

University of São Paulo
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Desorption kinetics and speciation of Zn, Pb and Cd in a soil contaminated by mining activities amended with calcite, phosphate, biochar and biosolids

Frederico Prestes Gomes

Thesis presented to obtain the degree of Doctor in
Science. Area: Soil and Plant Nutrition

Piracicaba
2019

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versão revisada de acordo com a resolução CoPGr 6018 de 2011

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Gustavo, por todo apoio, amor e
cumplicidade*

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*Aos meus pais Rosa e Adalberto
pelo amor incondicional e por todo
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RESUMO

Cinética de dessorção e especiação de Zn, Pb and Cd em um solo contaminado por atividades de mineração e tratado com calcita, fosfato, biocarvão e biossólido

Áreas de mineração produzem grandes quantidades de resíduos que são importantes fontes de elementos potencialmente tóxicos (EPT), tais como os metais pesados. Esses EPTs podem contaminar o meio ambiente e causar sérias ameaças ao ecossistema e à saúde humana. A remediação in-situ pela adição de condicionadores é alternativa eficiente para a imobilização de contaminantes e para redução dos riscos associados a esses poluentes. Fosfato, calcita e compostos orgânicos são os condicionadores mais utilizadas para remediação in-situ. Neste estudo foi avaliado o efeito da aplicação de condicionadores na cinética de dessorção e especiação de Zn, Cd e Pb em um solo contaminado por atividades de mineração. O solo foi coletado em uma área desativada de mineração de Zn, localizada na cidade de Vazante, MG. A solo contaminado foi incubado com fosfato, carbonato de cálcio, biocarvão ou biossólido. A cinética de dessorção foi avaliada pelo método fluxo constante com a solução de Mehlich-3. A especiação foi realizada por espectroscopia de absorção de raios-x (XAS) e extração sequencial, enquanto a análise absorção de raios-x próxima da borda (XANES) foi realizada para Pb e Zn. Também realizamos o mapeamento por μ -XRF (microfluorescência de raios-x) e em alguns pontos no mapa realizamos a especiação por μ -XANES do Zn no solo tratado com fosfato. Foi também conduzido um experimento com colunas para avaliar a lixiviação de Zn, Pb e Cd no solo tratado com fosfato. A adição de fosfato afetou as espécies de Zn. No entanto, algumas espécies de Zn que foram formadas e assim podem ser mobilizadas com mais facilidade. O Zn foi mais facilmente mobilizado na maior taxa de fosfato, provavelmente devido à diminuição do pH. Os tratamentos com biossólido, biocarvão e calcita não alteraram as espécies de Zn. No entanto, em algumas doses, a dessorção de Zn diminuiu, enquanto o teor de Zn aumentou na fração recalcitrante. As principais espécies no solo sem alterações foram a bentonita Pb e a anglesita. O solo corrigido com calcita diminuiu a cinética de dessorção do Pb e aumentou o Pb extraído na fração residual, o que pode ser devido à formação de piromorfita. Os solos tratados com biossólido e com biocarvão aumentaram o teor de Pb associado à matéria orgânica e diminuíram na fração residual. Nestes tratamentos parte das espécies de Pb presentes neste solo foi transformada em Pb ligado a citrato. Essas alterações orgânicas aumentaram substancialmente a cinética de dessorção do Pb em todas as doses adicionadas. Os tratamentos com biocarvão e com biossólido foram efetivos para diminuir a dessorção de Cd. Nestas alterações orgânicas o Cd associado à matéria orgânica aumentou. Os tratamentos com fosfato e calcita também aumentaram o teor de Cd na fração orgânica. Essas alterações inorgânicas também foram eficazes para diminuir a cinética de dessorção do Cd.

Palavras-chave: Cinética de dessorção; Espectroscopia por absorção de raios-x; Remediação de solos; Metais pesados; Poluição do solo

ABSTRACT

Desorption kinetics and speciation of Zn, Pb and Cd in a soil contaminated by mining activities amended with limestone, phosphate, biochar and biosolids

Mining areas produce large amounts of waste that are important sources of potentially toxic elements (PTE), such as heavy metals. These PTEs can contaminate the environment and cause serious threats to the ecosystem and human health. The in-situ remediation by the addition of amendments is an efficient alternative for the immobilization of contaminants and for reduction of the risks associated with these pollutants. Phosphate, lime, and organic compounds are the most used amendments for in-situ remediation. We evaluated the effect of rates of amendments in desorption kinetics and speciation of Zn, Cd, and Pb in a soil contaminated by mining activities. The soil was collected in a disabled Zn mining area in the city of Vazante, state of Minas Gerais, Brazil. The contaminated soil was incubated with either phosphate, or calcium carbonate, or biochar, or biosolid. Desorption kinetics was evaluated by the "stirred-flow" method that consists of a constant flow with a Mehlich-3 solution. The speciation was performed by X-ray absorption spectroscopy (XAS) and sequential extraction. The analysis with synchrotron radiation X-ray absorption near the edge (XANES) was performed for Pb and Zn. We also performed a mapping by μ -XRF (micro X-ray fluorescence) and in some spots on the map we performed the speciation by μ -XANES for Zn in the soil amended with phosphate. An experiment with columns was carried out with samples from the soil amended with phosphate to evaluate leaching of Zn, Pb, and Cd. The treatment with phosphate affected the species of Zn. However, some Zn species that were formed and can be mobilized most easily. Zn was more easily mobilized in the highest rate of phosphate probably because of the decrease of the pH. The treatments with biosolid, biochar and calcite did not change Zn species. However, in some rates, Zn desorption decreased while Zn contents increased in the recalcitrant fraction. The main species in the unamended soil was Pb-bentonite and anglesite. The soil amended with calcite and pyromorphite decreased the desorption kinetics of Pb and increased the Pb extracted in the residual fraction, and this could be due to formation of pyromorphite. The soil amended with biosolid and biochar increased the Pb extracted in the organic fraction and decreased in the residual fraction. In these treatments part of the species of Pb present on this soil was transformed in Pb-citrate. The addition of biochar and biosolid increased the desorption kinetics of Pb in all rates applied. The treatment with either biochar or biosolid was effective to decrease the Cd desorption. In these organic amendments, the content of Cd associated to organic matter (OM) increased. The treatments with phosphate and calcite also increased the Cd associated to OM extracted in the F3. These inorganic amendments were effective to decrease the desorption kinetics of Cd.

Keywords: Desorption kinetics; X-ray absorption spectroscopy; Remediation of soils; Heavy metals; Soil pollution

1 INTRODUCTION

Activities of mining and processing of metals are of important because it ensures the production of raw material for the manufacture of goods which are indispensable for the man and provide many other benefits to society and the development of the country. However, the environmental damage they cause can be large, thus posing a serious threat to ecosystems and human health. These activities have resulted in a generation of high amount of waste, which is a great source of trace elements, such as cadmium (Cd), lead (Pb) and zinc (Zn), and consequently, may cause a substantial environmental contamination (Alloway, 2013).

The metals/pollutants can enter the human body through ingestion, inhalation, dermal contact, which represents a considerable threat to humans (Bi et al., 2006; Pelfrêne et al., 2011). Adverse environmental impacts of contaminated mining areas include the risk to human health, the phytotoxicity, contamination of water and soil and the ecotoxicity (Anju; Banerjee, 2010). In response, the development of technologies to remediate heavy metals contaminated soils has been encouraged (Gray et al., 2006).

Techniques for remediation of soils based on the excavation and the deposition on the landfill are highly effective in reducing the risk, but they are very expensive (Basta; McGowen, 2004). Furthermore, the engineering technologies are often invasive and do not allow natural recovery of the environment (Lombi et al., 2002). Innovative and low-cost techniques are required for decontamination of soils. A promising technology is the stabilization in situ of heavy metals in soil by the addition of amendments, such as phosphates (Baker et al., 2014; Sanderson et al., 2015) alkaline materials (Ok et al., 2010; Basta et al., 2004), biochars (Puga et al., 2016; Abdelhafez et al., 2014) and organic compounds (Ahumada et al., 2014; Sindhu et al., 2016).

In situ stabilization of metals is based on the reduction of metal mobility and availability, either by precipitation or by increased sorption (Lee et al., 2009). The use of soil amendments may decrease the solubility of metals and reduce their harmful effects on microorganisms, plants, aquatic organisms and humans (Lombi et al., 2002).

Possible mechanisms to explain the increase in retention and/or immobilization of metals, in the presence of P, include (i) the formation of phosphate of metals, which are low soluble precipitates in soils (Crannell et al., 2000), (ii) increase in negative net charge (Peres-Novo et al., 2009) and availability of surface phosphate groups in which metals can associate to form ternary complex (Guilherme; Anderson, 1998). Phosphorus is able to neutralize completely or partially or even reverse the positive charge prevalent on the surface of Fe and Al hydroxides in acidic soils (Lima et al., 2000).

The addition of alkaline compounds such as calcium carbonate increases the retention of metals in soils due to the increase in pH and has a great influence on the solubility of metals (Adriano, 2001). A high soil pH may precipitate the metals as hydroxides, phosphates, and carbonates and also promote the formation of quite stable metal-organic complexes (Kabata, 2011). However, precipitates formed due to the application of calcium carbonate can be easily dissolved and released into the soil solution. Carbonates of Pb can be easily dissolved by organic acids released by the rhizosphere of plants, easily extracted by acidic solutions and easily dissolved in the gastrointestinal tract of humans and animals (Essington, 2005).

Organic materials such as organic fertilizer and biochar can immobilize the metals by means of adsorption, complexation, and precipitation reactions. This occurs because of: (i) the increase of cationic exchange capacity (CEC) of the soils that promotes the increase of adsorption of metals, and (ii) the formation of insoluble and soluble complex with the organic constituents because of high affinity for heavy metals by functional groups of the organic compounds (Bolan et al., 2014).

One of the objectives of the addition of amendments is to reduce the leaching of metals in the soil profile, thus decreasing the risks of contamination of groundwater. A leaching study in columns can give us important information about the potential of remediators in decreasing the leaching of metals. This study is necessary to evaluate the immobilization and to evaluate if the treatment has reduced or increased concentrations of metals in the leachate. Houben et al. (2012) evaluated the leaching of heavy metals in a Technosol in an urban area from Liège, eastern Belgium, and observed that the addition of calcium carbonate reduced the concentrations in the leachate in 88% for Cd, 98% for Zn and 57% for Pb.

The speciation of metals in contaminated soils is an important tool for development and understanding of processes and reaction mechanisms that control the transport of nutrients and contaminants. By knowing the species present in soil, it is possible to obtain information on which phases control the bioavailability of metals and their kinetics of release (Sparks, 2014).

The distribution of heavy metals in soil fractions may be evaluated by indirect methods, such as the sequential extraction. However, direct methods of determination based on the spectroscopy absorption of X-rays have been developed. Methods of analysis spectral features of X-rays provide information about the dispersion of the elements and contribute to

identify the phases of mineral in the soils, for obtaining the mechanisms of sorption on a molecular level and the speciation of atomic structure site (Lombi and Susini, 2009). Such methods guarantee the selectivity and sensitivity of the local structure of a wide variety of elements, a high spatial resolution, and limit of detection and a simple preparation of the sample, which makes this method the most accurate in the study of the composition of contaminants in soils (Nevidomskaya et al., 2015).

The X-ray absorption near the edge (XANES) and the X-ray absorption fine structure (EXAFS) are spectroscopic techniques that provide essential information about the forms of heavy metals in the soil (Manceau et al., 2002). XANES is used to assist in the study of the electronic structure of substances, the determination of the symmetry and the energy of molecular orbitals vague in molecules (Soldatov, 2008). This method can provide information about the degree of oxidation and the symmetry of its sphere of coordination (Singh and Graefe, 2010). The absorption of X-rays is widely used in the speciation of metals in soils after addition of amendments (Baker et al., 2012, 2014; Montenegro et al., 2015; Sanderson et al., 2015).

The integration of studies of kinetics, leaching, and speciation provide important information about which chemical processes (precipitation, complexation, a formation of complexes of the internal or external sphere) will occur with metals present in the soil after the addition of amendments. With this information, one can create new strategies for remediation in situ of contaminated soil, thereby minimizing its mobility and bioavailability.

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2 ORGANIC AND INORGANIC AMENDMENTS ON THE SPECIATION AND DESORPTION KINETICS OF ZINC FROM MINE-WASTE IMPACTED TROPICAL SOIL

Abstract

Mining activities play an important role in business endeavors in the Brazilian economy. However, they may generate several environmental problems such as soil pollution. Zinc (Zn) is an element essential to plants and humans, but it can also be toxic to human beings, plants, animals, and microorganisms in high concentrations. The in-situ stabilization of heavy metals by the addition of amendments may be an effective and cost-effective strategy to decrease the risks associated with such heavy metals. The soil utilized in our study was collected from a deactivated mining area located in Vazante, in the state of Minas Gerais, Brazil and was amended with rates of phosphate, calcite, biochar, and biosolids to immobilize the Zn on the soil. After the addition of these amendments, the soil was incubated for 60 days with deionized water at 70% of maximum water retention. The soil was chemically and mineralogically characterized, and we performed sequential extraction, desorption kinetics and speciation using synchrotron-based techniques, such as μ -XANES, μ -XRF, and bulk XANES. The soil amended with phosphate was the only one that had different species of Zn identified by using linear combination fitting. In the course of these treatments gahnite, Zn-LDH, $Zn_3(PO_4)_2$, ZnO were identified by bulk XANES, while Zn-ferrihydrite, Zn-montmorillonite and Scholzite were also identified by μ -XANES. The best fit combination for bulk XANES were standards for all other treatments including Zn-montmorillonite, Zn-kerolite, Zn-ferrihydrite and gahnite, and these species were also identified by the μ -XANES. The soil amended with phosphate had total correlation and partial correlation with Ni, Co, Fe, Cr, Mn, Si, P, Cd, Pb and Cd, while the unamended soil had correlation with Cu, Pb, Fe and Si. Excluding the highest rate of P, the quarter rate and half rate which decreased the desorption kinetics of Zn. Calcite and the organic amendments (biochar and biosolids) were also effective in reducing the Zn desorption kinetics.

Keywords: X-ray absorption near edge structure; Soil pollution; Remediation of soils; heavy metals

2.1 Introduction

More than 2,647 mining areas in Brazil account for almost 5% of the Brazilian Gross Domestic Product and 20% of total jobs.¹ Mining and smelting activities, however, are projected to generate 11.4 million metric tons of waste between 2010 and 2030.¹ In 2014, Brazil produced 170 kiloton of Zn, which is about 1.5% of world production.² Part of this production is from mining areas in the Vazante region, located in the state of Minas Gerais,³ home to one of the major known deposits of non-sulfide zinc in the world.⁴

Mining wastes typically present a high content of potentially toxic elements such as zinc (Zn), lead (Pb) and cadmium (Cd) that are usually found on the surface of soils.⁵ Once mobilized in soils, these elements can be transferred to groundwater and plants, and present a potential threat to threaten human health.⁶ Although Zn is an element essential to the metabolism of plants and animals,⁷ in excess it can lead to toxicity.

