6
C1CaP	2.3

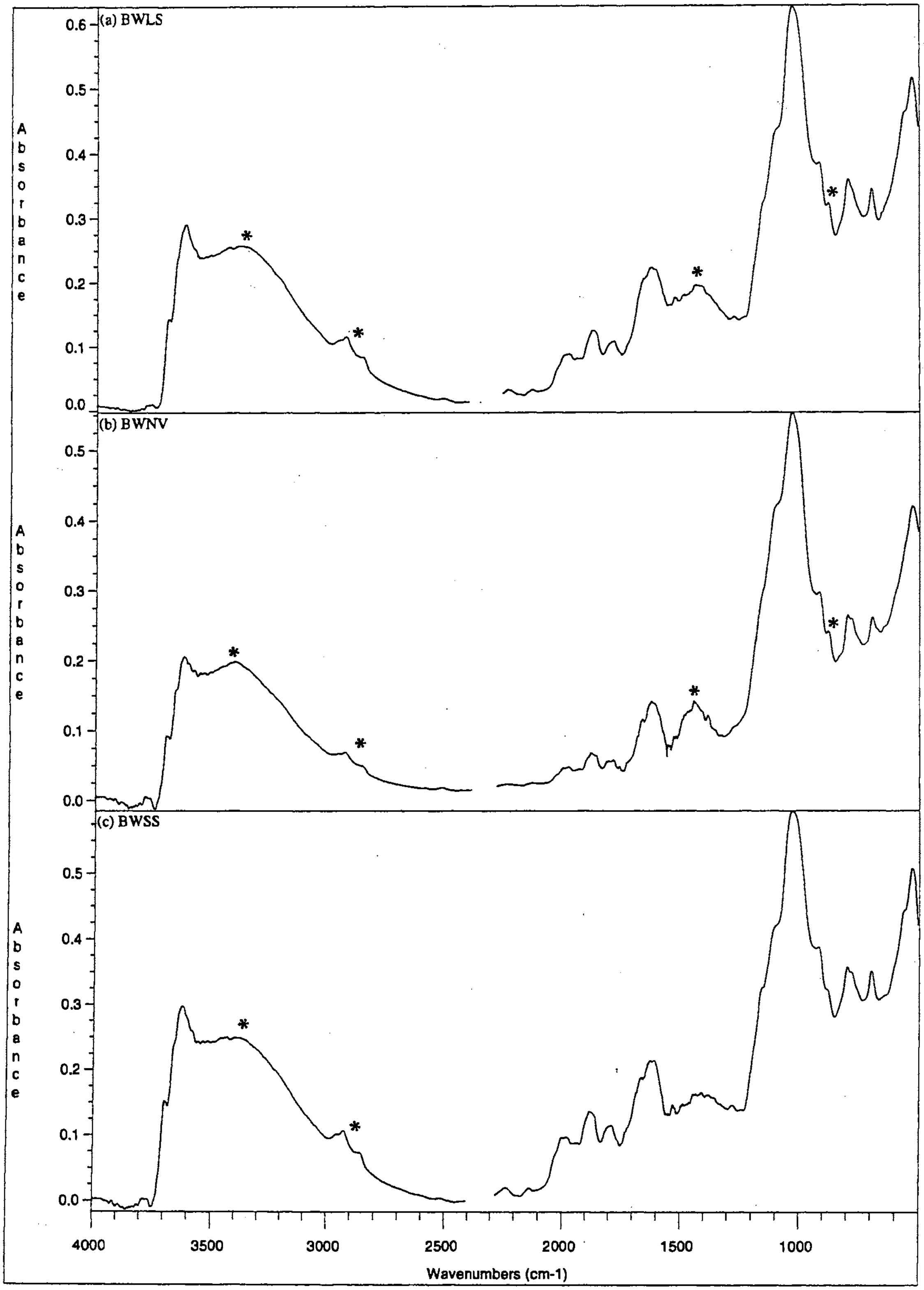

Figure 1. DRIFTS spectra of amended soils (a) BWLS, (b) BWNV, and (c) BWSS. * denote bands attributed to amendment in soil-amendment mixture spectra.

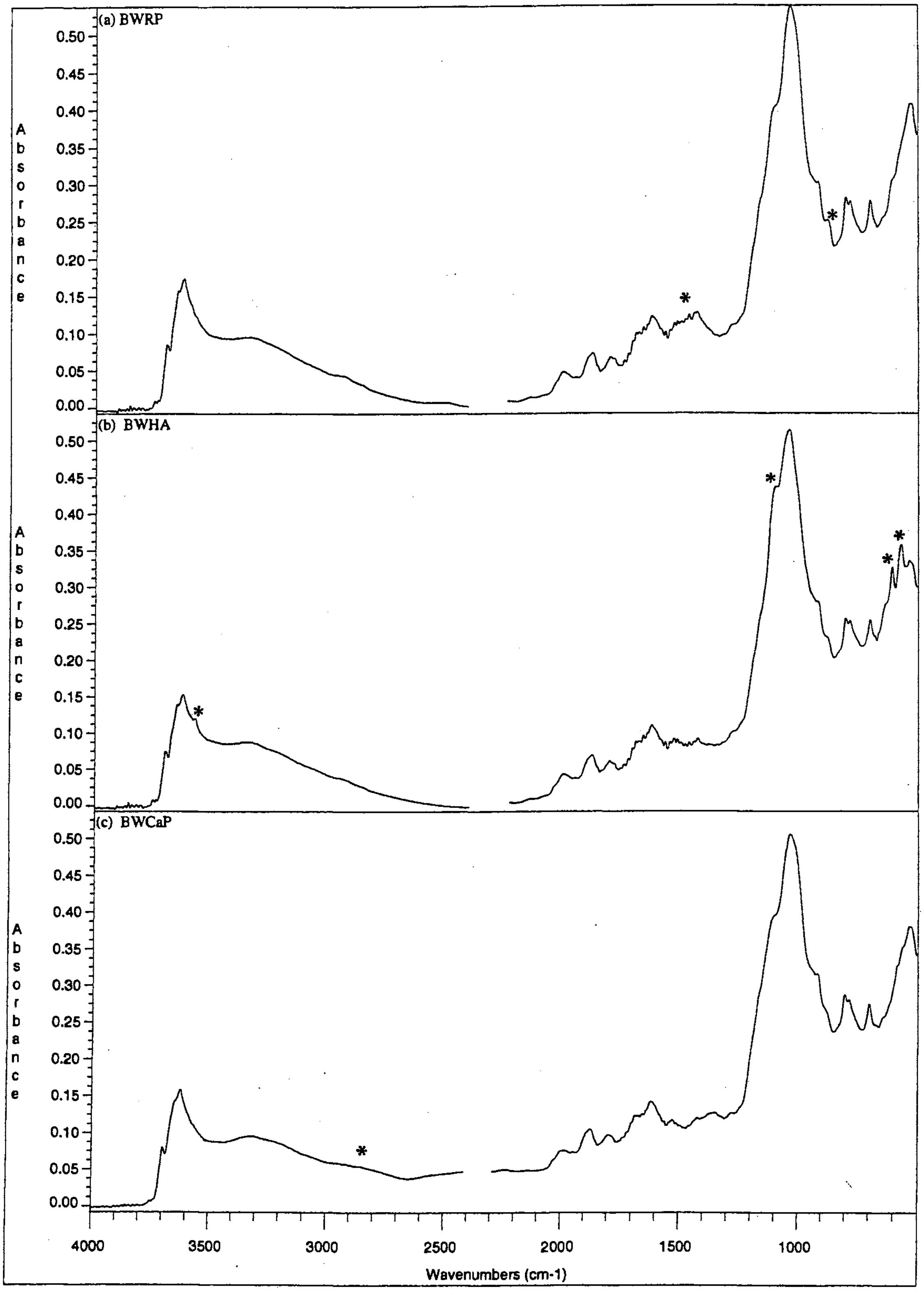

Figure 2. DRIFTS spectra of amended soils (a) BW(b)RP, (b) BW(b)HA, and (c) BW(b)CaP. * denote bands attributed to amendment in soil-amendment mixture spectra.