Most soils from the humid tropics are particularly unique because they are highly weathered (e.g., Oxisols) and rich in Fe, Al, and Mn (hydr)oxide minerals that have predominantly pH-dependent surface charge.⁸ These (hydr)oxide minerals immobilize heavy-metal cations such as Zn^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} at high pH (> 7),⁹ and oxyanions such as H_2AsO_4^- and HSeO_3^- at low pH (< 7).¹⁰ Mine soils usually present pH values near to 7.¹¹ However, this value can decrease over time due to high precipitation and temperature, thereby increasing the availability of toxic trace elements.⁸ Brazil has the potential to increase soil contamination by zinc and other metals as a result of different processes, such as fertilizer application and smelter and mining activities.¹² New strategies are necessary to reduce the risks associated with these heavy metals because the utilization of techniques based on excavation and deposition at landfills becomes unfeasible.

Innovative and cost-effective techniques are required for the decontamination of soils. A promising technology is the in situ stabilization of heavy metals by the addition of amendments such as phosphate,^{13,14} alkaline materials,^{15,16} biochar,^{17,18} and organic compounds.^{19,20} These amendments are reported to reduce the environmental risks associated with heavy metals in soils by the formation of low soluble salts or precipitates, and increased sorption.²¹ Understanding the chemical environment of heavy metals in the soils is an important step towards a rational use of the amendments, which can optimize the effects of such treatments. Synchrotron radiation techniques such as X-ray fluorescence microanalysis (Micro-XRF) and X-ray Absorption Near Edge Spectroscopy (XANES) are the best techniques to know the metal speciation and their possible associations in complex environmental media due to their selectivity of elements studied and due to their high resolution. These techniques are state-of-art tools that can probe Zn local atomic structure in soils, minerals and sediments.^{22–25}

In this study we aimed to characterize Zn desorption and speciation from a mine-waste affected Brazilian soil. Zinc speciation and desorption kinetics were investigated before and after the addition of the following amendments: $\text{NH}_4\text{H}_2\text{PO}_4$, CaCO_3 , Biochar, and Biosolid. We used the synchrotron-based Micro-XRF and XANES, stirred-flow kinetic approach, and sequential extraction. The information provided in this study will be important to creating new strategies for in-situ stabilization of Zn in tropical soils impacted by mine-waste.

2.2 Materials and Methods

2.2.1 Soil Sampling and Characterization

Soil samples of a Technosol were collected from the surface layer (0-20 cm) of a Zn mining area located in Vazante, in the state of Minas Gerais, Brazil (close to geographic coordinates (17°59'11''S, 46°54'27''W)). The soil was air dried at room temperature and passed through a 2-mm sieve for further analysis. Soil organic C content was determined with a Shimadzu TOC-5000. The pseudo-total concentrations of Cd, Pb and Zn in the soil sample were extracted according to the EPA3051a method (1:3 HCl/HNO₃, v/v)²⁶ and quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES). Other chemical analyses (exchangeable ions and pH) followed the methods of Ingram and Anderson.²⁷ XRD was performed in the bulk soil, the clay, sand, and silt fractions. We also performed XRD in the clay fraction after both concentrating the iron oxides with 5 M NaOH,²⁸ and applying treatment with sodium dithionite-citrate-bicarbonate (DCB) for removing the free iron oxides.²⁹ More information about the XRD procedure can be found in the Supporting Information Available section.

2.2.2 Production and Characterization of Biochar and Biosolid

The biochar was produced from sugarcane (*Saccharum officinarum*) straw with pyrolysis at 450°C. Detailed information about the production and characterization are described in Feola Conz et al.³⁰ The biosolid was produced from the composting of wood chips (eucalyptus) and sewage sludge. The composting took place in aerated rows for 60 days and was sieved through a mesh with 36 mm² holes. In the composting process, about 2% of dolomitic limestone was added to the sludge. The sewage sludge was collected at a sewage treatment station located in Jundiai, in the state of São Paulo, Brazil and was composed, for the most part, of domestic rather than industrial sludge. The pH of biosolid was determined in water extracts (1:5 v/v), CEC was determined as described by Sparks³¹ and organic C content was determined by the Walkley and Black method. The total concentration of Cd, Pb, Zn, P, K, Ca and Mg in the biochar and biosolid were determined following the EPA3051a method.²⁶

2.2.3 Amendments and Incubation Time

The soil was amended individually in triplicate with biochar, biosolid, calcite (CaCO_3), and ammonium phosphate monobasic ($\text{NH}_4\text{H}_2\text{PO}_4$). Phosphorus (P) was applied evenly to the soil at 0 (control), 0.5 (quarter rate), 1 (half rate), and 2:1 (full rate) molar ratio of P as related to the sum of Pb, Cd, and Zn. These rates were based on the stoichiometric (P:M =3:5) form of the following precipitate $\text{M}_5(\text{PO}_4)_3\text{OH}$ (M= sum of Zn, Pb and Cd).³² Treatment with calcium carbonate (CaCO_3) was based on the formation of metal-carbonate precipitates, with general formula $[\text{MCO}_3]$, where $\text{M}=\text{M}_{\text{total}(\text{Zn}+\text{Pb}+\text{Cd})}$.¹⁶ M: CO_3 (full rate) molar ratio of 0.5:1 (half rate) and 0.25:1 (quarter rate) were also utilized. The biochar was applied at the rates of 2.5, 5.0, and 10%,³³ and biosolid at 5, 10, and 20% relative to the mass of soil.²⁰ The amendments were homogenized with the soil through mixing and incubated in the lab with deionized water at $25\pm 2^\circ\text{C}$ for 60 days at 70% of the maximum water retention capacity. Water was added every three days based on the mass loss of water to maintain this degree of humidity.

2.2.4 Bulk XANES

Zn-K edge XANES analysis was carried out on the samples that received the highest rate of each treatment at the XAFS2 beamline at the LNLS (Brazilian Synchrotron Light Laboratory), located in Campinas, in the state of São Paulo. The measurements were performed in transmission mode using a Si (111) double crystal monochromator. Energy calibration was performed using a Zn metal foil positioned between the second and the third ionization chamber. The soil samples were ground and 150 mg was pressed down to 5 mm diameter pellets, 1.3 cm^2 in size. Three XANES spectra were collected per sample and the spectra were acquired across the energy range of -130 to 340 eV relative to the Zn-K edge energy at 9659 eV. These spectra were energy calibrated, aligned, merged, and normalized using the Athena program within the IFEFFIT package. Linear combination fitting (LCF) analysis were carried out across an energy range of -20 to 80 eV relative to E0 using the method developed by Manceau et al.³⁴ to deconvolute different Zn species present and their relative contributions to the observed Zn spectrum (Figure S3). Additional information about the bulk XANES procedure and standards (Table S2) utilized for the LCF analysis are in the Supporting Information Available Section below.

2.2.5 Micro-XRF and Micro-XANES Measurements.

Micro-XRF imaging and spectroscopy were performed on the phosphate-amended and unamended soil sample that was air-dried, ground, and prepared as thin sections of ~20 μm thickness. For the P-amended soil we used sub-micron resolution X-ray (SRX) Beamline (5-ID) of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory, located in Upton, New York, USA. A focused spot of 1 μm x 0.7 μm controlled by Kirkpatrick–Baez mirrors and Si (111) horizontal double-crystal monochromator crystals were used at this beamline.

Micro-XRF analysis was carried out using an incident beam energy of 15 keV and the fluorescence signals were received by a three-element Si drift detector. The map plotted a 120 μm x 120 μm area of the sample, using a step size of 1 μm and a 1 s acquisition time. The μ -XRF mapping technique was used to image the distribution of Zn, Si, P, Ca, Fe, Al, Mg, K, Pb, Mn, Cu and Ni. For the unamended soil, the analyses were completed using μ -XRF and μ -XANES at the D09B-XRF Beamline at the LNLS.

A focused 20 μm diameter spot size controlled by a KB mirror system and Si (111) crystal monochromator were used. Micro-XRF analysis was carried out using an incident beam energy of 15keV and the fluorescence signals were measured by a silicon drift detector (SDD; AXAS-A, KETEK GmbH, Germany). The map was plotted across a 4,000 x 3,000 μm area of sample, using a step size of 30 μm and 0.3 sec acquisition time. The μ -XRF mapping technique was used to image the distribution of Zn, Fe and Si.

Zinc K-edge μ -XANES were collected from ten and then three additional Zn spots across the μ -XRF map in the P-amended soil and un-amended soil, respectively. Five XANES spectra were collected per sample and were acquired across the energy range of -100 to 200 eV relative to the Zn-K edge energy at 9659 eV. These spectra were energy calibrated, aligned, merged, and normalized using the Athena program in the IFEFFIT package. LCF analysis was carried out across an energy range of -20 to 80 eV and -20 to 40 eV relative to E0 for the P-amended and unamended soil, respectively. The fit results were obtained using the Manceau approach described above for bulk XANES. Additional information about μ -XANES procedure and standards (Table S2) utilized for the LCF analysis are in the Supporting Information Available section below.

2.2.6 Statistical Analyses of μ -XRF Images

Natural log-transformed μ -XRF intensity data normalized to the incoming X-ray intensity (I_0) was used to develop a statistical relationship between Zn and other matrix elements (Ca, Cr, Co, Fe, Mn, Ni, Pb, Cd, P, Cu, Si). Pearson correlation and also partial correlation analyses were done to remove the effects of other confounding variables. All statistical analyses were carried out using the R statistical software package (version 3.2.3). Correlations were considered significant where $\alpha = 0.05$.

2.2.7 Desorption Experiments

Zinc desorption kinetics were carried out using a stirred-flow reactor equipped with a piston displacement pump designed for use in an HPLC system (Figure S7 in SI). A 12 mL stirred-flow chamber was used in these experiments to which 0.2 g of <2 mm sieved of each amended soil samples were added. Mehlich-3 solution (0.2M CH_3COOH + 0.25M NH_4NO_3 + 0.013M HNO_3 + 0.015M NH_4F + 0.001M EDTA) solution was the desorption agent. The use of Mehlich-3 has been reported to estimate the heavy metals availability for plants³⁵ and to estimate your bioaccessibility.³⁶ A 25-mm diameter cellulose filter membrane with a 0.45 μm pore size was used in the reaction chamber. The solution flowed through the chamber at a rate of 1 mL min^{-1} and the suspension in the reaction chamber was stirred at 300 rpm. The effluent was collected from the reactor at 2 min intervals over a period of 2 h, and Zn concentration was determined by ICP-OES. The desorption kinetic of Zn was calculated according to Yin et al.³⁷ and plotted in cumulative Zn desorption percentages.

2.2.8 Sequential Fractionation Procedures

The sequential fractions of the humid tropical soils were determined following the procedure developed by Silveira et al.³⁸. The original method numbers seven fractions, but in the present study we extracted the following sequentially with 0.1 M CaCl_2 for readily exchangeable (F1); 1 M NaOAC (pH 5) for carbonates forms (F2); NaOCl (pH 8.5) for organic-matter bound (F3); 0.2M oxalic acid + 0.2M NH_4 oxalate (pH 3) for iron-oxides

bound (F4); and the residual (F5) was obtained after digestion following the EPA3051a method ²⁶. The Zn concentration in each fraction was quantified by ICP-OES.

2.3 Results

2.3.1 Soil, Biochar, and Biosolid Characteristics

Soils from the mining area were considered hazardous because the concentrations of Zn, Pb, and Cd in these soils exceeded the intervention values adopted by the state of São Paulo for industrial or residential areas, which were 10,000 mg kg⁻¹ of Zn, 4,400 mg kg⁻¹ of Pb, and 14.0 mg kg⁻¹ of Cd ³⁹ (Table 1; Table S1 in SI).

Table 1. Selected chemical properties of soils from the mining area that received the highest rates of phosphate, calcite, biosolid and biochar. See Table S1 for properties of all treatments.

Treatments	pH H ₂ O	Exchangeable							Total		
		C g kg ⁻¹	P mg kg ⁻¹	K	Ca mmolc kg ⁻¹	Mg	H+Al	Al	Cd mg kg ⁻¹	Pb g kg ⁻¹	Zn g kg ⁻¹
Phosphate	6.3	16	8991	0.4	79	186	166	119	98 ± 7	4.3 ± 0.3	13.0 ± 0.6
Calcite	8.5	19	125	0.6	356	198	0	0	110 ± 10	4.3 ± 0.4	13.3 ± 0.8
Biosolid	7.7	31	344	18.2	194	166	0	0	98 ± 10	3.4 ± 0.5	12.0 ± 1.1
Biochar	8.4	85	65	24.5	115	115	0	0	104 ± 13	3.7 ± 0.6	12.4 ± 1.0
Control	8.3	16	90	0.9	183	215	0	0	111 ± 11	4.1 ± 0.4	13.1 ± 0.7

The unamended soil sample had a pH of 8.3, but the addition of the amendments decreased the pH by up to two units, particularly for the samples amended with P. Soil C contents increased by 5.3 fold when amended with biochar and 1.9 fold when amended with biosolid. The XRD indicated the presence of Goethite (α -FeO(OH)), Hematite (Fe₂O₃), Kaolinite (Al₂Si₂O₅(OH)₄), Gibbsite (Al(OH)₃), Muscovite (KAl₃Si₃O₁₀(OH)₂), Clinocllore ((Mg,Fe²⁺)₅Al₂Si₃O₁₀(OH)₈), Montmorillonite ((Na,Ca)_{0.3}(Al,Mg)₂Si₄O₁₀(OH)₂•n(H₂O)), and Quartz (SiO₂) (Figure S1 in SI). The organic amendments had a high pH and high CEC (Table 2). The biochar had 4.3 times more carbon than biosolids, whereas biosolids had a higher concentration of macronutrients (P, Mg, Ca,) and trace elements (Cd, Pb, Zn) than biochar.

Table 2. Chemical properties of biochar and biosolid.