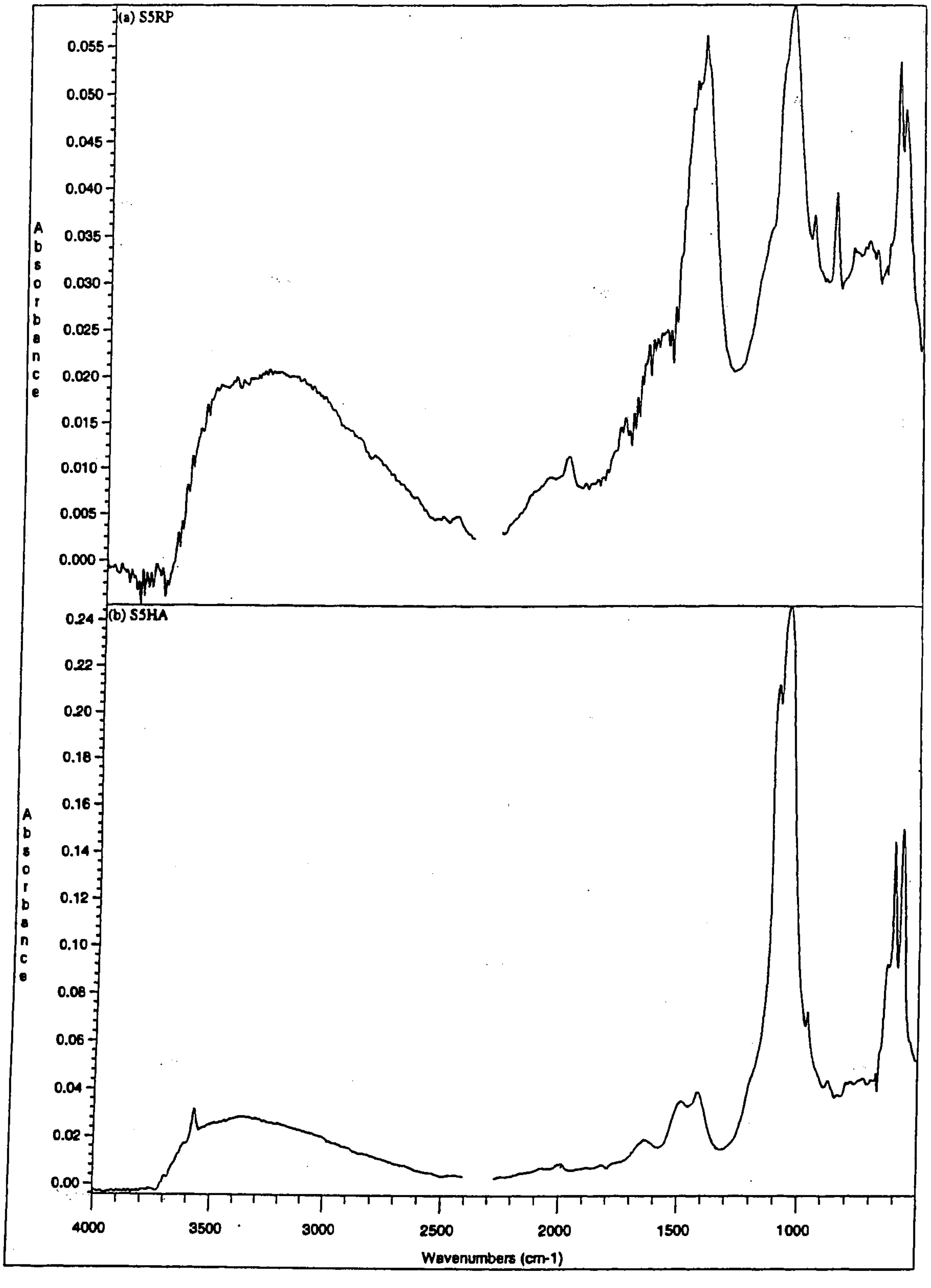

Figure 3. DRIFTS spectral subtractions for the S5 amended soils, (a) S5RP and (b) S5HA.

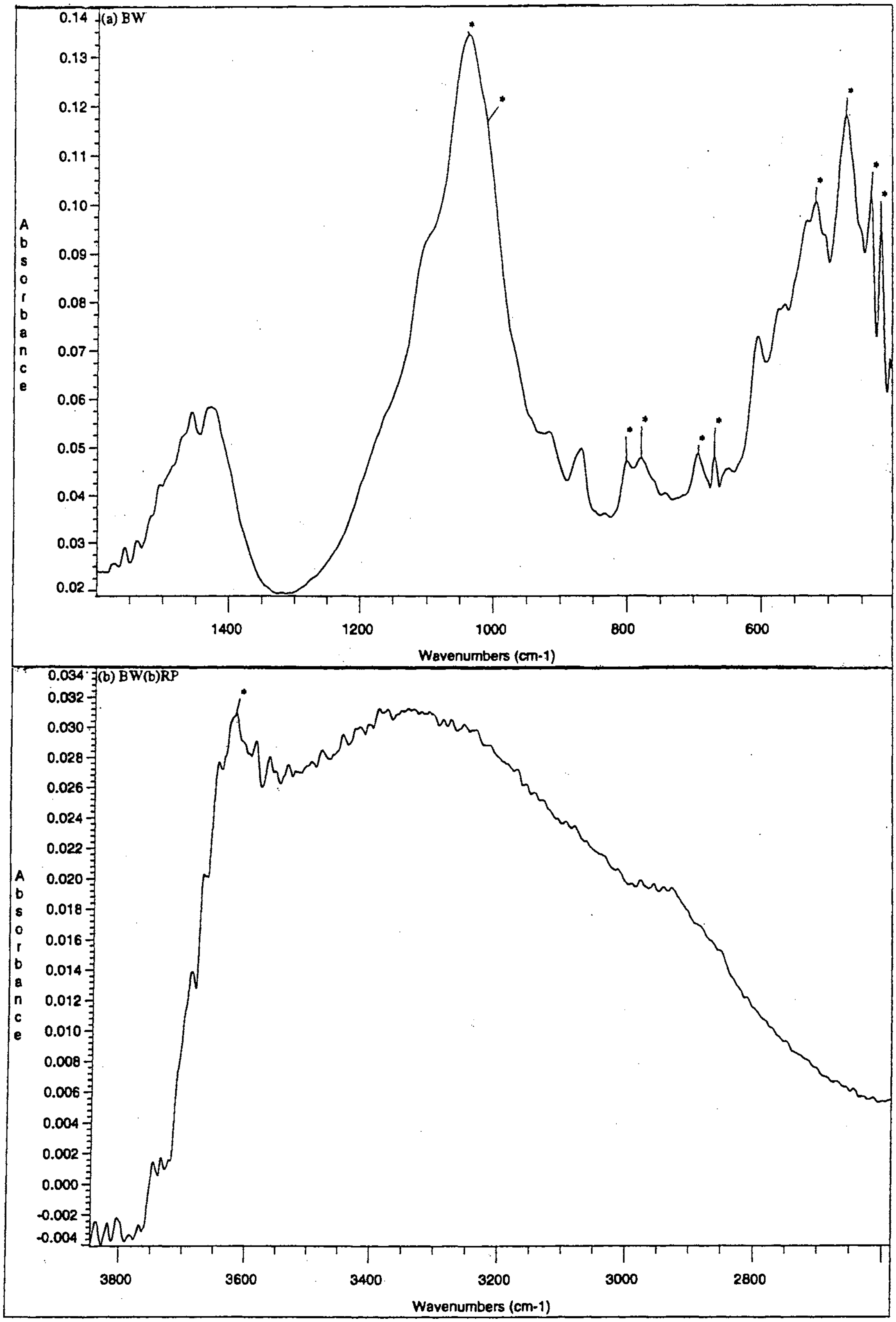

Figure 4. DRIFTS subtraction spectra of BW(b)RP soil. (a) 1600 to 400 cm^{-1} and (b) 3800 to 2700 cm^{-1}. * denotes new bands which are discussed in the text.