Amendments	pH H ₂ O	CEC mmolc kg ⁻¹	C	P	K	Ca	Mg	Cd	Pb	Zn
Biosolid	7.4	270	150	7	8	38	13	< 0.1	19.1	314
Biochar	8.8	200	650	2	10	3	3	0.0	0.0	0.03

2.3.2 Zinc Speciation and Elemental Distribution

2.3.2.1 Bulk-XANES Analysis

Zinc K-edge XANES spectra for the control (unamended) soil samples from mining area and after treatments were nearly identical, except for the P-amended samples (Figure 1). Consistent with the XANES spectra, LCF results also showed similar fits for all treatments, except for the P-amended samples (Table 3). When the P amended samples were excluded, the best fit combination of standards for all other treatments included 26-30% Zn-montmorillonite, 40-41% Zn-kerolite ($\text{Zn}_{2.1}\text{Mg}_{0.9}\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$), 18-24% Zn-ferrihydrate, and 10-14% Gahnite (ZnAl_2O_4). The treatment with P had a fit with Gahnite (20%), Zn-LDH (Zn Layered double hydroxides) (16%), $\text{Zn}_3(\text{PO}_4)_2$ (49%), and ZnO (15%).

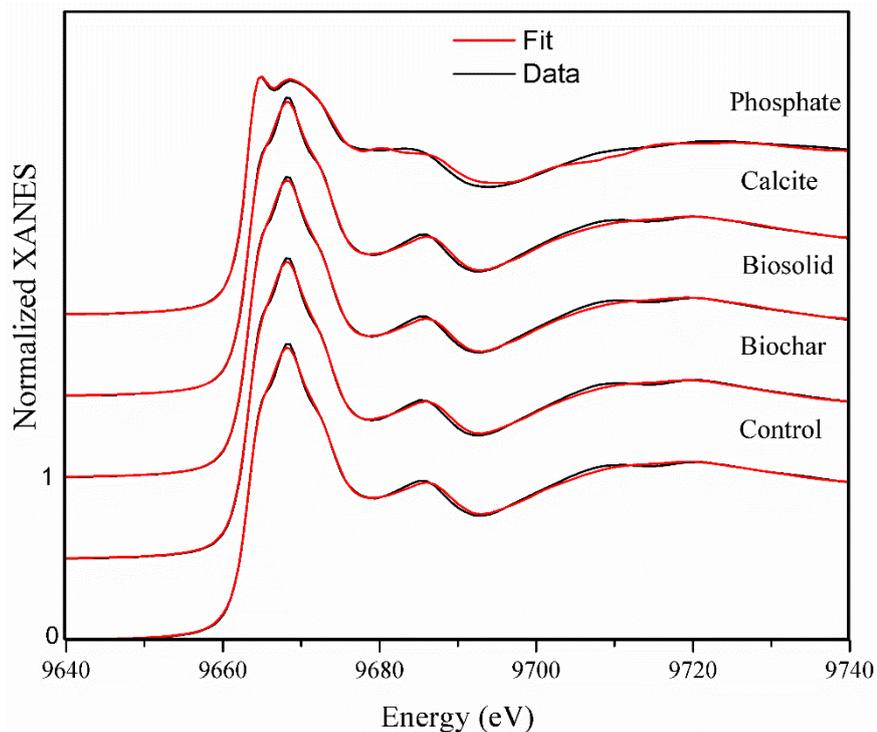


Figure 1. Zinc K-edge XANES spectra and overlaid best fits from linear combination fitting (LCF) analysis of mining area soil in the highest treatment of phosphate, calcite, biosolid, and biochar. Fitting was done across an energy range of -20 to 80 eV relative to E0 (first-derivative maximum).

Table 3. Combinations of standards yielding the best fits to zinc K-edge XANES spectra for mining area soil in the highest treatment of biochar, calcite, biosolid, and phosphate for a linear-combination fitting (LCF) energy range of -20 to 80 eV relative to E0 (first-derivative maximum)[¶].

Treatment	Zn-montmorillonite	Zn-kerolite	Zn-ferrihydrite	Gahnite	Zn-LDH	Zn ₃ (PO ₄) ₂	ZnO	10 ⁴ x R-factor [‡]
-----Proportion of standard ± uncertainty (%)†-----								
Control	26 ± 2	40 ± 2	24 ± 2	10 ± 1				6.0
Biosolid	29 ± 2	41 ± 3	19 ± 2	11 ± 1				5.8
Biochar	30 ± 2	41 ± 3	18 ± 2	11 ± 1				6.8
Calcite	28 ± 2	40 ± 3	18 ± 2	14 ± 1				6.7
Phosphate				20 ± 1	16 ± 1	49 ± 3	15 ± 1	11.7

[†] All data have been re-normalized to sum to 100 %; uncertainties were calculated in Athena.

[§] Suspected contamination.

[‡] R-factor is a measure of goodness of fit = $\sum(\text{data-fit})^2 / \sum(\text{data})^2$.

2.3.2.2 Micro-XRF Maps, Statistical Analyses of μ -XRF images and μ -XANES

The μ -XRF images in the P-amended soil showed the spatial distribution of Zn, Si, P, Ca, Fe, Al, Mg, K, Pb, Mn, Cu, and Ni (Figure 2). Zinc was co-localized with Fe, Si, Al, Mg and Ni, and the P was co-localized with Cu, Zn, Ni, Fe, and Ca. Similarly, the hotspot of Pb and Mn were co-localized, but its spatial distribution was different from Zn. The two hotspots from Zn (spot 10 and 4 on the XRF map) also co-localized with two hotspots of Ni. In our study, Zn had strong significant correlation with Ni ($r = 0.62$), Co ($r = 0.56$), Fe ($r = 0.53$), and Cr ($r = 0.51$) (Table S3 in SI). However, the partial correlation analysis carried out to remove the confounding effects of other elements had highest correlation with Ni ($r' = 0.56$), Mn ($r' = 0.38$), and Pb ($r' = -0.29$). The partial correlation coefficients decreased when compared to the Pearson correlation coefficient, implying the dependent spatial relationship between Zn and Ni, Co, Fe, and Cr on other co-localized elements present. The μ -XRF image in the unamended soil showed the spatial distribution of Zn, Cu and Si (Figure S3 in SI). Zn had significant ($p < 0.05$) correlation with Cu ($r = 0.19$), Pb ($r = 0.20$), Si ($r = 0.08$), and Fe ($r = 0.20$) (Table S4 in SI), whereas partial correlation had significant correlation only with Cu ($r = 0.20$) and Si ($r = 0.09$).

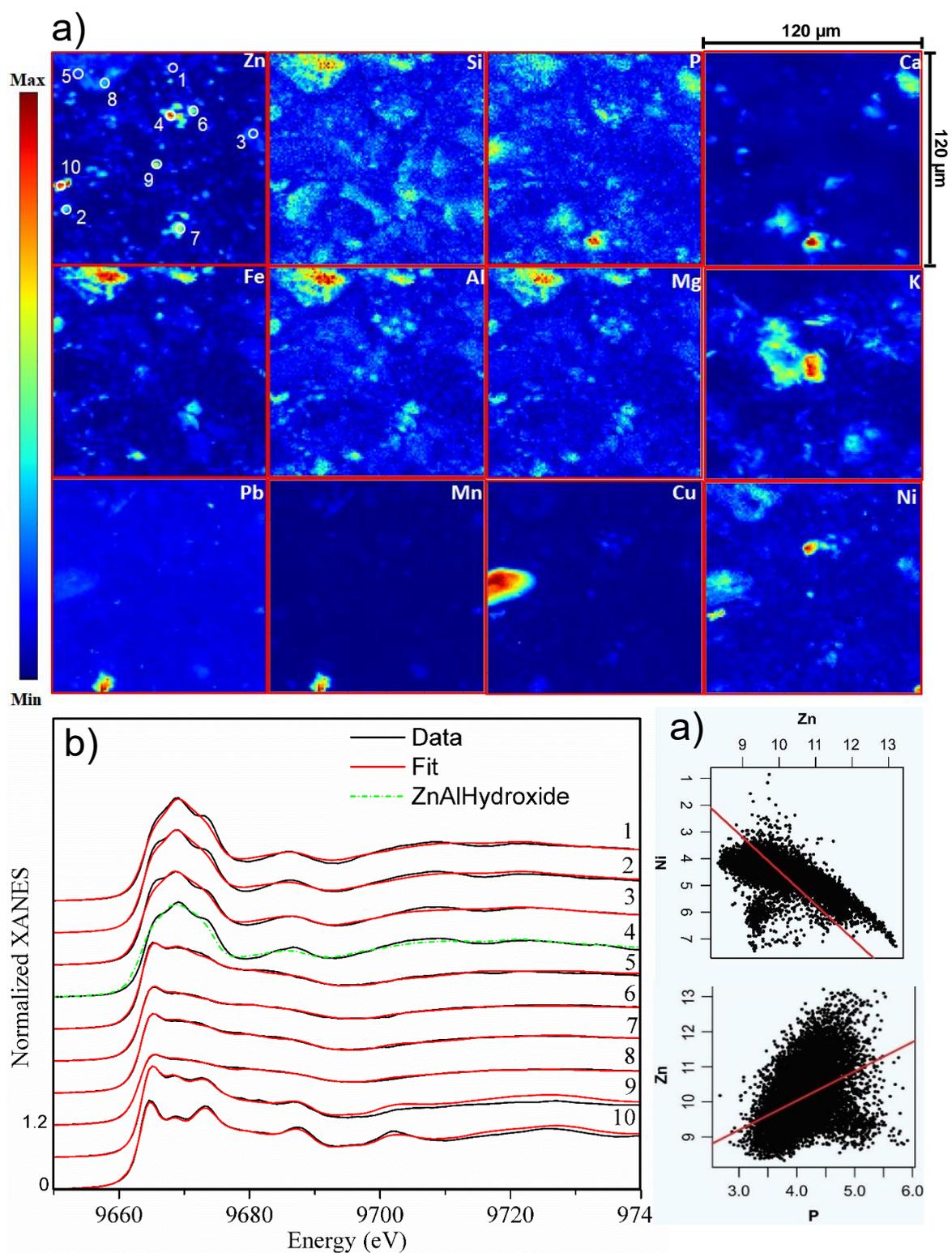


Figure 2. (a) Distribution of the selected elements (Zn, Si, Ca, Fe, Al, Mg, K, Pb, Mn, Cu, Ni) in the thin section of phosphate-amended soil sample determined by μ -XRF mapping and correlation between Zn and P and Ni; and (b) μ -XANES spectra, at the Zn K-edge taken at 10 different Zn spots.

Micro-XANES spectra of the un-amended soil collected from three spots confirmed the predominance of fit with Zn-montmorillonite (41-59%) followed by Gahnite (21-41%) (Table S5 in SI). Spots 1 and 2 had a fit with Zn-ferrihydrite (10-16%) and only spot 1 had a fit with Zn-kerolite (20%). These data agreed with the LCF performed in the bulk XANES, where the same species were identified (Table 3).

Micro-XANES spectra in the P-amended soil collected from ten spots showed variations (Fig. 2). However, the merge of these ten spectra was very similar to the spectra of the bulk XANES (Figure S2 in SI). Considering the size of the microprobe beam ($10 \mu\text{m}^2$) and bulk beam ($10^7 \mu\text{m}^2$), $10 \mu\text{-XANES}$ spectra represented only 0.0001% of the lateral sample area irradiated by the bulk beam. This result shows that the $\mu\text{-XANES}$ can be representative of the bulk XANES analyses and has the advantage of being able to identify species that cannot be deconvolved using bulk XANES.

The best-fit combination of standards for all ten spots included 8-35% $\text{Zn}_3(\text{PO}_4)_2$, 19-35% Scholzite ($\text{CaZn}_2(\text{PO}_4)_2 \cdot 2(\text{H}_2\text{O})$), 21-40% Gahnite, 23-100% Zn-LDH, 8-30% Zn-montmorillonite, 20-24% Zn-ferrihydrite (Table 4), whereas bulk XANES fit results did not show any fit with the standards of Scholzite and Zn-montmorillonite. However, the Zn-montmorillonite standard had a significant fit in the $\mu\text{-XANES}$ and bulk XANES results of the unamended soil. The greater proportion of gahnite in the fit was found in two ‘‘hot spots’’ (spots 9 and 10), consistent with results obtained by Kirpichtchikova et al.⁴⁰

Table 4. Combinations of standards yielding the best fits to zinc K-edge Micro-XANES spectra for mining area soil treated with phosphate for a linear-combination fitting (LCF) energy range of -20 to 80 eV relative to E0 (first-derivative maximum)[†].

Spots	$\text{Zn}_3(\text{PO}_4)_2$	Scholzite	ZnO	Gahnite	Zn-LDH	Zn-montmorillonite	Zn-ferrihydrite	$10^4 \times \text{R-factor}^\ddagger$
	-----Proportion of standard \pm uncertainty (%) [†] -----							
1					70 \pm 4	30 \pm 4		52.4
2	10 \pm 1				69 \pm 4	21 \pm 4		46.2
3				15 \pm 2	57 \pm 6	28 \pm 3		41.1
4					100			-
5	30 \pm 2		21 \pm 2	17 \pm 2		8 \pm 1	24 \pm 3	14.2
6	29 \pm 1	19 \pm 3	40 \pm 2	12 \pm 1				6.7
7	24 \pm 1	35 \pm 2	20 \pm 1	22 \pm 1				7.9
8	19 \pm 1	31 \pm 1	36 \pm 2	14 \pm 1				5.1
9	35 \pm 1			42 \pm 1	23 \pm 1			7.4
10	8 \pm 2			72 \pm 3			20 \pm 4	6.8

[†] All data have been re-normalized to sum to 100 %; uncertainties were calculated in Athena.

[§] Suspected contamination.

[‡] R-factor is a measure of goodness of fit = $\sum(\text{data-fit})^2 / \sum(\text{data})^2$.

2.3.3 Desorption Kinetics

Stirred-flow desorption experiments were conducted using Melich-3 solution to assess the bioavailable of Zn in each treatment with different rates. To compare the desorption behavior of treatments and their rates, the amount of Zn desorbed was normalized to the total soil Zn concentration and plotted as a function of time (Figure 3; Figure S5 in SI). For each treatment receiving a higher rate, the amount of Zn desorbed after 2 h ranged between 21 to 18 % for biosolid and biochar, respectively. During the initial time of desorption, the P-amended soil had the highest desorption, and the calcite amended soil had the lowest. The soil amended with lower rates of calcite and P desorbed less Zn after 2h compared to the higher rates. For the treatments with biochar and biosolid the rates that desorbed less Zn were the 5% and 10% respectively.