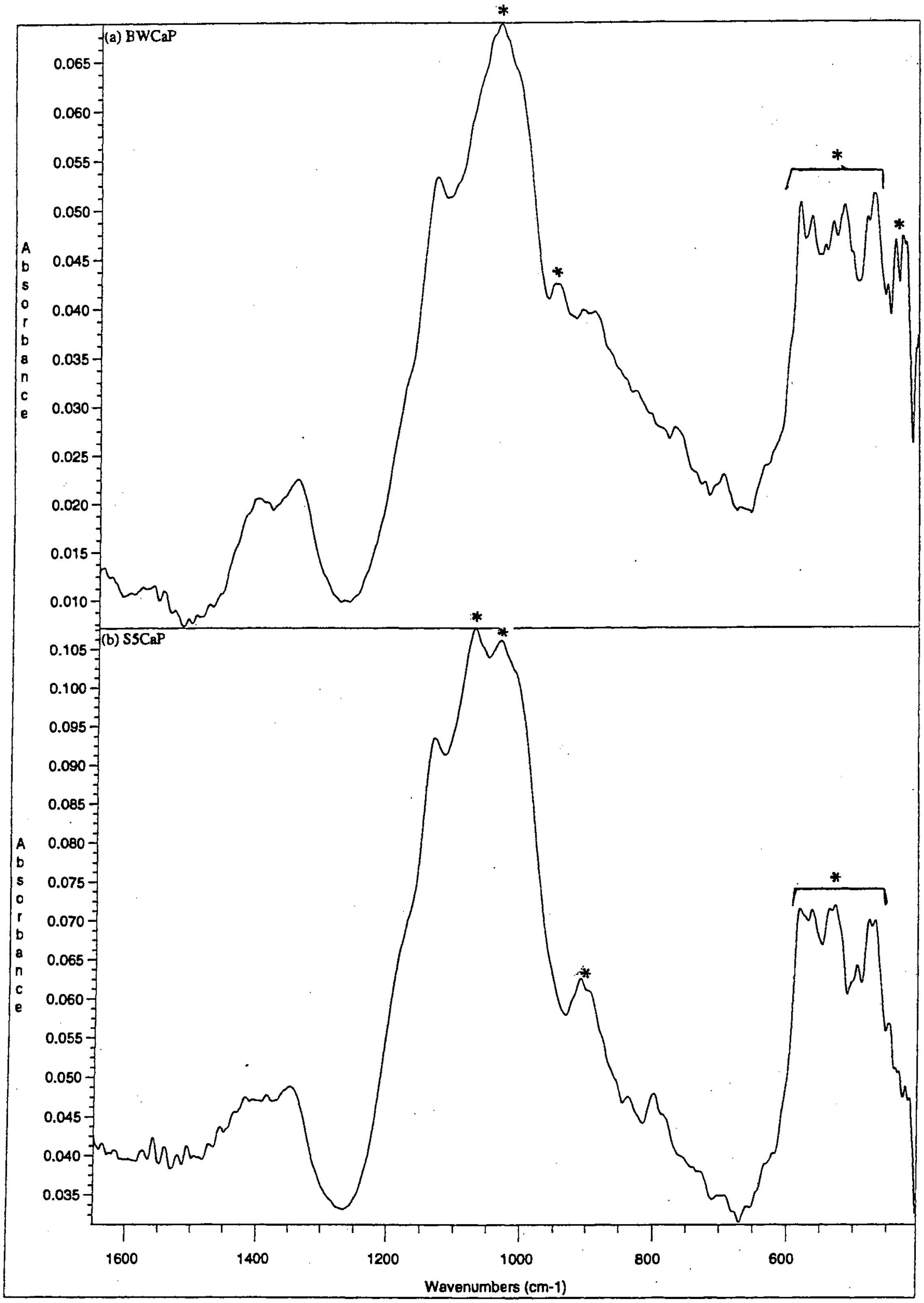

Figure 5. DRIFTS subtraction spectra of (a) BW(b)CaP and (b) S5CaP soils from 1600 to 400 cm^{-1}. * denote bands which are discussed in the text.

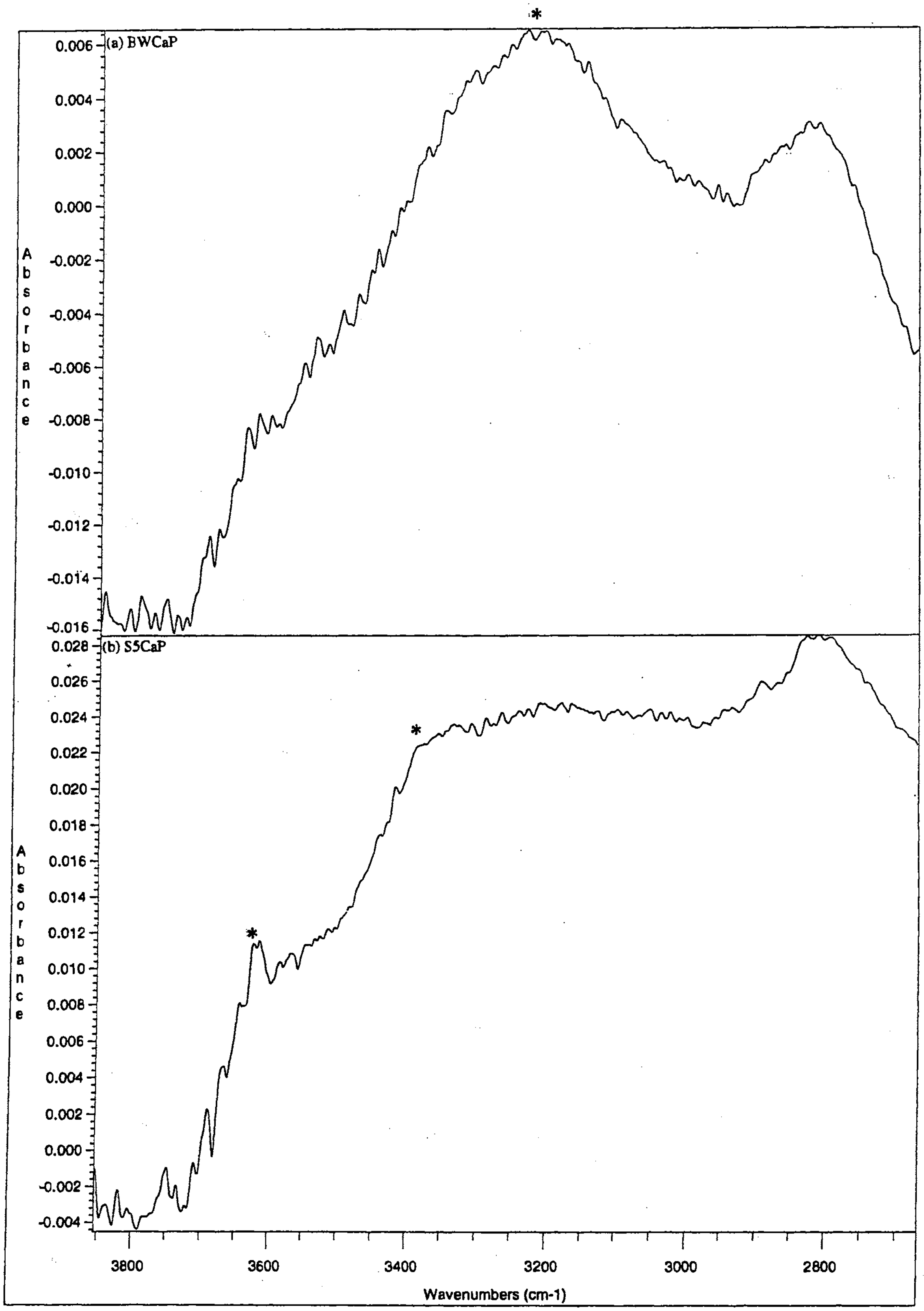

Figure 6. DRIFTS subtraction spectra of (a) BW(b)CaP and (b) S5CaP soils from 3800 to 2700 cm^{-1}. * denote bands which are discussed in the text.

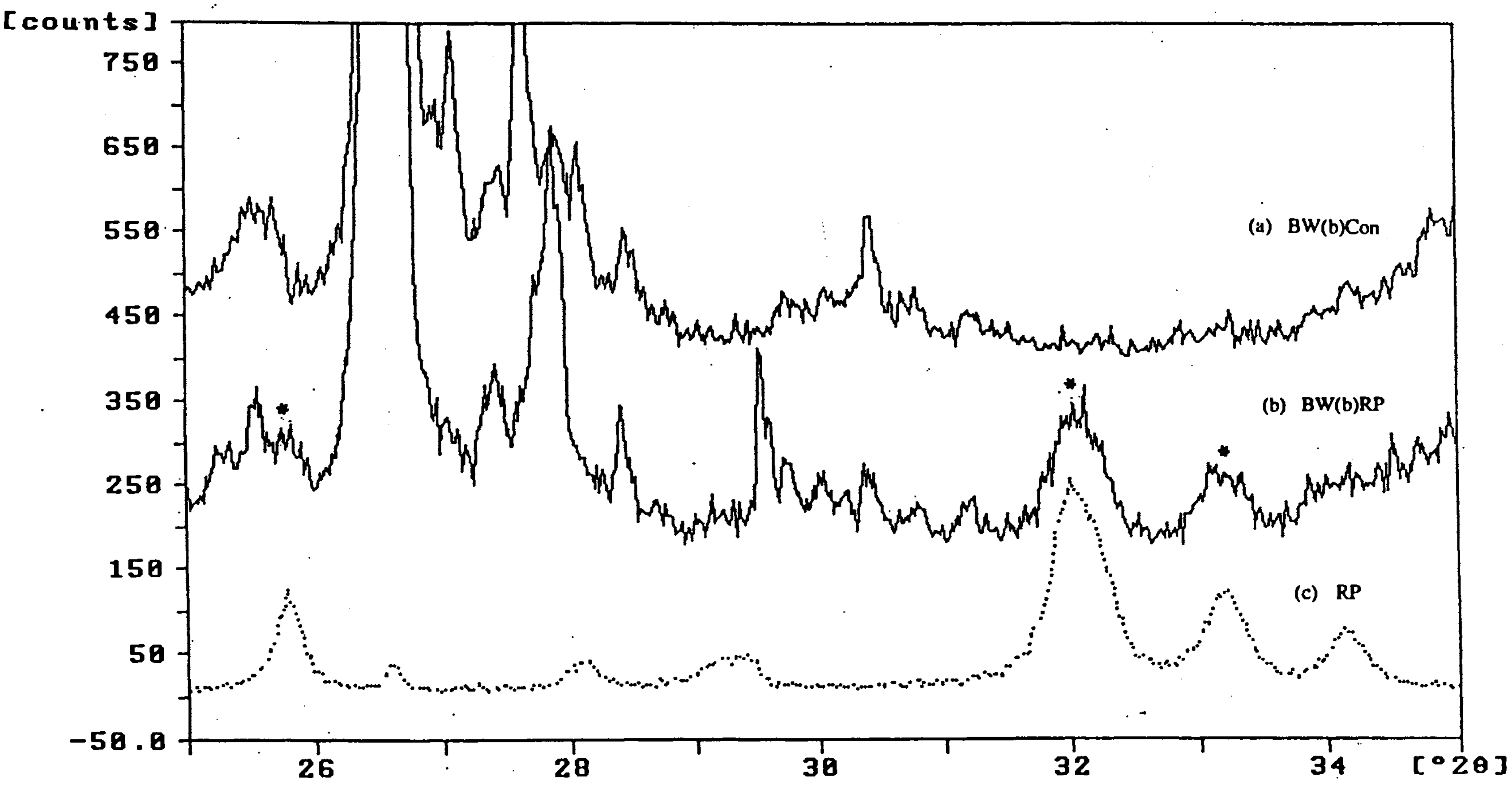

Figure 7. Powder XRD patterns for (a) BW(b)Con, (b) BW(b)RP, and (c) RP. * denotes peaks attributed to the amendment in the soil-amendment mixture pattern.