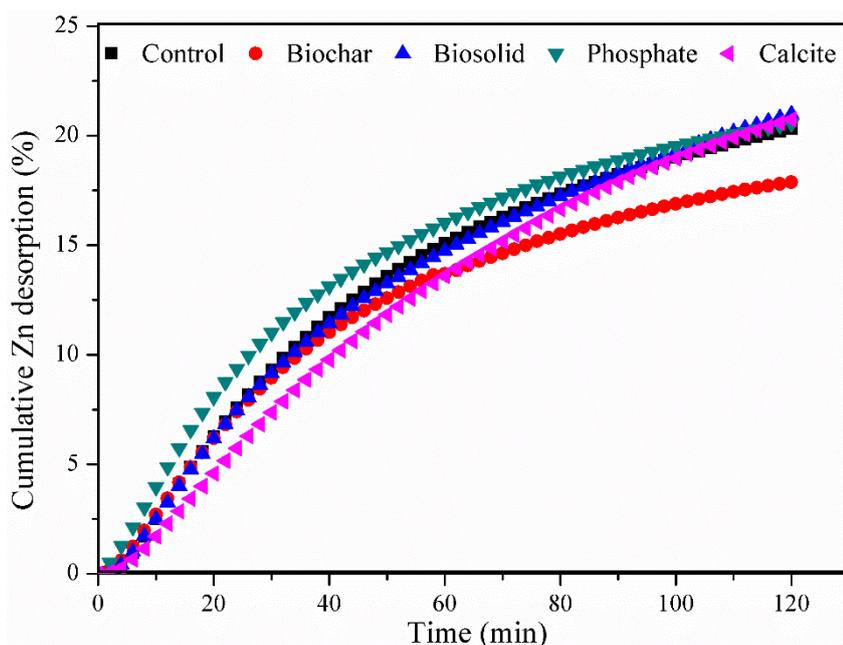


Figure 3. Cumulative Zn desorption (%) Mehlich-3 in the mining area treated with phosphate, calcite biochar and biosolid.

2.3.4 Sequential Extraction

The P-amended soil was the only one with detectable amounts of Zn in F1 extracted with 0.1 M CaCl_2 and increased the Zn in the F2 (extracted with 1M NaOAC (pH 5)) (Figure 4; Figure S6 in SI). Similarly, the treatments with calcite and biosolid also had increased Zn extracted in the F2 in a number of their lower rates (Figure S5 in SI). Except for the treatment

with calcite, all the treatments increased Zn in the F3 extracted with 5% NaOCl (pH 8.5). The soil amended with biosolid increased the Zn extracted in the F4, but the treatment with P decreased it. In the F5, extracted with HNO₃ + HCl, the treatments reduced the amount of Zn extracted, except for the soil amended with calcite. In general, the soil amended with P increased the Zn extracted in the initial fractions (F1, F2 and F3) and decreased in the most recalcitrant fractions (F4 and F5). The treatments with organic compounds (biochar and biosolid) increased the extracted Zn in F3 and F4 and decreased in F5. The higher rate of calcite did not differ ($p < 0.05$) from the control. However, the lower rates increased the Zn in F2 and F5 and reduced it in F4.

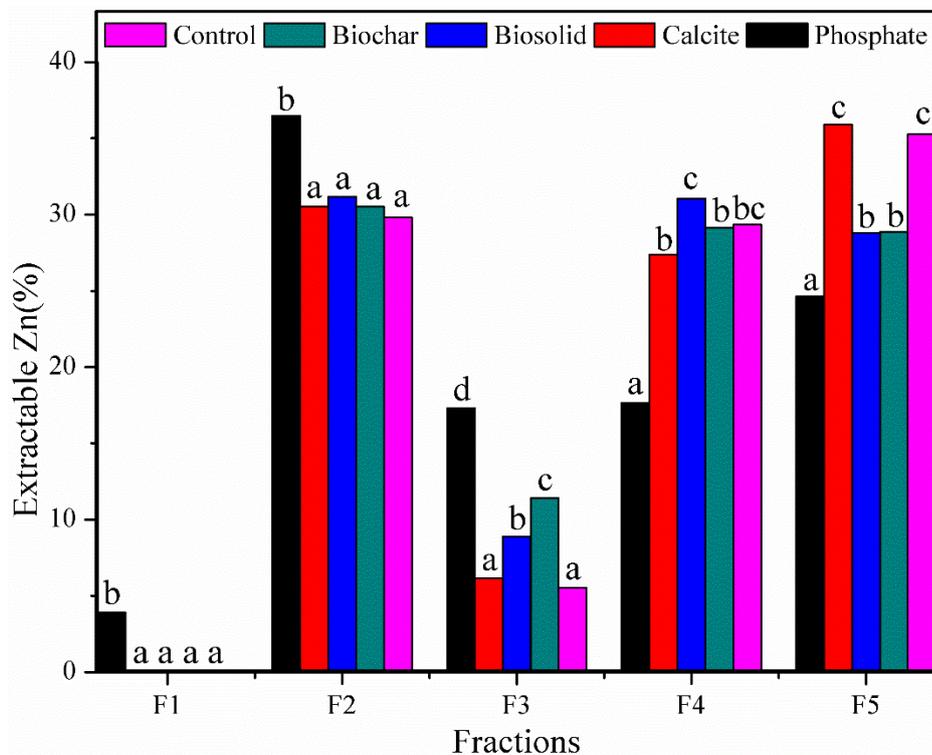


Figure 4. Relative distributions of Zn among the various soil fractions. F1= exchangeable, F2= carbonate-associated, F3 = organic-matter associated. F4 = oxide, and F5 = residual (most strongly bound). Column followed by the same letter in the same fraction did not differ at 0.05 by Tukey test.

2.4 Discussion

The city of Vazante has one of the major non-sulfide zinc deposits in the world,^{3,4} with Hemimorphite and Willemite having been previously reported in this region.⁴¹ However, the LCF results did not show any fit with these minerals in our soil samples which may be

explained by the formation of Zn pedogenic (soil-formed) species, including Zn in the structure of goethite, Zn sorbed to Fe and Mn oxides and Zn-bearing phyllosilicates-type precipitates.²⁴ A number of authors have reported that Zn released by the weathering of mining, smelting or foundry emissions can be precipitated and sorbed/complexed.^{40,42,43}

The bulk Zn K-edge XANES spectrum for the unamended soil indicated Zn-kerolite (40% of total Zn) and Zn-montmorillonite (26%) as major components, whereas Zn-montmorillonite had a predominant fit in the spots analyzed by μ -XANES. Zinc can form mononuclear inner-sphere complex at the edges of montmorillonite layers at low $[\text{Si}]_{\text{aq}}$ around $70\mu\text{M}$ and precipitates epitaxially as kerolite at relevant geochemical systems with concentrations around $500\mu\text{M}$.⁴⁴ Schuwirth et al.⁴⁵ investigated the speciation of Zn in different layers in a soil at a former tailings pond of a Zn/Pb/Ag ore mine in the northern Rhineland-Palatinate, Germany and observed that in the superficial layer (4 to 6 cm) the Zn species was predominantly in the form of Zn adsorbed on montmorillonite and Zn-rich phyllosilicates.

Zn-kerolite has been identified in many soils and sediments and is derived from the *in-situ* weathering of primary minerals.^{24,40,46-48} The prevalence of the Zn-montmorillonite standard in the fit is consistent with the presence of Zn^{2+} adsorbed on this secondary mineral, which was identified by XRD analysis in our soil sample (Figure S1 in SI). Zinc may be incorporated or sorbed on the octahedral sheet or a hydroxy-Al sheet in the interlayer region in the phyllosilicates.⁴⁹ The other species identified in the unamended soil were Zn-ferrihydrate (24%) and Gahnite (10%).

Zn-ferrihydrate is usually detected with phyllosilicates and frequently occurs as a background species in soil matrices.^{50,51} Similarly, Gahnite which is a primary mineral formed mainly in metamorphic high temperature⁵⁰ environments was identified in soils impacted by the dust of smelting activities,^{42,46} and acid mine drainage sites.⁵⁰ The positive correlation and partial correlation with Fe, Si are further evidence of the presence of Zn associated with phyllosilicates and ferrihydrate that were identified in the unamended soil. Kirpichtchikova et al.⁴⁰ investigated the speciation of Zn in a soil from Pierrelaye plain, a 1,200 ha truck farming area located about 30 km northwest of Paris, France in an area of urban and industrial suburbia. This site was irrigated for a hundred years with untreated sewage water from the city of Paris. The predominant Zn species identified at this place were Zn-sorbed ferrihydrate, Zn phosphate, Zn-kerolite, willemite and gahnite.

The P-amended soil was the only one that affected the bulk XANES spectrum (Figure 1). This treatment had a fit with ZnO, Zn₃(PO₄)₂, and Zn-LDH. Baker et al.⁵² evaluated the effect of sources of P, reaction times and distance of the application in the Zn speciation in a contaminated soil from an abandoned Pb/Zn smelter near Dearing, KS, USA. The authors verified the formation of Zn-P and ZnO (Zincite) due to P application in certain treatments. Although our LCF result for the control did not show the fit with Zn-LDH, it could still be present in the sample because it is common for Zn-LDH to be identified in soils with pH near 7 and high concentration of Zn.^{24,25,47,53} The fit with ZnO is not reasonable because this species is more soluble than Zn-kerolite and Zn-montmorillonite.⁵³ However, it could probably form due to the decrease in the pH caused by the treatment (Table 1). As pH decreases, the solubility of Zn increases.⁵⁴ In this treatment, we did not observe a fit with Zn-kerolite, Zn-montmorillonite, and Zn-ferrihydrite. This might be because of the unitability of Zn-kerolite under acid conditions,²⁴ the adsorption of Zn on Montmorillonite that occurs mainly in the electrostatic form,⁵⁵ and the adsorption of Zn on Ferrihydrite that is highly pH dependent.⁵⁶

Micro-XRF and μ -XANES confirmed the formation of Zn-P in the P-amended soil (Figure 2; Table 4). In the μ -XRF image, P is co-localized with Zn, and the significant partial correlation confirmed this association. Micro-XANES showed that the Zn-P species are dominant in most of the spots analyzed. In a number of these spots, we identified Scholzite (Zn, Ca-phosphate) which is more stable than Hopeite, but requires Ca to be present for such formation.⁵⁷ In a number of μ -XANES spots we also identified Zn-montmorillonite and Zn-ferrihydrite, which indicate that these species are present in the amended soil but are not sufficiently abundant to be detected by the bulk XANES.

Nickel, Mn, Pb and Fe had the highest partial correlation in the P-amended soil (Table 5). Iron and Mn are the constituents of the soil that have a high affinity for Zn and represent two possible reactive surfaces with which Zn may interact in the soil environment²⁵. Karna et al.⁵⁸ found a high positive correlation between Zn and Pb, Fe, and Mn in mine waste materials. According to Karna et al.⁵⁸, Zn and Pb could be adsorbed and co-precipitate with Mn and Fe hydr(oxides). Kirpichtchikova et al.⁴⁰ also reported positive correlation between Zn, and Pb with Fe in ferruginous clay particles. However, Kirpichtchikova et al.⁴⁰ found no correlation between Zn and Pb with Fe at spots that had low Fe concentration, suggesting that the different regions engendered different Zn and Pb species.

The Ni “hot spot” (spot 4 on Zn μ -XRF map; Figure 2) was co-localized with the Zn “hot spot”. The μ -XANES showed the predominance of Zn-LDH (100%) at this spot where

Ni and Zn could be precipitated on the mineral surface. Nickel can form a Ni-Al layered double hydroxide (LDH) which precipitates upon the reaction of Ni with Montmorillonite, Kaolinite, Pyrophyllite and Gibbsite.

Desorption kinetics and the chemical extraction confirmed the increased availability of Zn in the P treated soil that received the highest rate (Figure 3). More Zn was desorbed during the initial time of the desorption kinetics, which could be inferred from increased Zn extracted in the first fractions (F1, F2, and F3) of the sequential extraction. However, total Zn desorbed after 120 min was almost equal to that of the control. The first Zn species to be released may be from ZnO and Zn-phosphate followed by Zn-ferrihydrite and Zn-phyllsilicates. Kirpichtchikova et al.⁴⁰ performed an EXAFS with linear combination data before and after the chemical extraction with EDTA and observed that Zn-phosphate was entirely and selectively dissolved by EDTA. According to Kirpichtchikova et al.⁴⁰, the lower extraction level measured for Zn was due to the Zn phyllosilicate component, which is less soluble than Zn-phosphate and Zn-ferrihydrite.

Less Zn was desorbed from the samples that received lower rates of P in comparison to those that were unamended or received a high rate of P (Figure 3; Figure S5 in SI). This shows that P can be effective in the immobilization of Zn, which has also been demonstrated by several authors.^{59,60} The use of the lowest molar ratio, P:M, may be the best option for immobilizing Zn in soils with alkaline soil (high pH) and a high concentration of metals. A lower P rate will have a lower effect on pH and have less risk of eutrophication of groundwater and rivers.

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The treatments with calcite, biosolid and biochar had no effect in the speciation determined by the bulk XANES (Table 3; Figure 1). However, changes were observed in the results of sequential extraction and desorption kinetics. The lowest rate of calcite was probably better at immobilizing Zn as it had less Ca competing for binding sites with Zn on the montmorillonite. Calcite can decrease the availability of Zn due to the formation of Zn-

LDH.⁶¹ We observed an increase in Zn in the extraction of the residual fraction, which further supports the formation of Zn-LDH. The stability of the Zn-LDH phase has been well documented in the literature.^{23,24,47}

The speciation determined by bulk XANES may not have been effective in detecting modifications in the Zn species in the organic treatments. Mamindy-Pajany et al.⁶² used Micro-XRF and Micro-XANES to observe an increase in Zn bonded to organic matter and iron oxide in soils amended with biosolids. In our study, the biosolids and biochar increased the Zn extracted in the F3 (organic fraction) and in certain of their rates increased the Zn in the F4 (iron oxides). In the desorption kinetics, the biochar was more effective in decreasing the Zn desorption than biosolid. The greater affinity of biochar might be because of the high CEC and specific surface area.⁶³⁻⁶⁵ The biochar can increase the buffering capacity of the soil,⁶⁶ and this may also have contributed to decreased Zn desorption.

2.5 Environmental Recommendations

The organic and inorganic amendments utilized in our experiment had different behavior patterns according to the different rates applied. Considering only the highest rate of each amendment, the application of P affected the Zn species determined by bulk XANES. However, the sequential extraction and desorption kinetics results showed us that Zn species such as ZnO could be released easier. Nevertheless, the results from the desorption kinetics highlighted that the quarter rate and half rate of P were sufficiently effective to decrease Zn desorption. Although our soil was alkaline, the utilization of calcite was effective in decreasing Zn desorption on all rates, the quarter rate and half rates being the most effective. The organic amendments were also able to reduce the Zn desorption. The rate of 10% of biosolid and 5% of biochar were more effective in reducing the Zn desorption than the other rates. In general, the highest rate did not seem to be the most effective in immobilizing Zn in the soil. This information is very important in helping to develop remediation strategies that provide a cost-effective and sustainable solution.

2.6 Supporting Information

2.6.1 Soil Mineralogical Characterization

In order to obtain the clay, silt and sand, the sample of the unamended soil was dispersed using 0.1 M NaOH. The sand fraction was separated by sieving (2 - 0.05 mm) and

the clay ($< 2 \mu\text{m}$) was isolated from the silt (0.05 - 0.002 mm) by repeated siphoning of the dispersed material. The XRD analyses were carried out on a computer-controlled X-ray diffractometer (Philips PW 1877) with $\text{CuK } \alpha$ radiation (0.1542 nm) - (40 kV and 40 mA) and a graphite monochromator. The velocity of the goniometer was $0.02^\circ 2\theta \text{ s}^{-1}$, with a variable range between 3 and $60^\circ 2\theta$. The data were analyzed by the PANalytical X Pert HighScore software program.

2.6.2 Bulk XANES and Micro-XANES

Bulk XANES and Micro-XANES spectra were acquired across the energy range of -130 to 340 eV and -100 to 200 respectively, relative to the Zn-K edge energy at 9659 eV. For the bulk XANES we used a step size of 4 eV in the pre-edge (-130 to -10); 1 eV across the adsorption edge region (-10 to 50) and 4 eV in the post-edge region (50 to 340) with acquisition times of 2, 5 and 2 sec, respectively. For the μ -XANES we used a step size of 4 eV in the pre-edge (-100 to -10); 0.5 across the adsorption edge region (-10 to 50) and 2 eV in the post-edge region (50 to 200) with acquisition times of 2, 5 and 2 sec, respectively. The backgrounds of the bulk XANES and μ -XANES spectra were corrected using a linear pre-edge function between -70 to -30 eV and -90 to 30 eV a linear or quadratic function between 30 to 130 eV and 80 to 150 eV respectively, and a flattening function in the post-edge region for normalization was included.

2.6.3 Standards Utilized to Perform the Linear Combination Fitting (LCF)

The LCF was implemented using standards analyzed by us. On the other hand, in the other studies we utilized the spectra measured in different beamlines provided by researchers. Table S2 has a list of standards utilized and their references and sources. The standards obtained by the Alfa Aesar Company, Zn-montmorillonite and Zn-kaolinite were analyzed at XAFS2 beamline at the LNLS (Brazilian Synchrotron Light Laboratory) and followed the same setup utilized for the samples. The Zn adsorbed to montmorillonite and kaolinite was produced following the method described in Khaokaew et al.²

Table S1. Selected chemical properties of soils from the mining area for all treatments (and non-treated control) of phosphate, calcite, biosolid and biochar.

Treatments	pH		C g kg ⁻¹	P mg kg ⁻¹	K	Ca	Mg	H+Al mmolc kg ⁻¹	Al	Cd mg kg ⁻¹	Pb g kg ⁻¹	Zn g kg ⁻¹
	H ₂ O	CaCl ₂										
Control	8.3	7.5	15	90	0.9	183	215	0.0	0.0	111 ± 11	4.1 ± 0.4	13.1 ± 0.7
Phosphate												
Full rate	6.3	6.2	16	8991	0.4	79	186	166.0	119.5	98 ± 7	4.3 ± 0.3	13.0 ± 0.6
Half rate	6.4	6.1	14	6185	0.5	104	156	142.0	64.0	86 ± 9	4.3 ± 0.4	13.2 ± 0.7
One-fourth rate	6.7	6.0	13	3870	0.8	116	165	64.0	20.0	91 ± 8	4.2 ± 0.5	13.1 ± 0.9
Calcite												
Full rate	8.5	7.6	21	125	0.6	356	198	0.0	0.0	110 ± 10	4.3 ± 0.4	13.3 ± 0.8
Half rate	8.3	7.8	17	54	1	354	155	0.0	0.0	98 ± 10	4.0 ± 0.3	13.5 ± 0.7
One-fourth rate	8.5	7.8	15	46	0.7	298	152	0.0	0.0	95 ± 9	4.2 ± 0.3	13.3 ± 0.9
Biosolid												
5%	7.7	7.4	23	148	5.8	190	198	0.0	0.0	102 ± 10	4.0 ± 0.3	12.9 ± 0.6
10%	7.8	7.5	31	259	11.3	208	180	0.0	0.0	95 ± 9	4.0 ± 0.5	13.1 ± 0.9
20%	7.7	7.4	32	344	18.2	194	166	0.0	0.9	98 ± 10	3.4 ± 0.5	12.0 ± 1.1
Biochar												
2.5%	8.1	7.5	49	47	9.6	146	171	0.0	0.0	97 ± 9	3.9 ± 0.4	13.2 ± 0.9
5%	8.2	7.5	52	359	17.4	164	188	0.0	0.0	93 ± 10	3.9 ± 0.5	13.1 ± 1.1
10%	8.4	7.6	85	65	24.5	115	115	0.0	0.0	104 ± 13	3.7 ± 0.6	12.4 ± 1.0

Table S2. List of purchased standards or standards from other authors that were used in linear combination fitting (LCF) of Zn K-edge XANES spectra.

Standards	Chemical Formula	Reference or Source
Compounds		
Zincite	ZnO	Hettiarachchi et al. ²
Gahnite	ZnAl ₂ O ₄	Hettiarachchi et al. ²
Zn-Al-LDH	[M _{1-x} ²⁺ M _x ³⁺ .(OH) ₂] ^{x+} A _{x/n} ⁿ⁻ .mH ₂ O	Nachtegaal et al. ³
ZnO	ZnO	Alfa Aesar
Zinc Phosphate	Zn ₃ (PO ₄) ₂	Alfa Aesar
Hopeite	[Zn ₃ (PO ₄) ₂ · 4H ₂ O],	Baker et al. ⁴
Scholzite	[CaZn ₂ (PO ₄) ₂ · 2H ₂ O]	Baker et al. ⁴
Franklinite	(Zn _{0.6} Mn _{0.3} ²⁺ Fe _{0.1} ²⁺ Fe _{1.5} ³⁺ Mn _{0.5} ³⁺ O ₄)	Hettiarachchi et al. ²
Willemite	[Zn ₂ (SiO ₄)]	Hettiarachchi et al. ²
Zinc Sulfate	ZnSO ₄ · 7H ₂ O	Hettiarachchi et al. ²
Hemimorphite	[Zn ₄ Si ₂ O ₇ (OH) ₂ · H ₂ O]	Baker et al. ⁴
Smithsonite	ZnCO ₃	Hettiarachchi et al. ²
Zinc Carbonate	ZnCO ₃	Alfa Aesar
Sphalerite	ZnS	Alfa Aesar
Zinc Nitrate	ZnNO ₃	Alfa Aesar
Zinc Iron Oxide	ZnFe ₂ O ₄	Alfa Aesar
Hydrozincite	[Zn ₅ (CO ₃) ₂ (OH) ₆]	Hettiarachchi et al. ²
Zn-kerolite	(Zn ₃ Si ₄ O ₁₀ [OH] ₂ · H ₂ O)	Nachtegaal et al. ³
Zn Sorbed on Organic Compounds		
Humic	C ₁₈₇ H ₁₈₆ O ₈₉ N ₉ S ₁	Nachtegaal et al. ³
Fulvic	C ₁₄ H ₁₂ O ₈	Nachtegaal et al. ³
Standards with sorbed Zn		
Montmorillonite		
Ferrihydrite	(Fe ₂ ³⁺ O ₃ · 0.5H ₂ O)	
Goethite	Fe ³⁺ O(OH)	
Hematite	Fe ³⁺ ₂ O ₃	
Gibbsite	Al(OH) ₃	
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	
Birnessite	(Na, Ca) _{0.5} (Mn ⁴⁺ , Mn ³⁺) ₂ O ₄ · 1.5H ₂ O	Nachtegaal et al. ³

Table S3. Pearson correlation and partial correlation coefficients obtained between log-transformed Zn and detected soil matrix elemental data in the P-amended soil.

Matrix Elements	Correlation (r)	Partial correlation (r')
Ni	0.62*	0.56*
Co	0.56*	-0.07*
Fe	0.53*	0.20*
Cr	0.51*	-0.07*
Mn	0.43*	0.38*
Si	0.43*	0.11*
P	0.41*	0.14*
Cd	0.21*	-0.03*
Pb	0.11*	-0.29*
Ca	-0.01 ^{ns}	-0.17*

^{ns} = non-significant at $\alpha = 0.05$, * = significant at $\alpha = 0.05$

Table S4. Pearson correlation and partial correlation coefficients obtained between log-transformed Zn and detected soil matrix elemental data in the un-amended soil

Matrix Elements	Correlation (r)	Partial correlation (r')
Cu	0.19*	0.20*
Pb	0.02*	0.01 ^{ns}
Si	-0.08*	-0.09*
Fe	0.02*	0.00 ^{ns}

^{ns} = non-significant at $\alpha = 0.05$; * = significant at $\alpha = 0.05$

Table S5. Combinations of standards yielding the best fits to zinc K-edge Micro-XANES spectra for mining area soil for a linear-combination fitting (LCF) energy range of -20 to 40 eV relative to E0 (first-derivative maximum)[†].

Points	Zn-montmorillonite	Gahnite	Zn-ferrihydrite	Zn-kerolite	10 ⁴ x R-factor [‡]
	-----Proportion of standard \pm uncertainty (%) [†] -----				
1	41 \pm 3	21 \pm 2	16 \pm 2	20 \pm 3	1.8
2	48 \pm 2	34 \pm 2	10 \pm 2		7.2
3	59 \pm 1	41 \pm 1			9.4

[†] All data have been re-normalized to sum to 100 %; uncertainties were calculated in Athena.

[§] Suspected contamination.

[‡] R-factor is a measure of goodness of fit = $\sum(\text{data-fit})^2 / \sum(\text{data})^2$.

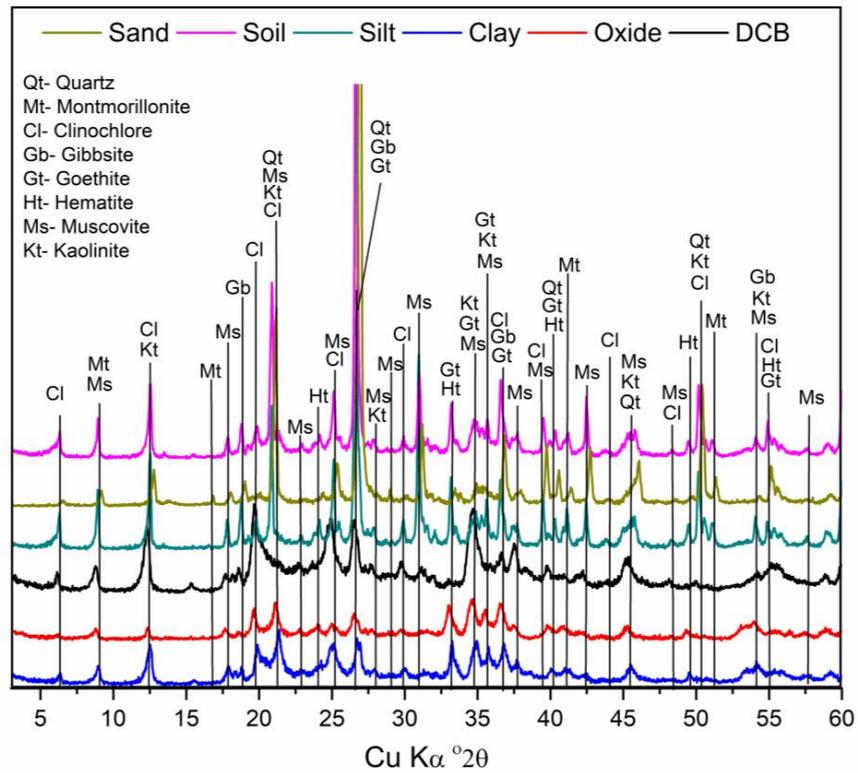


Figure S1. XRD of the sand, silt and clay fractions, and in the clay fraction after chemical treatments for remove iron oxides (DCB) and silicates (Oxides).

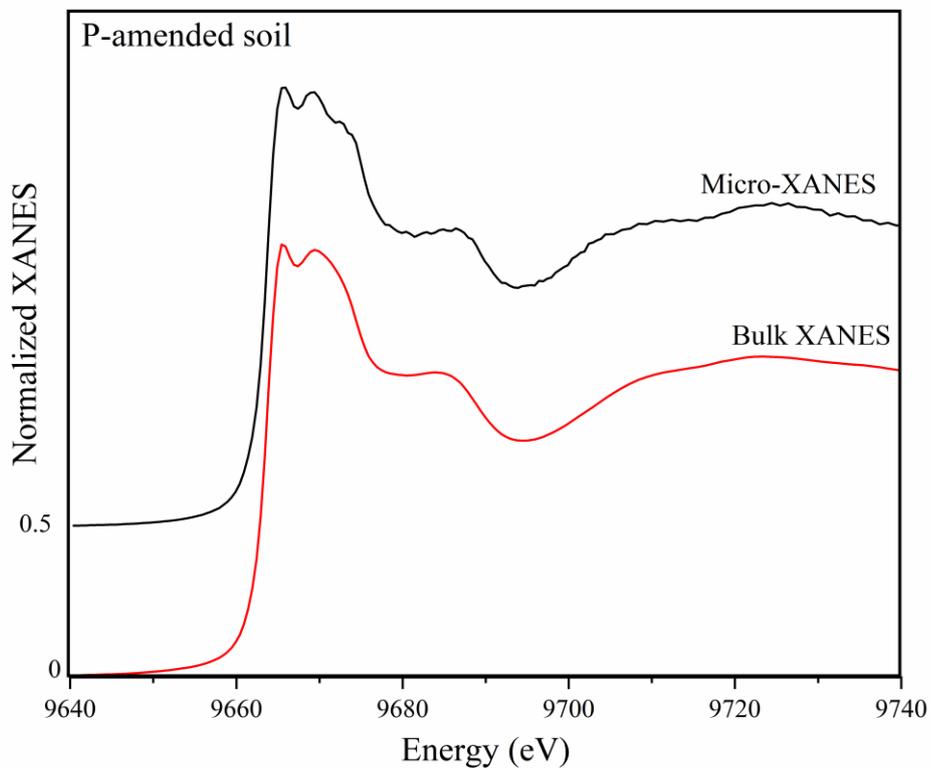


Figure S2. Comparison between bulk XANES and the merge of 10 Micro-XANES spectra's of the P-amended soil.