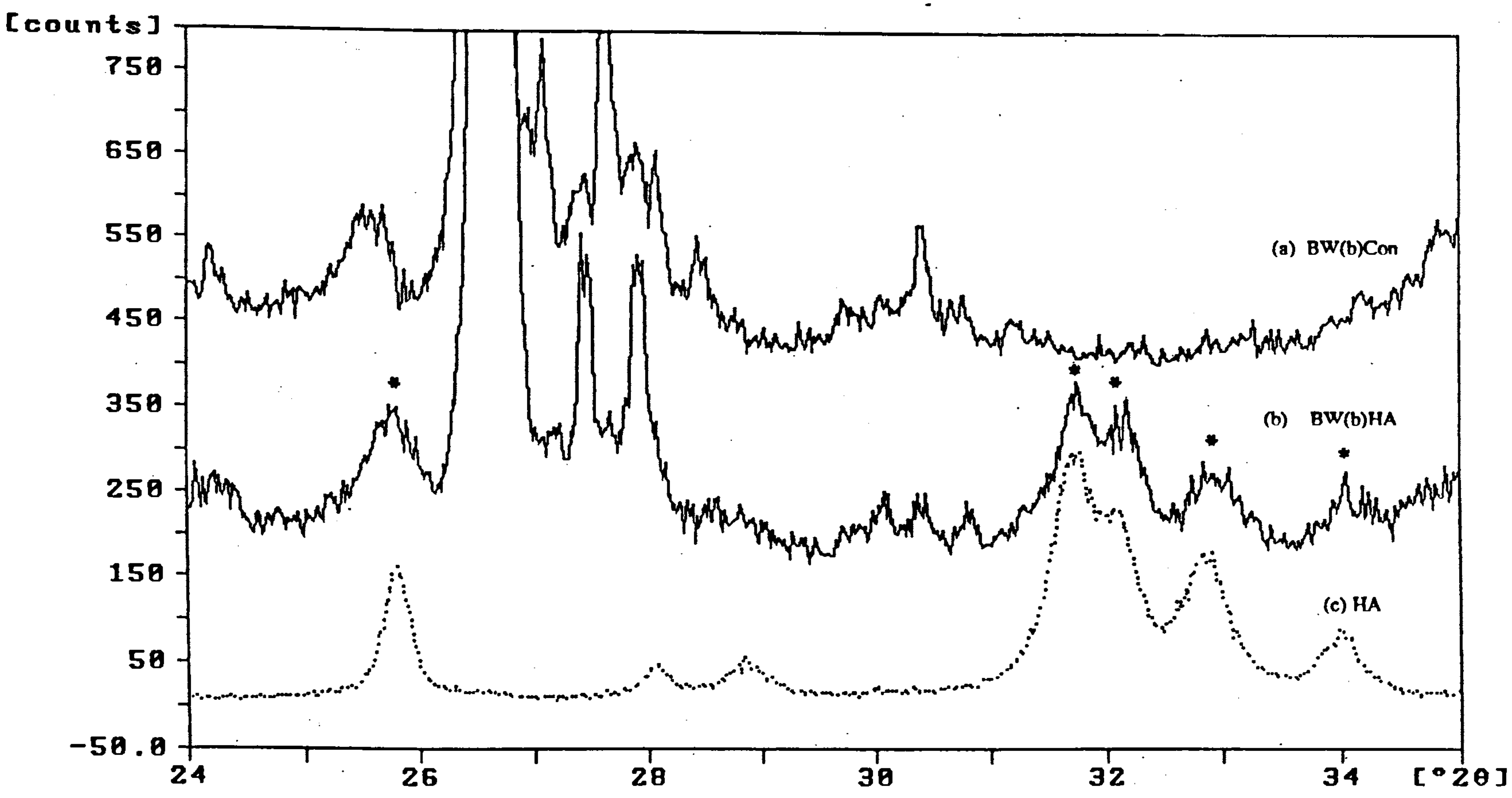

Figure 8. Powder XRD patterns for (a) BW(b)Con, (b) BW(b)HA, and (c) HA. * denotes peaks attributed to amendment in soil-amendment mixture pattern.

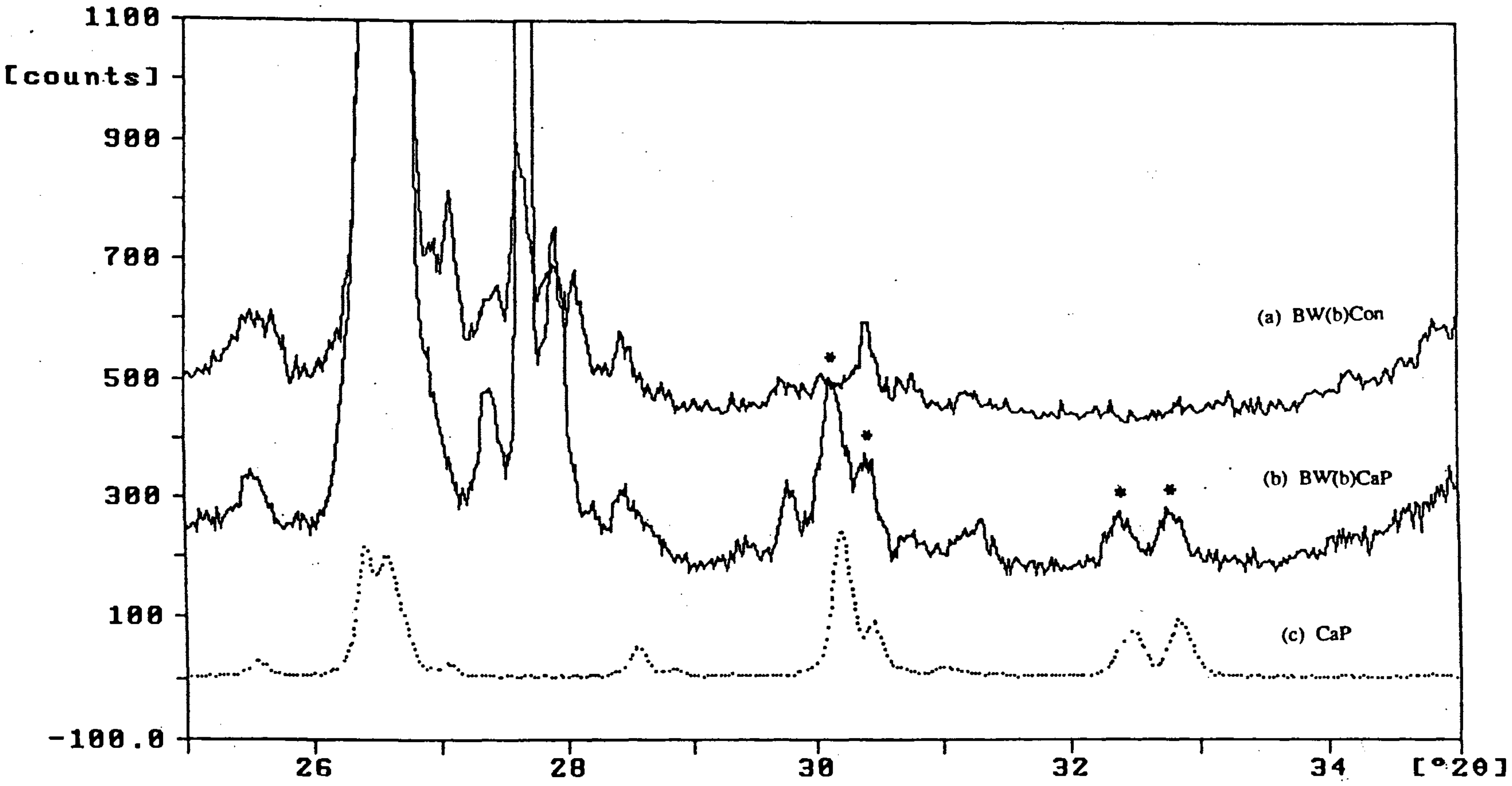

Figure 9. Powder XRD patterns for (a) BW(b)Con, (b) BW(b)CaP, and (c) CaP. * denotes peaks attributed to amendment in soil-amendment mixture pattern.

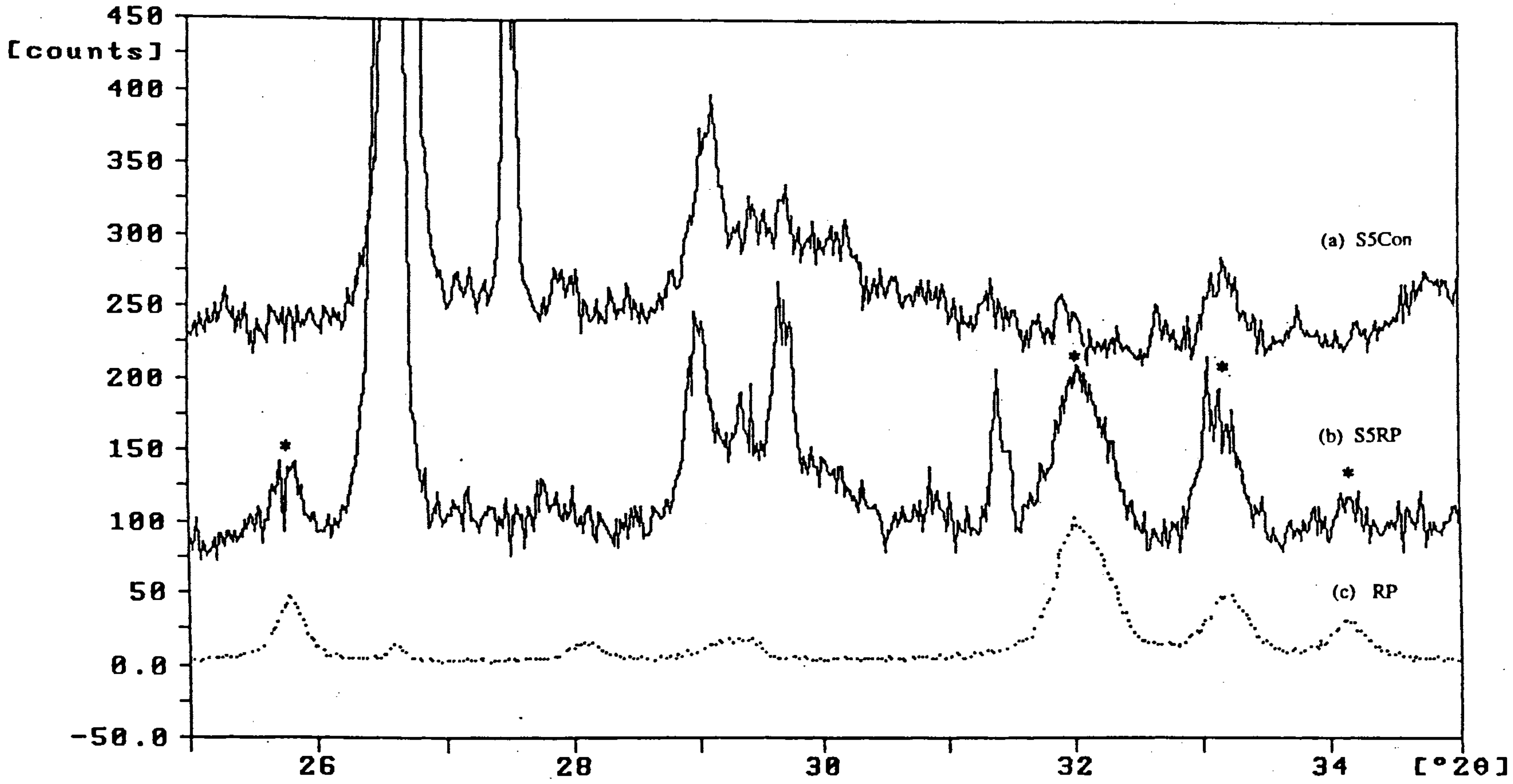

Figure 10. Powder XRD patterns for (a) S5Con, (b) S5RP, and (c) RP. * denotes peaks attributed to amendment in soil-amendment mixture pattern.

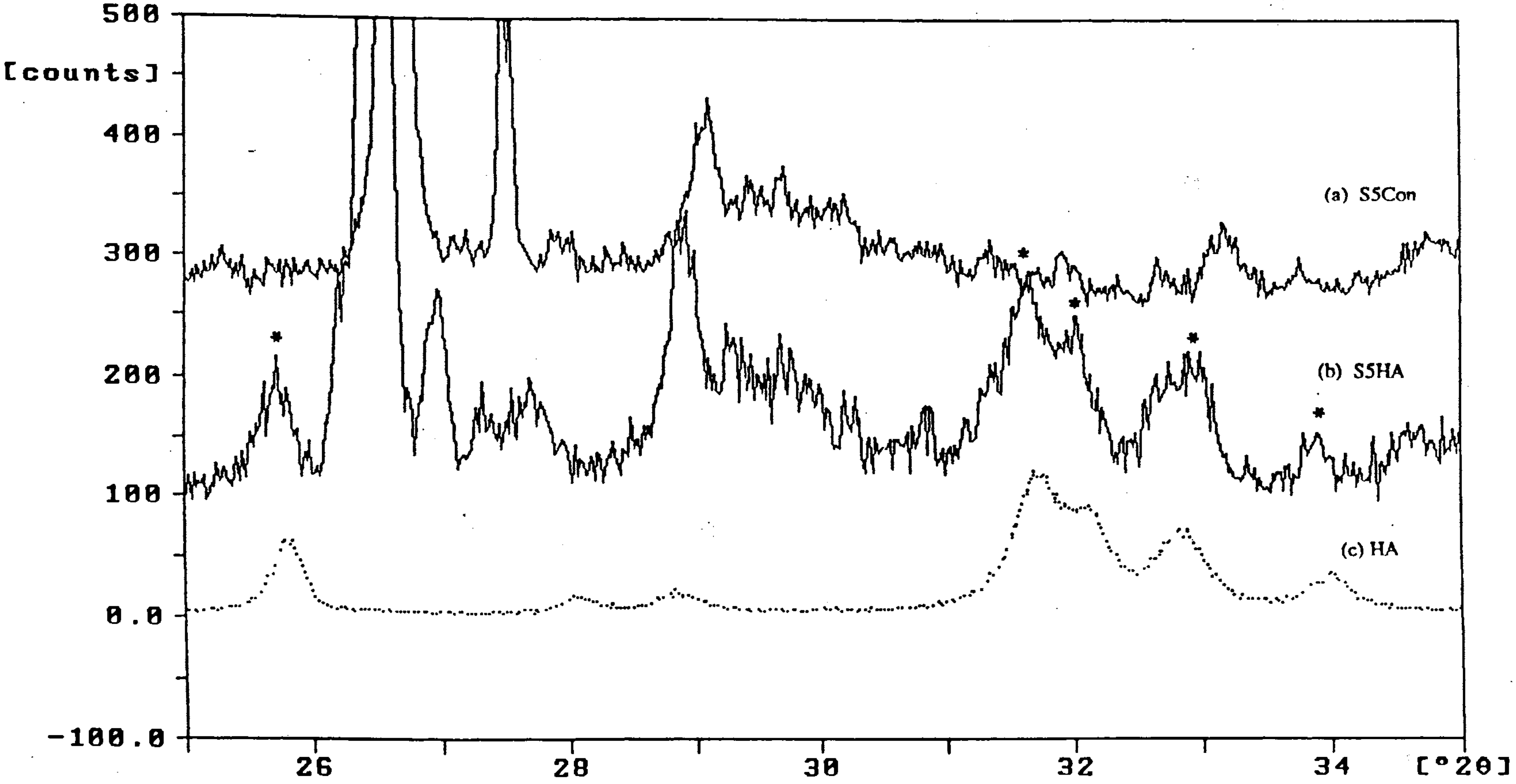

Figure 11. Powder XRD patterns for (a) S5Con, (b) S5HA, and (c) HA. * denotes peaks attributed to amendment in soil-amendment mixture pattern.