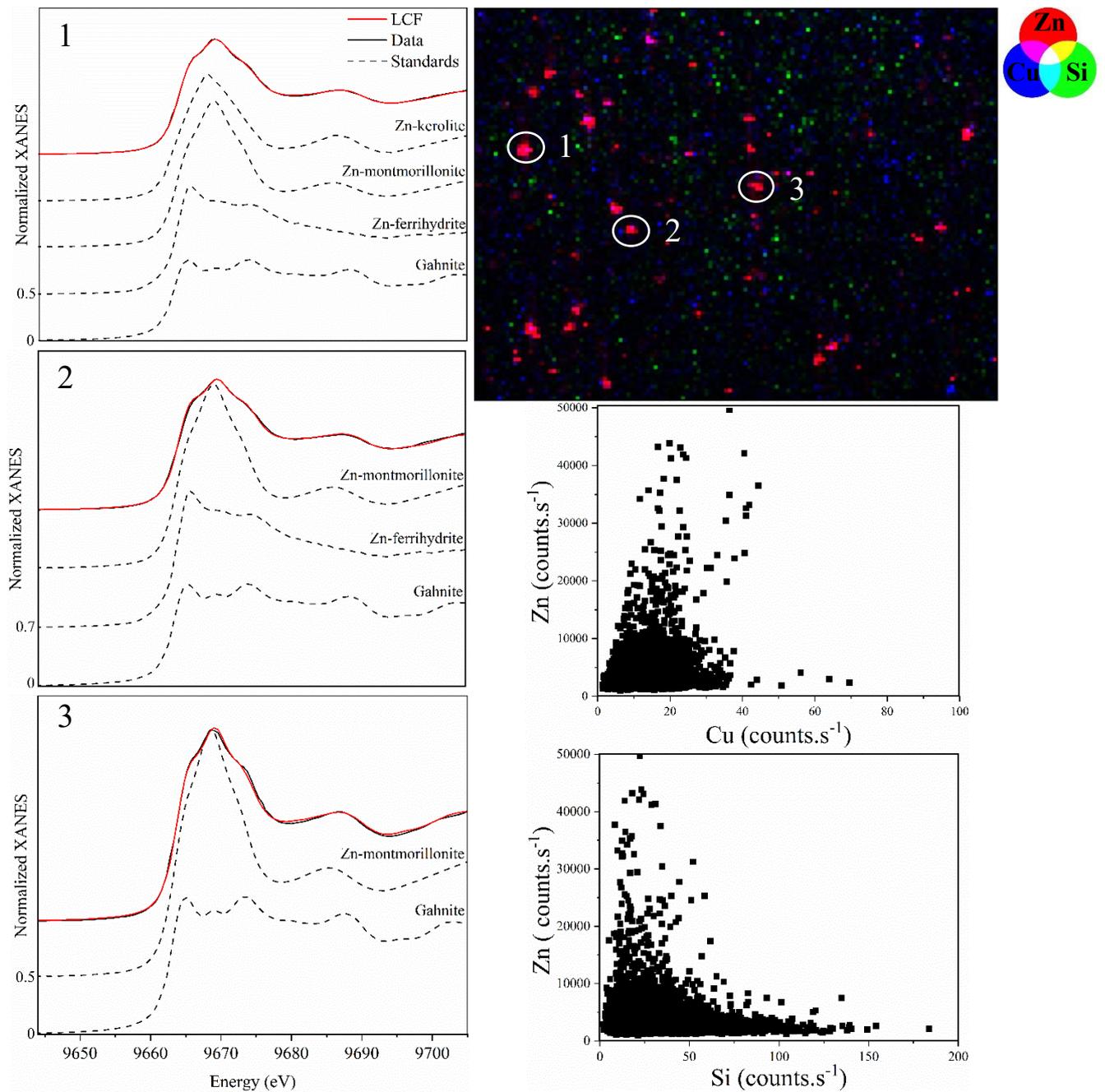


Figure S3. Microprobe XRF map and the correlation plots of Zn-Si and Zn-Cu from all pixels. On the μ -XRF map are indicated the spots 1-3 and in the left side is the correspondent μ -XANES of these spots and the standards that had fit. Fitting was performed across an energy range of -20 to 40 eV relative to E0 (first-derivative maximum).

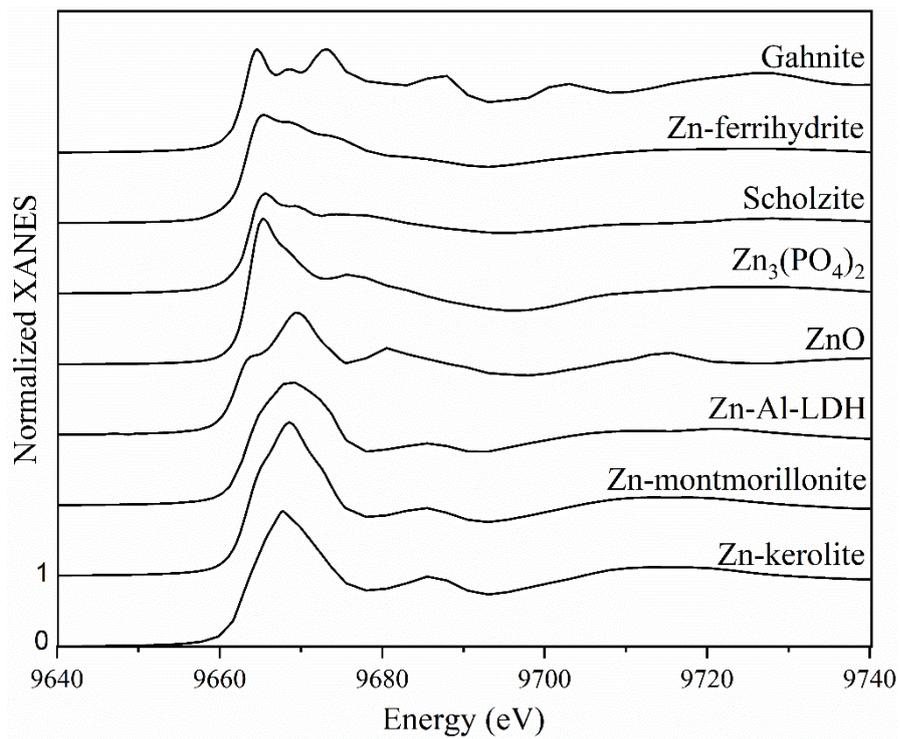


Figure S4 Zn-K edge XANES of Zn reference minerals that had a fit with the Bulk XANES and Micro-XANES samples.

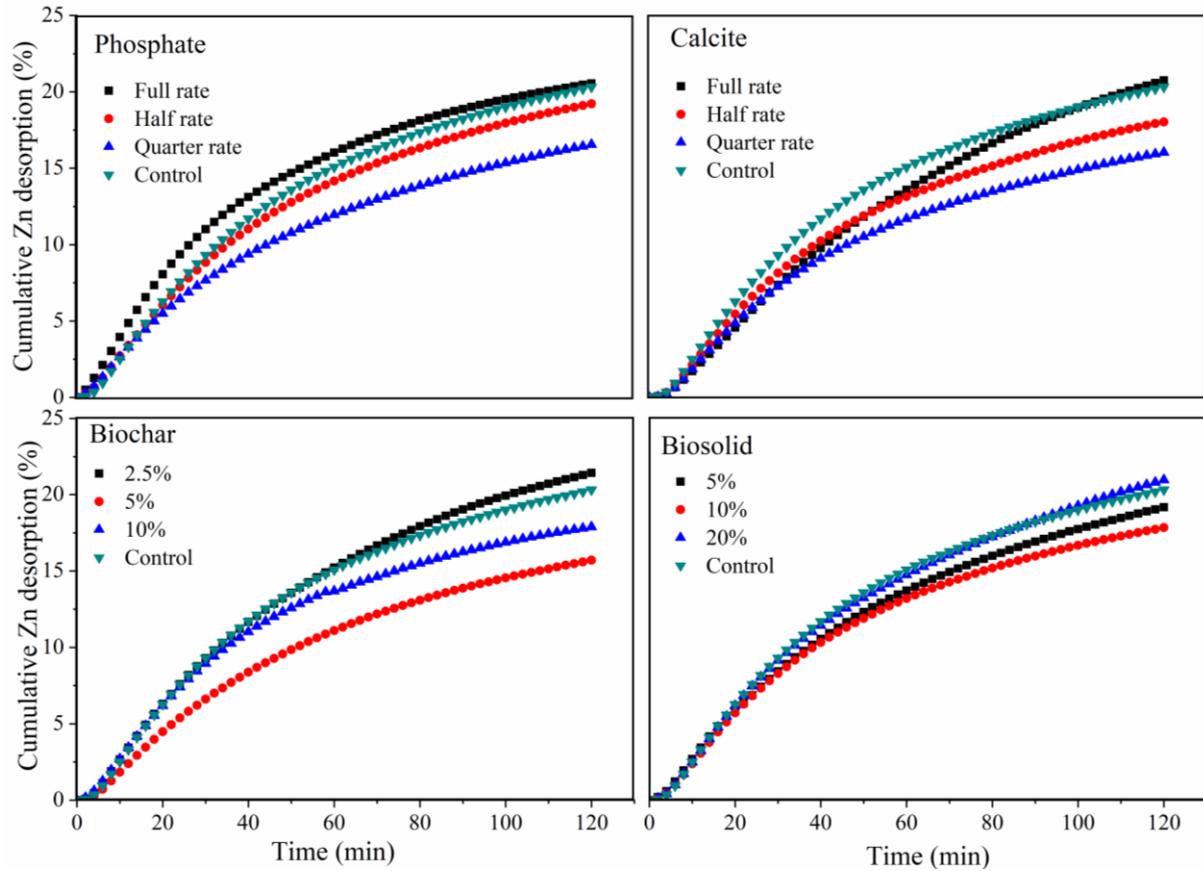


Figure S5 Cumulative Zn desorption by Mehlich-3 in the mining area amended with phosphate, calcite biochar and biosolid in different rates.

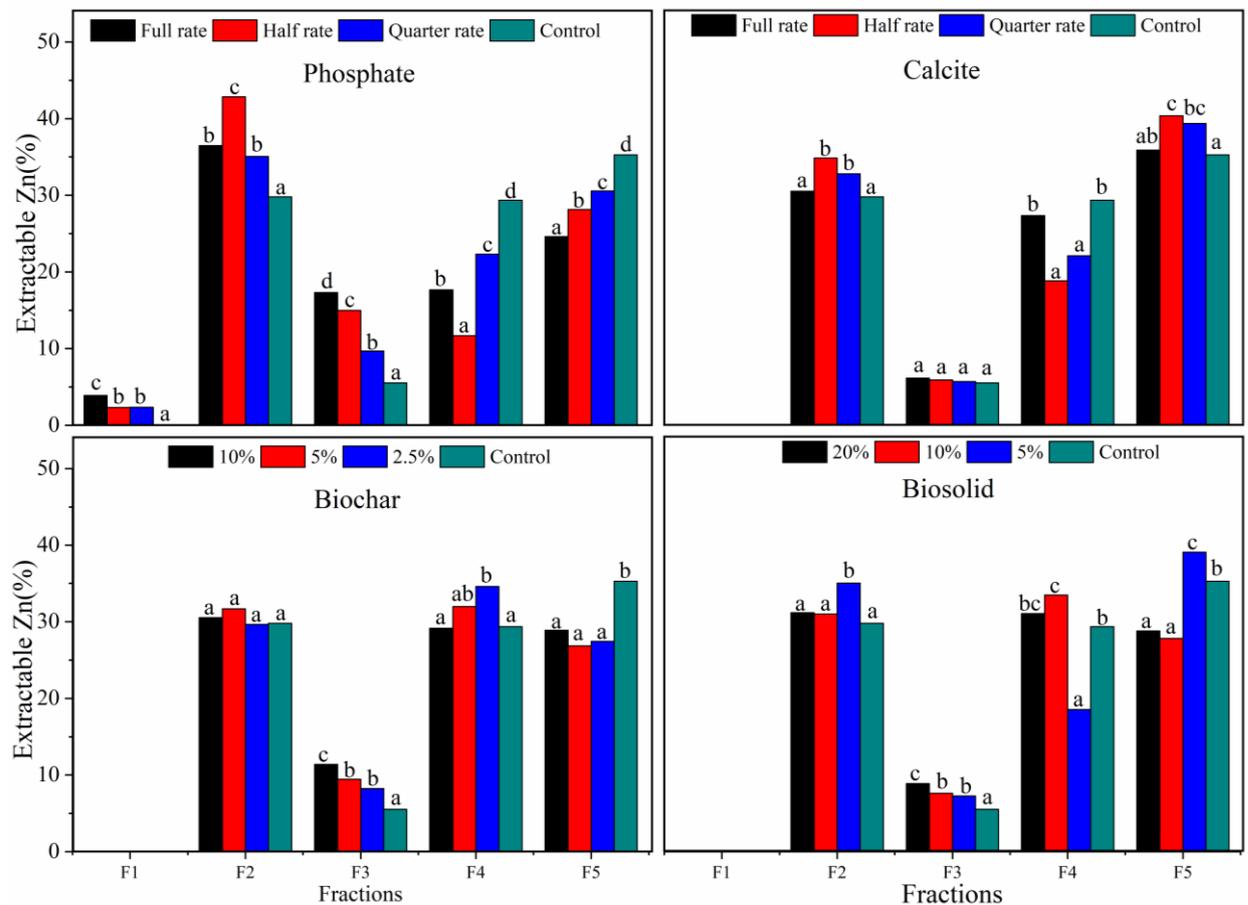


Figure S6. Relative distributions of Zn among the various soil fractions in different treatments and rates. F1= exchangeable, F2= carbonate-associated, F3 = organic-matter associated. F4 = oxide, and F5 = residual (most strongly bound). Columns followed by the same letter in each fraction did not differ at 0.05 (Tukey test).

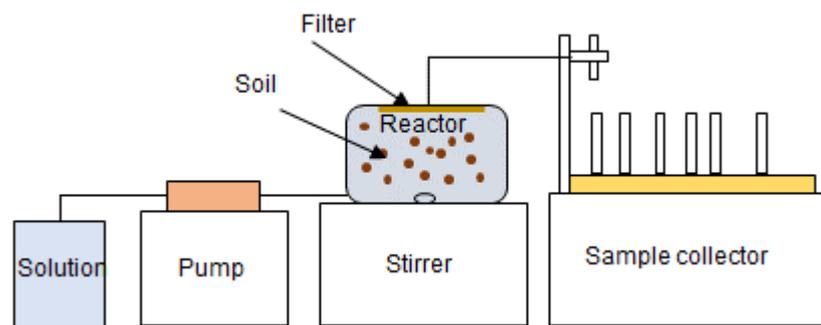


Figure S7. Schematic diagram of operation for stirred flow method.