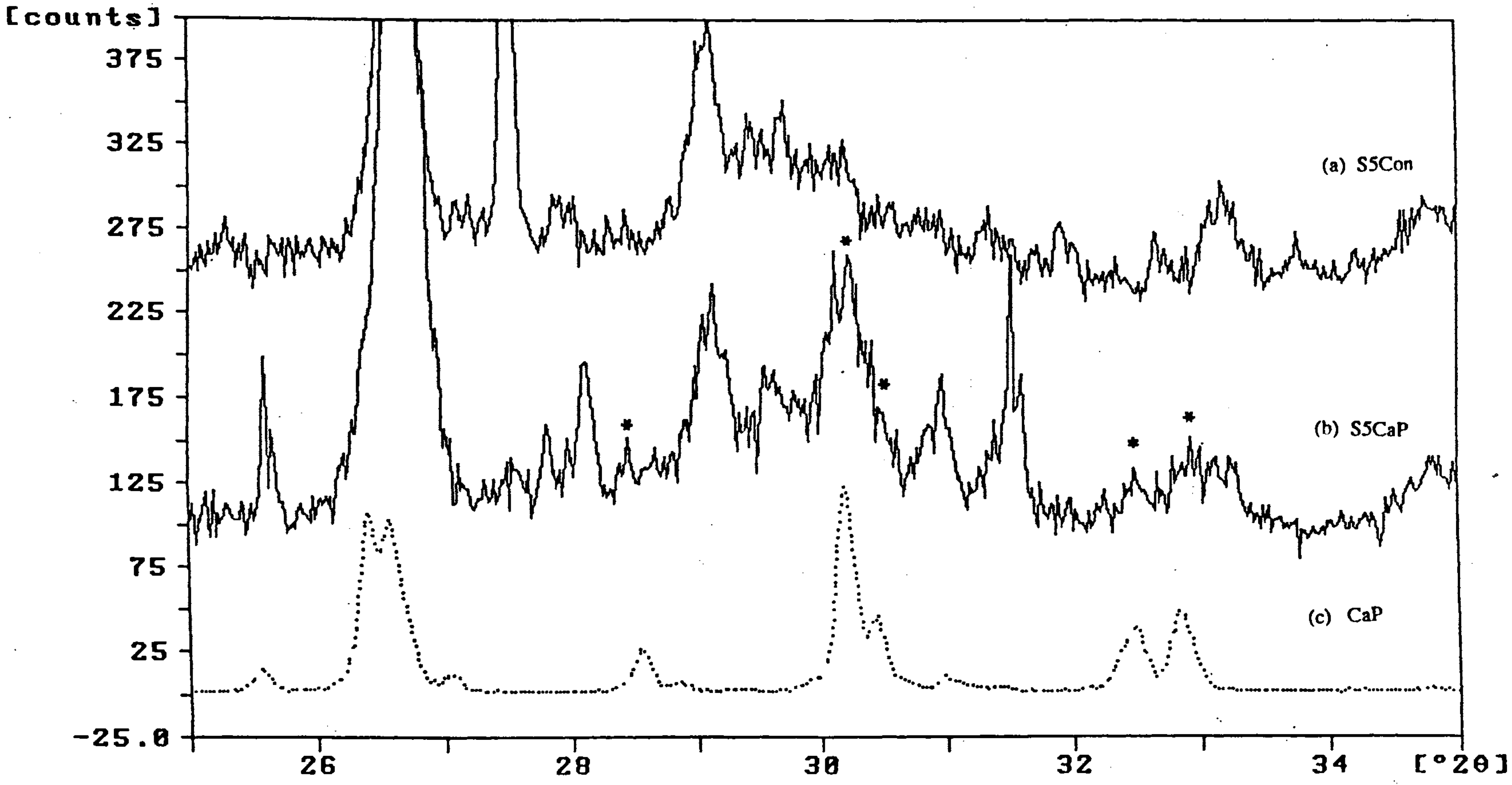

Figure 12. Powder XRD patterns for (a) S5Con, (b) S5CaP, and (c) CaP. * denotes peaks attributed to amendment in soil-amendment mixture pattern.

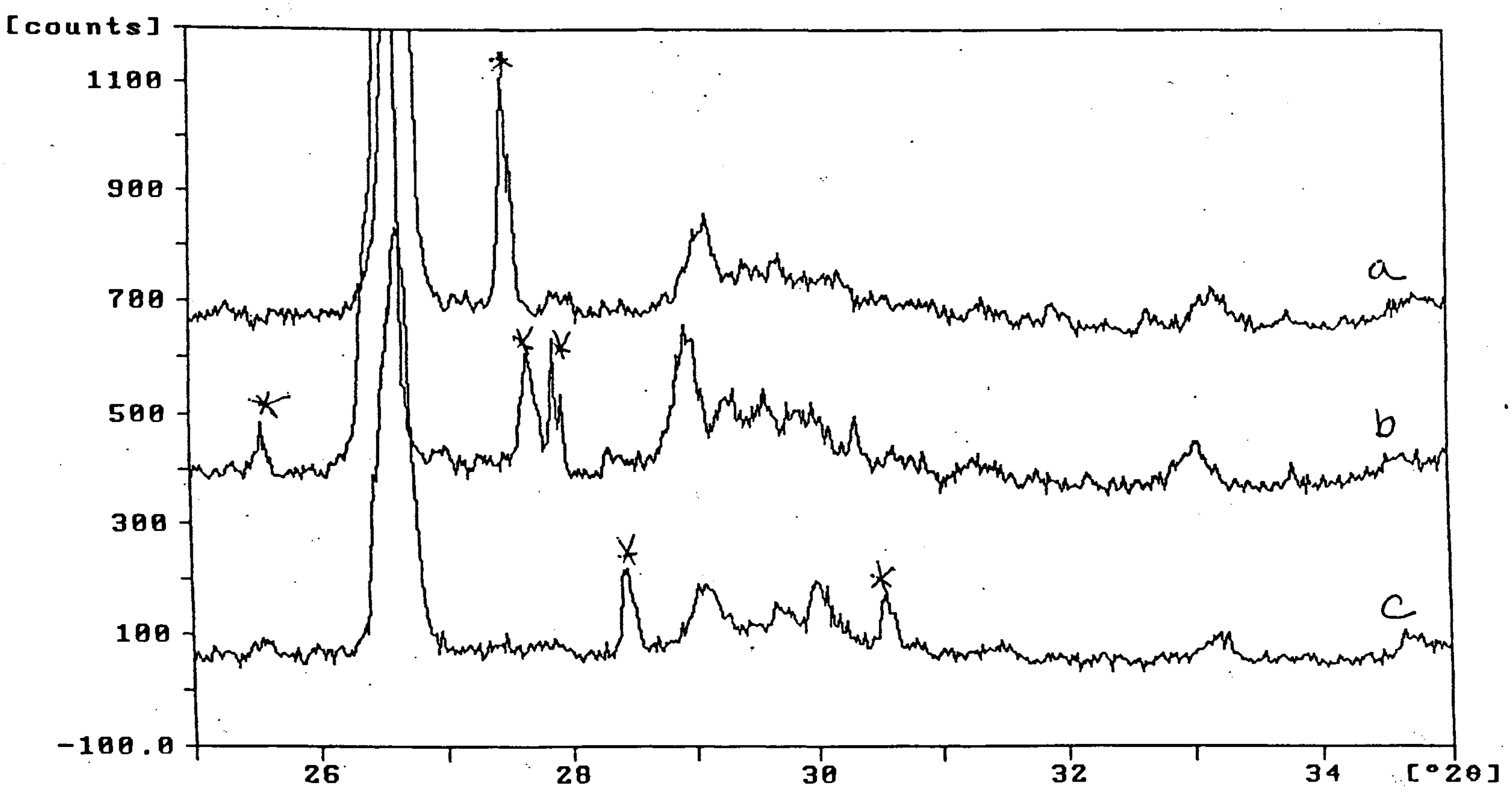

Figure 13. XRD powder patterns for the S5 control soil (a-c). * denote peaks discussed in the text.

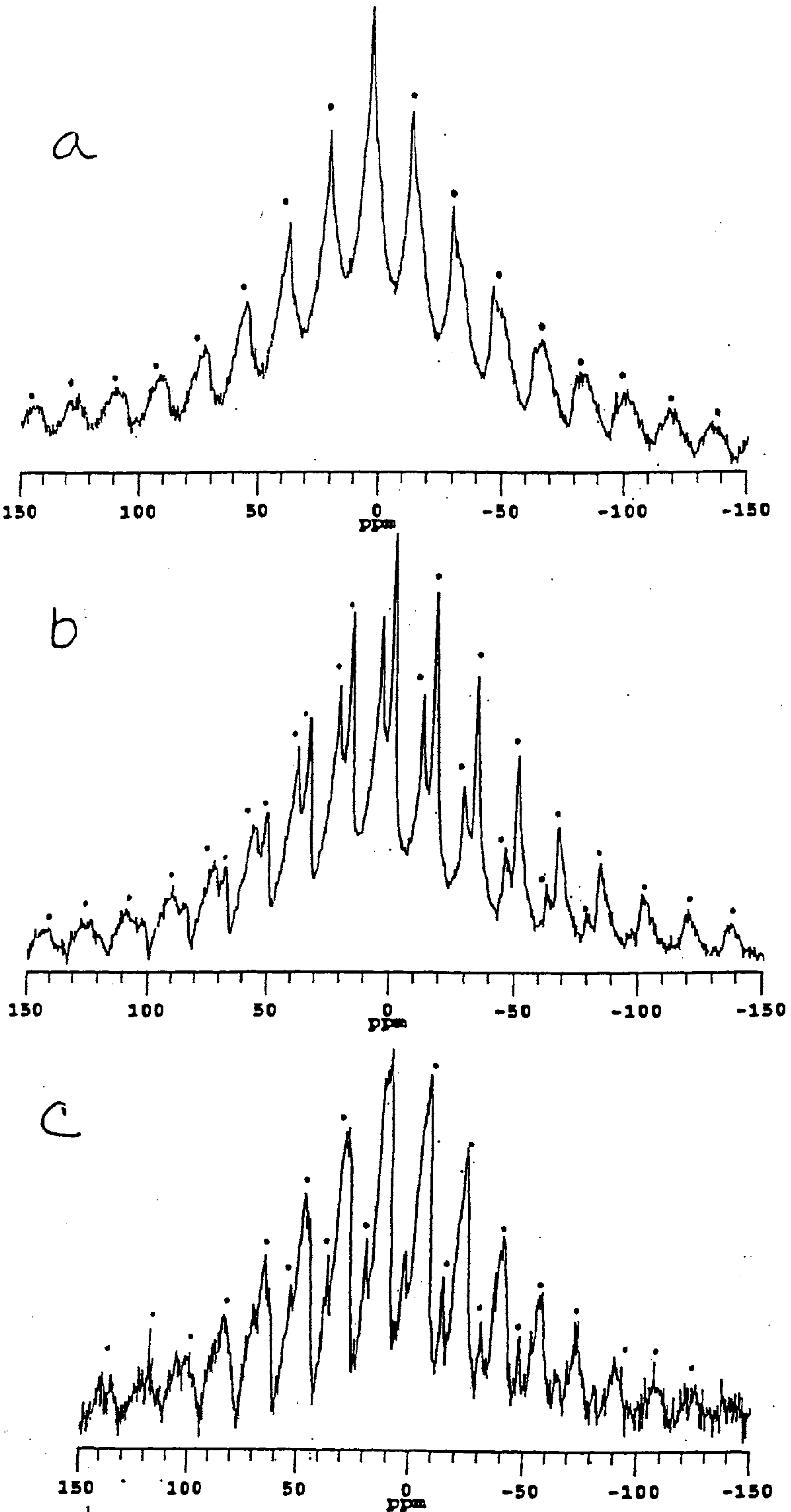

Figure 14. ^{1}H NMR spectra for BW(b) amended soils, (a) BW(b)RP, (b) BW(b)HA, and (c) BW(b)CaP. • denote spinning side bands.

CHAPTER VII

SUMMARY OF SEQUENTIAL EXTRACTION AND SPECTROSCOPIC STUDIES

A. Summary of Results

Sequential extraction studies (Chapter V) revealed that metal solubility was reduced when amendments were added to soils, verifying that in situ chemical immobilization is a viable technique for remediating heavy metal contaminated soils. The reduced metal extractability indicated that reactions occurred when the amendments were added to the soils which resulted in the formation of metal phases with reduced solubilities. This hypothesis was supported by the spectroscopic studies (Chapter VI) which confirmed that both new metal phases and surface reactions were occurring in the soil-amendment systems. Tables 1 and 2 summarize the findings for the sequential extraction and spectroscopic studies for the BW and S5 soils, respectively. The observation of spectroscopic changes associated with both precipitation and surface reactions indicates more than one mechanism of immobilization may be occurring.

The results of this study suggest the changes spectroscopy may be used to explain changes in metal extractability observed in sequential extraction studies, but changes in sequential extraction studies can not be used to predict when spectroscopic changes will be observed. For example, reductions in bioavailable metal of up to 46 % were observed in the sequential extraction study for the biosolids amended soils (Chapter V), but not spectroscopic evidence for the formation of new phases was observed.

Table 1. Summary of results for BW soil.

Evaluation Method	Amendment RP	 HA	 CaP
Sequential Extraction§	Cd, Pb, Zn: D (E1, E2) I (E3)	Cd, Zn: D (E1) I (E2,E3) Pb: D (E1, E2) I (E3)	Cd: D (E1) I (E2, E3) Pb, Zn: D (E1, E2) I (E3)
DRIFTS	Cd, Zn, and/or Pb phosphates; $PbCO_3$	-	Cd, Zn, and/or Pb phosphates; Reaction with OH
XRD	$Pb_5(PO_4)_3Cl$	-	$Pb_5(PO_4)_3Cl$
^{31}P NMR	-	-	-
^{1}H NMR	-	Reaction with OH	Reaction with OH
Conclusions	Form phosphate and carbonate ppt	Surface reactions, no ppt formation	Form phosphates and surface reactions

(-) = no new phases observed

§: D = decrease, I = increase, E = step in extraction scheme

Table 2. Summary of results for S5 soil.

Evaluation Method	Amendment RP	 HA	 CaP
Sequential Extraction§	Cd, Pb, Zn: D (E1, E2) I (E3)	Cd: D (E1), I (E2) Pb, Zn: D (E1, E2) Zn: I (E3) Pb: I (E3, E4)	Cd, Pb, Zn: D (E1, E2) I (E3 Zn)
DRIFTS	-	-	Cd, Zn, and/or Pb phosphates; Reaction with OH
XRD	$Cd_5(PO_4)_3OH$, $Zn_3(PO_4)_2 \bullet 4\ H_2O$	$Cd(OH)_2$, $PbHPO_4$	$Pb_{5-x}Ca_x(PO_4)_3OH$
^{31}P NMR	-	-	-
^{1}H NMR	-	Reaction with OH	Reaction with OH
Conclusions	Form phosphate	Form phosphate, surface reactions	Form phosphate, surface reactions

(-) = no new phases observed
§: D = decrease, I = increase, E = step in extraction scheme

B. Mechanism of Immobilization

Three mechanisms have been proposed for the interactions of the metals with the amendments: specific surface adsorption, ion exchange, and dissolution-precipitation.[1] Specific surface adsorption involves the accumulation of the metal at the interface between the surface and solution. This is a 2D process and does not involve 3D processes such as diffusion into the crystal or precipitation. Ion exchange involves the exchange of metal ions in the soil solution for Ca^{2+} ions in the amendment. Dissolution-precipitation involves the dissolution of the amendment, followed by precipitation of new metal containing phases.

In addition to the traditional explanations for metal-amendment interactions, another possible explanation for the reduced solubility of the metals in the soils could be the coating of the metal phases by the amendments. In a study conducted by Davis in 1994, the association of Pb containing phases with other mineral phases in the soil was investigated by electron microprobe analyses.[2] The study indicated that the coating or encapsulation of Pb bearing phases by less soluble phases reduced the bioavailability of Pb in soils. The tendency of soil organic matter to coat the reactive surfaces of minerals in soils is widely accepted phenomenon in soil science.[3,4]

The results of this study indicate that in addition to the formation of discrete insoluble precipitates, other mechanisms must be occurring during in-situ immobilization. If dissolution of the amendment followed by the formation of insoluble precipitates was the predominant mechanism for immobilization of the metals, the most soluble phosphate amendment should have been the most effective. This was not observed in this study.

C. Conclusions of Study

This study has demonstrated that in situ chemical immobilization can reduce metal solubility in smelter contaminated soils. The effectiveness of the amendments varies from amendment to amendment, from soil to soil, and from metal to metal. These results indicate that generalizations can not be made about amendment effectiveness and that information about the soil matrix and initial form of the metal in the soil need to be considered when choosing an amendment. Decisions regarding remediation of heavy metal contaminated soils by in situ chemical immobilization need to be tailored to a particular site.

In addition, this study has shown that the solubility of the phosphate amendment is not the controlling factor in the effectiveness of the amendments. Literature studies have proposed that the mechanism for the immobilization of Pb in phosphate amended soils is through the dissolution of the phosphate followed by the precipitation of Pb phosphate phases.[5] Although CaP was the most soluble phosphate amendment, it was not the most effective. These results indicate that even though dissolution-precipitation could be a mechanism for metal immobilization it does not determine the effectiveness of the amendment. Other immobilization reactions are important in controlling metal solubility. Spectroscopic characterization of the phosphate amendment revealed each amendment contained different structural and surface functionality which may be attributed to the differences in effectiveness of the amendments.

This study revealed that in some cases, spectroscopy can be used to identify the formation of new metal containing phases in the soil-amendment mixture. ^{31}P NMR does not provide any insight into the phases formed during in situ chemical immobilization. This study also revealed that multiple spectroscopic techniques must be used to study soil-amendment interactions. ^{1}H NMR provides information regarding the surface reactions between soils and amendments when surface hydroxyl groups exist in the amendment, but no information regarding the formation of new phases. XRD provides evidence for the formation of new crystalline phases, but no insight into possible surface reactions. DRIFTS spectral subtractions provided evidence for both the formation of new precipitates and the interaction amendment surface hydroxyl groups. Using different spectroscopic techniques has revealed the complexity of the soil-amendment immobilization process. Based on this study, it does not appear that predictions can be made regarding whether spectroscopic analyses will be successful or useful for a particular soil-amendment mixture.

D. Future Work

Many questions still need to be addressed regarding in situ chemical immobilization. Are there more effective amendments? What characteristics determine whether or not a contaminated soil is a good candidate for in situ chemical immobilization? What is the mechanism for immobilization of the metals?

Although the sequential extraction studies revealed that metal solubility had been reduced, metals were still extracted in the first and second steps of the sequential extraction scheme. The extremely low metal solubilites observed for the C1 soil indicate the formation of metal phases with very low solubilities is possible in soil systems.