2.6.4 References (Support Information)

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3 ORGANIC AND INORGANIC AMENDMENTS TO IMOBILIZE LEAD FROM A MINE-WASTE IMPACTED SOIL

Abstract

Lead (Pb) is a heavy metal that may cause several human health problems, such as neuromuscular weakness, hearing deficits, and impaired cognitive functions. The Pb present on the soils may be leached to groundwater, accumulated by plants and animals and then enter in the food chain. Chemical stabilization is an in-situ remediation that uses inexpensive amendments to reduce contaminant availability in polluted soil. Rates of phosphate, calcite, biochar, and biosolids were evaluated on Pb speciation and mobility. The soil was collected in a Zn mining area located in Vazante, state of Minas Gerais, Brazil and was incubated for 60 days with deionized water at 70% of the maximum water retention. Chemical and mineralogical characterization, desorption kinetics, sequential extraction, leaching columns and speciation using X-ray absorption near edge structure (XANES) were performed. Pb adsorbed on bentonite and on anglesite were the predominant species in the unamended soil. The treatments with phosphate and calcite transformed part of the Pb species to pyromorphite. Conversely, in the soil amended with biochar and biosolids, part of Pb species was transformed to Pb adsorbed on citrate and $PbCl_2$ in the biosolids. Biosolids and biochar treatments decreased the Pb in the residual fraction and increased it in the fraction associated to organic matter (OM) after the addition of biosolids. These organic amendments increased the desorption kinetics of Pb in all rates applied. Calcite and phosphate increased the Pb extracted in the residual fraction, thus showing that more recalcitrant species, such as pyromorphite, were formed. Calcite and phosphate were effective to immobilize Pb and to decrease Pb desorption kinetics. The soil amended with phosphate decreased the Pb leached in the experiment with leaching columns.

Keywords: X-ray absorption near edge structure; Desorption kinetics; Soil pollution; Remediation of soils

3.1 Introduction

Lead (Pb) is one of the most hazardous environmental pollutants that affect biological systems through exposure to air, water and food sources¹. It is also associated with behavioral abnormalities, neuromuscular weakness, hearing deficits, and impaired cognitive functions.² In Brazil, Pb exposure has been widely recognized as a significant public health problem in recent decades. One example is the region of Santo Amaro (state of Bahia where a lead smelter operated for 33 years before closing in 1993. It has been reported that some children living close to the former plant have high levels of Pb and Cd in their blood.³

In situ stabilization of heavy metals in soil using amendments is a promising technology to decrease the risks associated with these elements.^{4,5} This technique is based on the reduction of metal availability and mobility, either by precipitation or increased sorption.⁶ The soil amendments may decrease the metals solubility and thus reduce the detrimental effects on environmental receptors, such as humans, animals, plants and microorganisms, as

well as water bodies.⁷ Numerous amendments have been used and tested for in situ stabilization of Pb in soils, including alkaline materials^{5,8,9}, phosphate⁹⁻¹¹, biochar¹²⁻¹⁴ and biosolids^{15,16}.

Phosphate compounds increase the immobilization of heavy metals through different chemical processes, such as adsorption/substitution by phosphorus (P) compounds, P anion-induced metal adsorption, and precipitation.¹⁷ The soil amended with phosphate may form pyromorphite, which is the most stable Pb form in the environment.¹⁸ The formation of this mineral in a contaminated soil environment reduces Pb bioavailability and improves ecosystem health.¹⁹ Alkaline materials are also increasingly being accepted as an important amendment to reduce the toxicity of heavy metals in soil.¹⁷ These materials enhance the sorption of heavy metals by increasing the negatively charged sites through reduction in the H⁺ concentration¹⁷, with the pH increase resulting in the precipitation of these metals.⁸

Biochar has been accepted to be used to immobilize heavy metals in the recent years. This amendment may change soil properties such as increasing soil buffering capacity, cation exchange capacity (CEC) and soil pH. Biochar may immobilize Pb by electrostatic interactions, precipitation and other reactions according to current research.²⁰⁻²² However, all biochar materials may not be suitable for all cases of remediation.¹⁷ Feedstock type and pyrolysis condition are the main factors influencing sorption behavior of biochars.²³ Some researchers have revealed that biochar may increase the mobility of some toxic metals in soils.¹⁷

Another material that may be a suitable amendment is biosolids, the semi-solid residues generated during the treatment of domestic sanitary sewage, providing that it contains no appreciable amount of heavy metals.²⁴ This amendment contains an abundant amount of nutrients and organic matter that may improve soil biological, physical and chemical properties.²⁵ Stabilization of heavy metals by biosolids is achieved through complexation adsorption and redox reactions.¹⁷ Biosolids has been used to successfully restore mine lands for more than 25 years^{26,27}. Despite its beneficial usage, it is necessary to be careful with the application of biosolids because it may contain a significant amount of heavy metals originated mainly from industrial wastewater. The organic compounds may increase the dissolved organic carbon (DOC) on the soil solution. The DOC can decrease the sorption of Pb onto soil surfaces due to the competition for binding sites or by the formation of soluble Pb-organ-complexes.²⁸

Our research aim was to characterize Pb desorption and speciation from a mine-waste impacted soil from Brazil. The investigation was conducted using contaminated soil before and after the addition of $\text{NH}_4\text{H}_2\text{PO}_4$, CaCO_3 , biochar, and biosolids. We used leaching column, sequential extraction, stirred-flow kinetic approach and X-ray absorption near edge structure (XANES) to evaluate the effect of these amendments in the Pb speciation and mobility.

3.2 Materials and Methods

3.2.1 Soil Characterization

The soil sample was collected in a deactivated Zn mining area located in Vazante, Minas Gerais State, Brazil (coordinates 17°59'11''S, 46°54'27''W). The soil was collected from the surface layer (0-20 cm) and was air dried at room temperature (~25°C) and passed through a 2-mm sieve. The content of soil organic carbon was determined with a Shimadzu TOC-5000 carbon analyzer. To determine their total (or pseudo-total) concentrations, heavy metals in the soil were extracted following the EPA3051a method using a 1:3 HCl/HNO₃, v/v extraction method²⁹, and the metal contents were quantified by inductively couple plasma optical emission spectroscopy (ICP-OES). Exchangeable ions and pH analyses followed the methods of Ingram and Anderson et al.³⁰. XRD was performed in the clay, silt and sand fractions and bulk soil. XRD was also performed in the clay fraction after treatment with 5M NaOH³¹ for concentrating iron oxides and after treatment with sodium dithionite-citrate-bicarbonate (DCB) for removing the iron oxides.³² Based on the XRD data for different fractions and chemical treatments, the composition of the soil was qualitatively identified as goethite, hematite, kaolinite, gibbsite, muscovite, clinocllore, montmorillonite, and quartz in the non-amended soil (Figure 1).

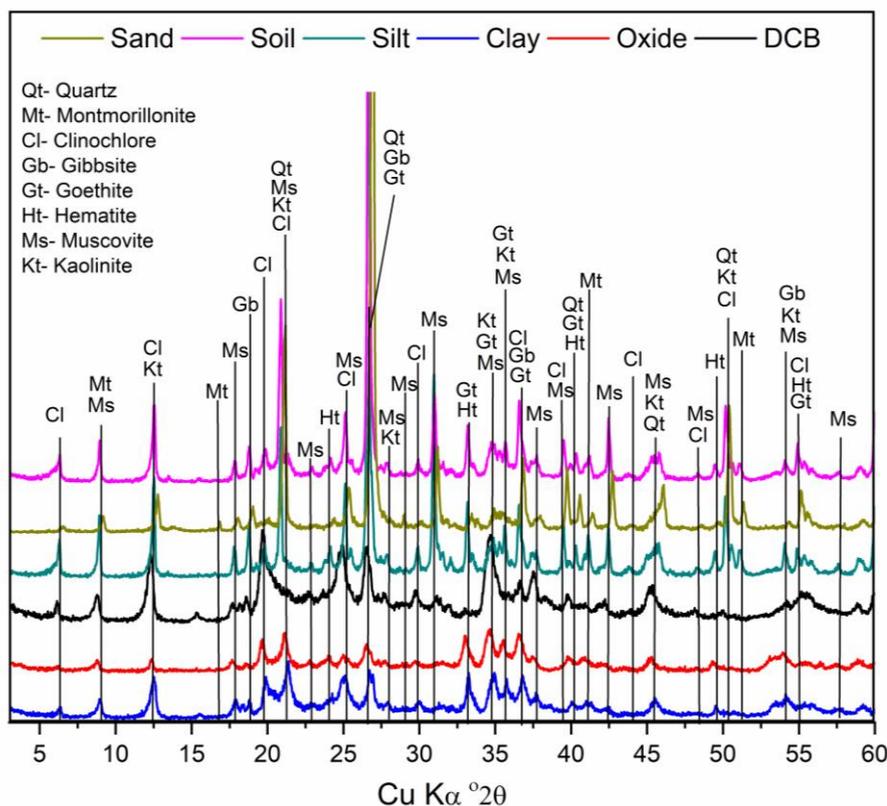


Figure 1. XRD of the sand, silt and clay fractions, and in the clay fraction after chemical treatments for remove iron oxides (DCB) and silicates (Oxides).

3.2.2 Biochar and Biosolids Characterization

Sugarcane (*Saccharum officinarum*) straw was used to produce biochar at the temperature of pyrolysis of 450 °C. For more details about the production and characterization of biochar materials used in the study see Feola Conz et al.³³. The biosolids was produced using wood chips (eucalyptus) and sewage sludge. It was composted in aerated rows for 60 days, in this process, about 2% of dolomitic limestone was added and after composted it was sieving in mesh with 36 mm². The sewage sludge was collected at a sewage treatment station located in Jundiai, São Paulo, Brazil and was composed in the major part by domestic than industrial sludge. The pH of biosolids was determined in water extracts (1:5 v/v), CEC was determined following the method described in Sparks³⁴ and organic C amount was determined by the Walkley and Black method. The total concentrations of heavy metals (Pb, Zn and Cd) and nutrients (P, K, Ca and Mg) in both organic amendments were determined following the EPA3051a²⁹ method.

3.2.3 Amendments and Incubation Time

The soil was amended individually in triplicate with rates of ammonium phosphate monobasic ($\text{NH}_4\text{H}_2\text{PO}_4$), calcite (CaCO_3), biochar and biosolids. The soil was amended with 2.5; 5 and 10% of biochar³⁵ and 5, 10 and 20% of biosolids³⁶. The $\text{NH}_4\text{H}_2\text{PO}_4$ was applied evenly to the soil at 0 (control); 0.5 (quarter rate); 1.0 (half rate) and 2:1 (full rate) molar ratio of P to the sum of Pb, Cd and Zn. These rates were based on the stoichiometry (P:M=3:5) form of the follow precipitate $\text{M}_5(\text{PO}_4)_3\text{OH}$ (M= sum of Pb, Zn, Cd).³⁷ The CaCO_3 was applied evenly to the soil at 0 (control); 0.25 (quarter rate); 0.5 (half rate) and 1:1 (full rate) molar ratio of CO_3 to the sum of Pb, Cd, and, Zn⁵. The amendments were added and mixed homogeneously with the soil and incubated with deionized water at 70% of the maximum water retention at $25\pm 2^\circ\text{C}$ in the lab for 60 days. To maintain the humidity, water was added every 3 days based on the mass loss of water.

3.2.4 Bulk XANES

The Pb- L_3 -edge XANES analysis was performed on the samples that received the highest rate of each amendment using the Beamline XAFS2 at LNLS (Brazilian Synchrotron Light Laboratory) Campinas, Brazil. About 65 mg of each amended soil was ground and mixed with 65 mg of boron nitrate for dilution and then pressed as ~5 mm diameter pellets with 1.3 cm^2 of surface area. The Si (111) monochromator energy was calibrated to 13035 eV based on the first inflection point in the L_3 -edge derivative spectra from a Pb foil. Spectra were collected in fluorescence mode using a Canberra 15 element Ge solid state detector. We collected 5 spectra for each sample across the energy range of -150 to 200 eV relative to the $\text{Pb}L_3$ -edge energy at 13,035 eV, using a step size of 0.5 eV in the pre-edge (-150 to -35), 0.2 eV across the absorption edge region (-35 to 65) and 1 eV in the post-edge region (65 to 200) with 1 sec of acquisition time.

The XAS scans were aligned, merged and processed using the Athena program, an interface to IFEFFIT^{38,39}. The backgrounds of the spectra were corrected using a linear pre-edge function between -120 and -45 and a linear or quadratic function between 30 and 110 eV, included a flattening function in the post-edge region for normalization. Linear Combination fitting (LCF) analysis was done across -30 to 80 region using the method developed by Manceau et al⁴⁰ to deconvolute different Pb species present and their relative contributions to the observed Pb spectrum.

Reference materials for LCF included Pb complexes of Pb-citrate, Pb-acetate, Pb-fulvic, Pb-humic and adsorbed on bentonite, birnessite, goethite, ferrihydrite, gibbsite, kaolinite and hematite. We also used the following minerals: pyromorphite, galena, litharge, cerussite, hydrocerussite, chloropyromorphite, anglesite, hydroxypyromorphite. The references of PbO, PbCl₂, PbCO₃, PbO₂, Pb(NO₃)₂ were purchased from Sigma-Aldrich.

3.2.5 Desorption Kinetics

A Stirred-flow reactor equipped with a piston displacement pump designed for use in an HPLC system was used to conduct the Pb desorption kinetics. The mass of the amended soils used was 200 mg placed in a 12 mL stirred-flow chamber (Figure 2). A Mehlich-3 (0.2M CH₃COOH + 0.25M NH₄NO₃ + 0.013M HNO₃ + 0.015M NH₄F + 0.001M EDTA) solution was used as a desorption agent. A 25-mm diameter cellulose filter membrane with a 0.45 μm pore size was used in the reaction chamber. The suspension in the reactor was stirred at 300 rpm and the liquid portion of it was flowed through the filter in the chamber at a rate of 1 mL min⁻¹. The effluent was collected by a fraction collector at 2 min intervals and the concentration of Pb was quantified by ICP-OES. The amount of Pb desorbed was calculated according to Yin et al.⁴¹ and plotted in cumulative Pb desorption percentages.