What characteristics determine whether or not a contaminated soil is a good candidate for in situ chemical immobilization? The results of our sequential extraction study and those of others showed that amendment effectiveness varies from soil to soil. This could be attributed to the initial form of the metal in the soil or the characteristics of the soil matrix. Electron microprobe analyses is a promising new technique which can be used to determine the initial form of the metal in soils.[2]

Another question would be what is the mechanism for immobilization of the metals? Possible experiments which could provide insight in to the mechanism of immobilization are: 1. monitoring the changes in solution concentrations of calcium and phosphorous during incubation, 2. Timed sequential extraction studies to monitor changes in metal solubility as a function of time, 3. Geochemical modeling to identify the solid phases which may be controlling the metal solubility. In addition, investigations of the interactions of metal phosphates of different structures and surface reactivities may provide information regarding the varying effectiveness of the phosphate amendments investigated in this study.

E. References

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APPENDIX

Table A1. Sequential extraction data for Cd model compounds.

Sample	Step 1	Step 2	Step 3	Step 4
	mg kg^{-1}			
$CdPO_4$	7089	80224	327392	95364
$Cd_3(PO_4)_2$	456	88190	266143	261741
HA Ads Cd	46727	28324	30504	1275
HA Ppt Cd	59171	78972	59772	2063
Cd Phal	62370	180364	44770	379
Fe Ads Cd	9.0	185	309	880
Fe Ppt Cd	26	163	120	5092
0.6 pH4	31222	3333	275	202
0.6 pH 10	4400	44035	5551	1511

Table A2. Sequential extraction data for Pb model compounds.

Sample	Step 1	Step 2	Step 3	Step 4
	mg kg^{-1}			
$PbPO_4$	5850	720	406288	278190
$Pb_3(PO_4)_2$	253	161460	462643	88463
PbS	6535	47914	41018	67669
HA Ads Pb	45502	53653	125180	4958
HA Ppt Pb	29474	105194	212224	6574
Fe Ads Pb	0.0	258	870	808
Fe Ppt Pb	6.0	2986	27040	8355

Table A3. Sequential extraction data for Cd, greenhouse incubation soil samples.

Sample	Step 1	Step 2	Step 3	Step 4
	mg kg^{-1}			
BWCon	185.9	83.0	7.3	17.1
BWLS	32.6	206.1	18.1	19.6
BWNV	19.9	215.3	12.9	17.3
BWSS	93.0	103.6	19.1	18.9
BWRP	97.7	83.1	73.4	28.9
H12Con	22.8	41.5	9.8	15.8
H12LS	7.0	50.3	11.4	14.7
H12NV	5.0	52.6	9.3	15.2
H12SS	20.0	35.6	11.2	13.3
H12RP	19.4	35.7	11.7	14.3
B4Con	24.0	51.8	15.6	13.8
B4LS	6.7	63	17.9	13.4
B4NV	4.7	64.8	16.1	14.2
B4SS	20.7	45.8	19.4	13.8
B4RP	20.5	53.8	18.2	14.3

Table A4. Sequential extraction data for Pb, greenhouse incubation soil samples.

Sample	Step 1	Step 2	Step 3	Step 4
	mg kg^{-1}			
BWCon	5.4	253.0	37.0	87.1
BWLS	0.6	158.3	134.0	79.1
BWNV	0.1	232.2	36.3	75.9
BWSS	3.4	136.7	148.9	84.8
BWRP	3.7	183.3	146.3	96.7
H12Con	5.1	652.8	994.6	919.9
H12LS	0.8	461.1	1021.4	889.2
H12NV	0.4	576.9	809.8	883.7
H12SS	5.4	387.9	1073.2	798.2
H12RP	4.3	563.8	828.9	731.6
B4Con	1.3	225.9	522.8	241.1
B4LS	0.7	171.4	549.2	248.1
B4NV	0.8	211.3	490.5	351.5
B4SS	1.6	150.8	613.3	257.7
B4RP	1.4	235.5	523.2	205.1

Table A5. Sequential extraction data for Zn, greenhouse incubation soil samples.

Sample	Step 1	Step 2	Step 3	Step 4
	mg kg^{-1}			
BWCon	1089.5	6781.4	1796.1	2237.9
BWLS	8431	6754.0	2387.2	2221.6
BWNV	20.1	6665.6	2109.4	2308.4
BWSS	739.8	6247.1	2588.7	1950.5
BWRP	1200.7	5929.6	2123.0	2286.8
H12Con	472.0	9175.6	4893.0	6044.9
H12LS	85.8	7905.8	4800.5	5692.0
H12NV	26.6	7977.0	4421.5	6082.6
H12SS	756.6	7224.5	4992.7	5109.1
H12RP	407.1	8368.8	5381.3	3637.9
B4Con	492.1	2662.6	2175.4	3087.3
B4LS	64.2	2564.5	2109.7	2971.2
B4NV	23.1	2605.0	2121.1	2912.2
B4SS	542.7	2194.7	2219.9	2780.7
B4RP	435.8	2595.2	2217.5	2181.6

Table A6. Sequential extraction data for Cd, slurry incubation soil samples.

Sample	Step 1	Step 2	Step 3	Step 4
	mg kg^{-1}			
BW(b)Con	225.2	88.0	16.6	108.8
BW(b)RP	57.4	84.9	80.2	109.8
BW(b)HA	44.4	111.3	81.4	101.1
BW(b)CaP	55.1	121.5	75.0	97.2
H12(b)Con	22.8	57.3	20.1	15.8
H12(b)RP	13.8	48.3	24.9	16.5
H12(b)HA	6.8	50.1	30.6	25.4
H12(b)CaP	17.7	51.3	20.3	23.7
S5Con	4.1	35.3	67.1	72.5
S5RP	3.7	30.3	65.2	63.1
S5HA	2.3	37.7	64.8	67.4
S5CaP	3.6	28.6	58.8	61.4
C1Con	1.5	0.7	0.0	17.3
C1RP	0.3	0.9	1.0	22.0
C1HA	0.0	0.5	0.9	19.0
C1CaP	0.2	0.6	0.5	18.0

Table A7. Sequential extraction data for Pb, slurry incubation soil samples.

Sample	Step 1	Step 2	Step 3	Step 4
	mg kg^{-1}			
BW(b)Con	27.6	643.4	512.8	341.4
BW(b)RP	3.9	335.4	723.3	286.3
BW(b)HA	1.4	84.7	943.6	349.1
BW(b)CaP	4.0	310.1	809.1	307.1
H12(b)Con	4.5	739.7	1494.0	816.3
H12(b)RP	1.9	509.4	1352.7	629.7
H12(b)HA	0.1	169.9	1715.3	1373.3
H12(b)CaP	3.4	519.7	1443.0	1283.0
S5Con	2.5	1344.3	4344.3	9758.3
S5RP	1.6	858.2	4108.0	8137.7
S5HA	0.5	339.4	4883.3	9772.3
S5CaP	0.9	670.3	4091.7	8014.3
C1Con	0.1	5.0	48.3	6417.3
C1RP	0.0	3.1	29.4	6327.3
C1HA	0.0	2.4	23.1	6426.7
C1CaP	0.0	3.3	27.8	6506.0

Table A8. Sequential extraction data for Zn, slurry incubation soil samples.

Sample	Step 1	Step 2	Step 3	Step 4
	mg kg^{-1}			
BW(b)Con	4898.7	11883.0	8675.7	11889.7
BW(b)RP	639.9	10507.7	10133.0	8662.3
BW(b)HA	938.2	14021.3	9464.7	9620.0
BW(b)CaP	480.7	9530.3	12627.3	8895.0
H12(b)Con	495.4	9673.7	8366.3	6091.13
H12(b)RP	300.2	8464.7	8640.7	4000.0
H12(b)HA	181.9	8197.3	8733.3	9166.7
H12(b)CaP	366.8	8562.7	9750.0	7879.0
S5Con	7.1	457.1	274.1	4208.0
S5RP	6.4	382.8	525.1	3301.3
S5HA	2.4	321.2	457.3	3725.7
S5CaP	7.7	341.3	373.2	3417.7
C1Con	89.0	17.3	16.5	1177.0
C1RP	8.6	18.4	55.1	1285.0
C1HA	3.3	5.4	46.9	1241.0
C1CaP	14.0	17.2	37.7	1241.5

VITAE

Lisa Phegley

Candidate for the Degree of

Doctor of Philosophy

Thesis: SPECTROSCOPIC AND CHEMICAL EVALUATION OF IN SITU CHEMICAL IMMOBLIZATION FOR THE REMEDIATION OF HEAVY METAL CONTAMINATED SOILS

Major Field: Chemistry

Biographical:

Education: Graduated from MacArthur High School, Lawton, Oklahoma, in May 1988; received Bachelor of Science degree in Chemistry from Cameron University, Lawton, Oklahoma in May 1993. Completed the requirements for the Doctor of Philosophy degree with a major in Chemistry at Oklahoma State University in July 1998.

Experience: Employed as a teaching and research assistant at Oklahoma State University, Department of Chemistry, 1993 to present. Served as an intern at Hoechst Celanese Technical Center, Corpus Christi, TX, 1996.

Professional Memberships: American Chemical Society, American Society of Agronomy Soil Science Society of America, International Humic Substances Society, Phi Lambda Epsilon, Phi Kappa Phi