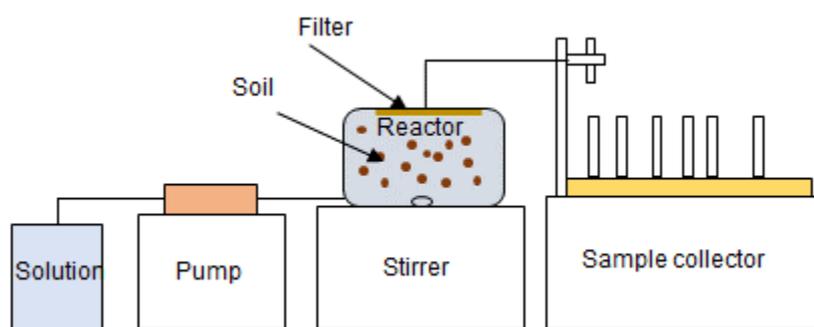


Figure 2. Schematic diagram of operation for stirred flow method

3.2.6 Sequential Extraction

The sequential extraction was performed according to the procedure developed by Silveira et al.⁴² The original method counts on seven fractions, but in the present study we extracted sequentially with 0.1 M CaCl₂, 1 M NaOAc (pH 5), NaOCl (pH 8.5), and 0.2M oxalic acid + 0.2M NH₄ oxalate (pH 3); and the residual was digested by EPA3051a method⁴²

to target Pb in readily exchangeable (F1), carbonate forms (F2), organic-matter bound (F3), iron-oxides bound (F4), and residual (F5), respectively.

3.2.7 Leaching Column

The leaching experiment was conducted using soil from the mine area and amended it with different rates of P. Four 5.05-cm diameter (20 cm² cross sectional area) columns made from polycarbonate, washed with acid and rinsed with distilled water were prepared for the study. Twenty-six g of air dried soil was packed at a bulk density of 1.3 g cm⁻³ (1 cm thick) over a 3-cm thick layer of washed sand in each column (Figure 3). Another 3-cm thick layer of washed sand was then packed on top of the soil before placing a cap with an outlet on top. Assuming a particle density of 2.65 g cm⁻³, one pore volume for the soil columns was approximately 10.1 cm³. Deionized water, adjusted to pH of 4.3 with 0.001 M HNO₃, was pumped through the column at a rate of approximately 10 mL/h. We selected this pH based on a previous study that determined the chemical characteristics of the rainwater at a southeastern part of Brazil⁴³. A total of 670 pore volumes of the solution was passed through each column and the outflow was collected on a fraction collector in 14-15 mL increments. We determined the concentration of Pb by ICP-MS and measured the pH in the outflow samples to establish breakthrough curves.

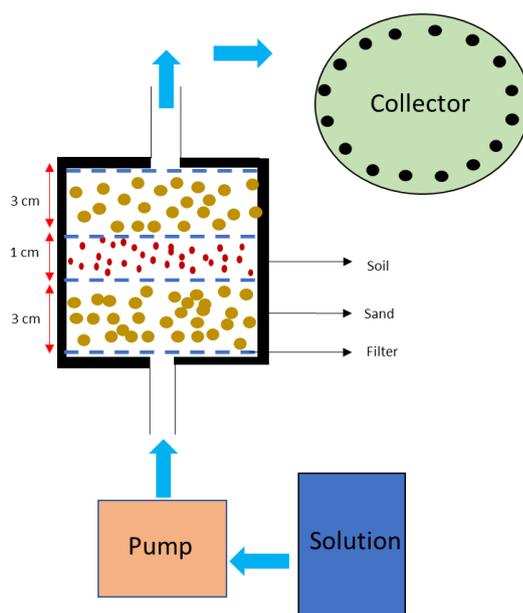


Figure 3. Diagram of the leaching column apparatus.

3.3 Results

3.3.1 Soil, Biochar and Biosolids Characterization

The amount of Pb, Zn and Cd in the soil samples were considered hazardous because their concentrations exceeded the intervention values adopted by the Environmental Agency of the State of São Paulo⁴⁴ for residential and industrial areas (Table 1). The treatment with phosphate and biosolids reduced the pH by 2 and 0.5 units, respectively. The other amendments did not affect the pH. Soil carbon (C) contents were increased more in the biochar than biosolids treatment. The highest rate of phosphate increased the exchangeable P by almost 100 times and the calcite amendment increased the Ca content by 60 to 90%.

Table 1. Selected chemical properties of soils from the mining area for all treatments (and non-treated control) of phosphate, calcite, biosolids and biochar.

Treatments	pH	C	P	K	Ca	Mg	H+Al	Al	Cd	Pb	Zn
	H ₂ O	g kg ⁻¹	mg kg ⁻¹		mmol _c kg ⁻¹	mmol _c kg ⁻¹			mg kg ⁻¹	g kg ⁻¹	g kg ⁻¹
Control	8.3	15	90	0.9	183	215	0.0	0.0	111 ± 11	4.1 ± 0.4	13.1 ± 0.7
Phosphate											
Full rate	6.3	16	8991	0.4	79	186	166.0	119.5	98 ± 7	4.3 ± 0.3	13.0 ± 0.6
Half rate	6.4	14	6185	0.5	104	156	142.0	64.0	86 ± 9	4.3 ± 0.4	13.2 ± 0.7
Quarter rate	6.7	13	3870	0.8	116	165	64.0	20.0	91 ± 8	4.2 ± 0.5	13.1 ± 0.9
Calcite											
Full rate	8.5	21	125	0.6	356	198	0.0	0.0	110 ± 10	4.3 ± 0.4	13.3 ± 0.8
Half rate	8.3	17	54	1	354	155	0.0	0.0	98 ± 10	4.0 ± 0.3	13.5 ± 0.7
Quarter rate	8.5	15	46	0.7	298	152	0.0	0.0	95 ± 9	4.2 ± 0.3	13.3 ± 0.9
Biosolids											
5%	7.7	23	148	5.8	190	198	0.0	0.0	102 ± 10	4.0 ± 0.3	12.9 ± 0.6
10%	7.8	31	259	11.3	208	180	0.0	0.0	95 ± 9	4.0 ± 0.5	13.1 ± 0.9
20%	7.7	32	344	18.2	194	166	0.0	0.9	98 ± 10	3.4 ± 0.5	12.0 ± 1.1
Biochar											
2.5%	8.1	49	47	9.6	146	171	0.0	0.0	97 ± 9	3.9 ± 0.4	13.2 ± 0.9
5%	8.2	52	40	17.4	164	188	0.0	0.0	93 ± 10	3.9 ± 0.5	13.1 ± 1.1
10%	8.4	85	65	24.5	115	115	0.0	0.0	104 ± 13	3.7 ± 0.6	12.4 ± 1.0

The biochar and biosolids were slightly alkaline and both had a high CEC. The presence of heavy metals (Cd, Pb and Zn) were not found in the biochar, whereas biosolids had significant amount of Pb and Zn (Table 2). Also, the biosolids had more Ca, Mg and P than biochar, and they had almost the same amount of K.

Table 2. Chemical properties of biochar and biosolids.

Amendments	pH	CEC	C	P	K	Ca	Mg	Cd	Pb	Zn
	H ₂ O	mmol _c kg ⁻¹			g kg ⁻¹				mg kg ⁻¹	
Biosolids	7.4	270	150	6.99	8.1	38	13.2	< 0.1	19.1	314
Biochar	8.8	200	650	1.67	9.87	2.6	3.01	0.0	0.0	0.03

3.3.2 Bulk XANES

The Pb L₃-edge spectra and the LCF-XANES results for the non-amended and amended soils are shown in Figure 4 and Table 3, respectively. The LCF-XANES fitted results described the samples data quite well. The primary Pb species in the non-amended soil were Pb-bentonite (75%) and Anglesite (PbSO₄) (25%) (Table 3). The soil amended with phosphate and calcite had an LCF with the same species as the non-amended soil, plus the LCF with pyromorphite. The best fit combination for phosphate and calcite amended soil were 41-54% Pb-bentonite, 30-16% Anglesite, and 29-30% pyromorphite.

The formation of pyromorphite due the treatment with phosphate compounds has been well documented in the literature.^{19,45,46} The soil amended with the biochar and biosolids also had a fit with Pb-bentonite (66 and 38%, respectively), and the Pb-citrate (22 and 48%, respectively). However, the biosolids did not have a fit with anglesite but had a fit with PbCl₂ (14%). The Pb L₃-edge XANES spectra of the references that had a fit with our soil samples are show in Figure 5.

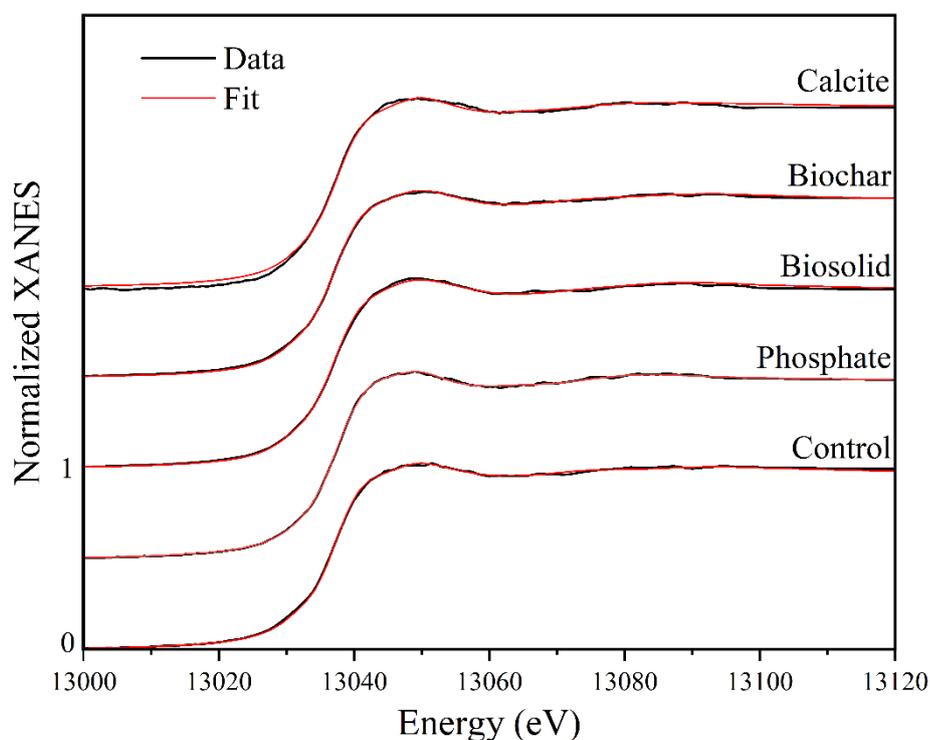


Figure 4. Lead L₃-edge XANES spectra and overlaid best fits from linear combination fitting (LCF) analysis of mining area soil in the highest treatment of phosphate, calcite, biosolids, and biochar. Fitting was done across an energy range of -30 to 80 eV relative to E₀ (first-derivative maximum).

Table 3. Combinations of standards yielding the best fits to Lead L₃-edge XANES spectra for mining area soil in the highest treatment of biochar, calcite, biosolids, and phosphate for a linear-combination fitting (LCF) energy range of -30 to 80 eV relative to E0 (first-derivative maximum)[¶].

Treatment	Pb-bentonite	Anglesite	Pyromorphite	Pb-citrate	PbCl ₂	10 ⁴ x R-factor [‡]
Proportion of standard ± uncertainty (%) [†]						
Control	75 ± 2	25 ± 2				1.90
Phosphate	41 ± 2	30 ± 1	29 ± 2			1.03
Biochar	66 ± 2	12 ± 2		22 ± 1		1.08
Calcite	54 ± 4	16 ± 3	30 ± 3			13.10
Biosolids	38 ± 3			48 ± 3	14 ± 2	3.71

[†] All data have been re-normalized to sum to 100 %; uncertainties were calculated in Athena.

[‡] Suspected contamination.

[‡] R-factor is a measure of goodness of fit = $\sum(\text{data-fit})^2 / \sum(\text{data})^2$.

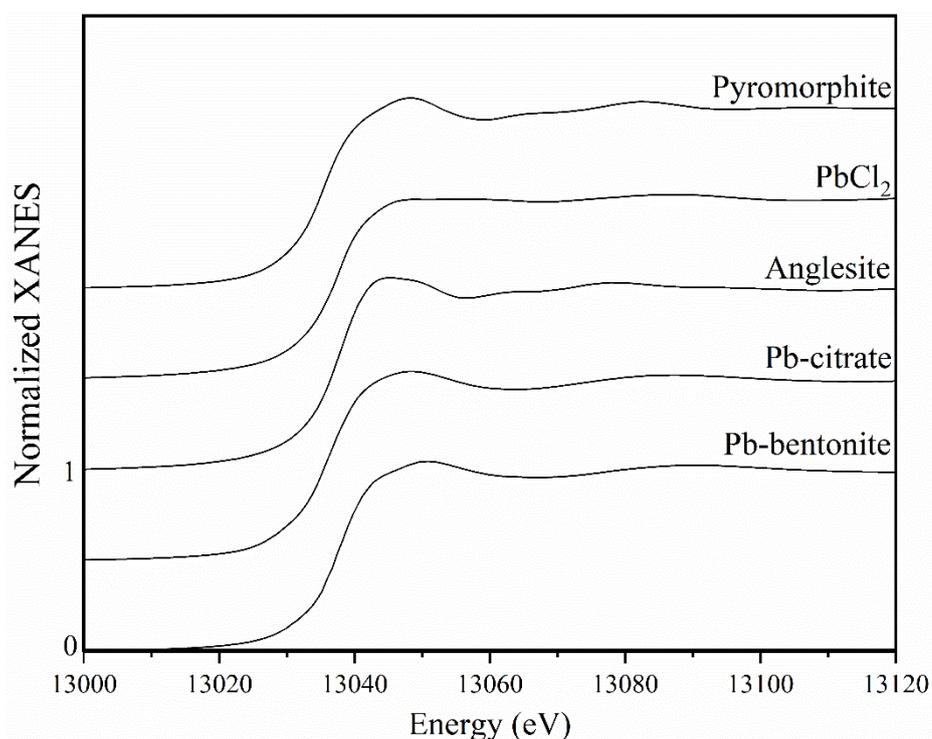


Figure 5. Pb-L₃ edge XANES of Pb reference minerals that had a fit with the bulk XANES samples.

3.3.3 Desorption Kinetics

The cumulative Pb desorbed with Mehlich-3 in the non-amended soil (control) and the soil amended with rates of phosphate, calcite, biochar, and biosolids are presented in Figure 6. The data indicated a rapid desorption of Pb in the non-amended soil within the first 30 min. The cumulative desorption at 30min was 6% and after 2 h was 10%.

The inorganic amendments (phosphate and calcite) were efficient in decreasing Pb kinetics desorption than organic amendments (biosolids and biochar). The phosphate amendment was the most effective treatment to decrease Pb desorption. While the lowest P amendment had the lowest desorption (5% after 2 h), the half and full rate were also effective in reducing Pb desorption (up to 8% after 2 h). The calcite amendment was also effective in reducing Pb desorption, but without any appreciable difference among calcite rates, with a cumulative Pb desorption around 8%.

The biochar and biosolids amendments were not effective in decreasing the desorption kinetics of Pb. Biosolids increased the desorption of Pb in the early times more than biochar. However, both amendments had very similar Pb cumulative desorption after 2 h.

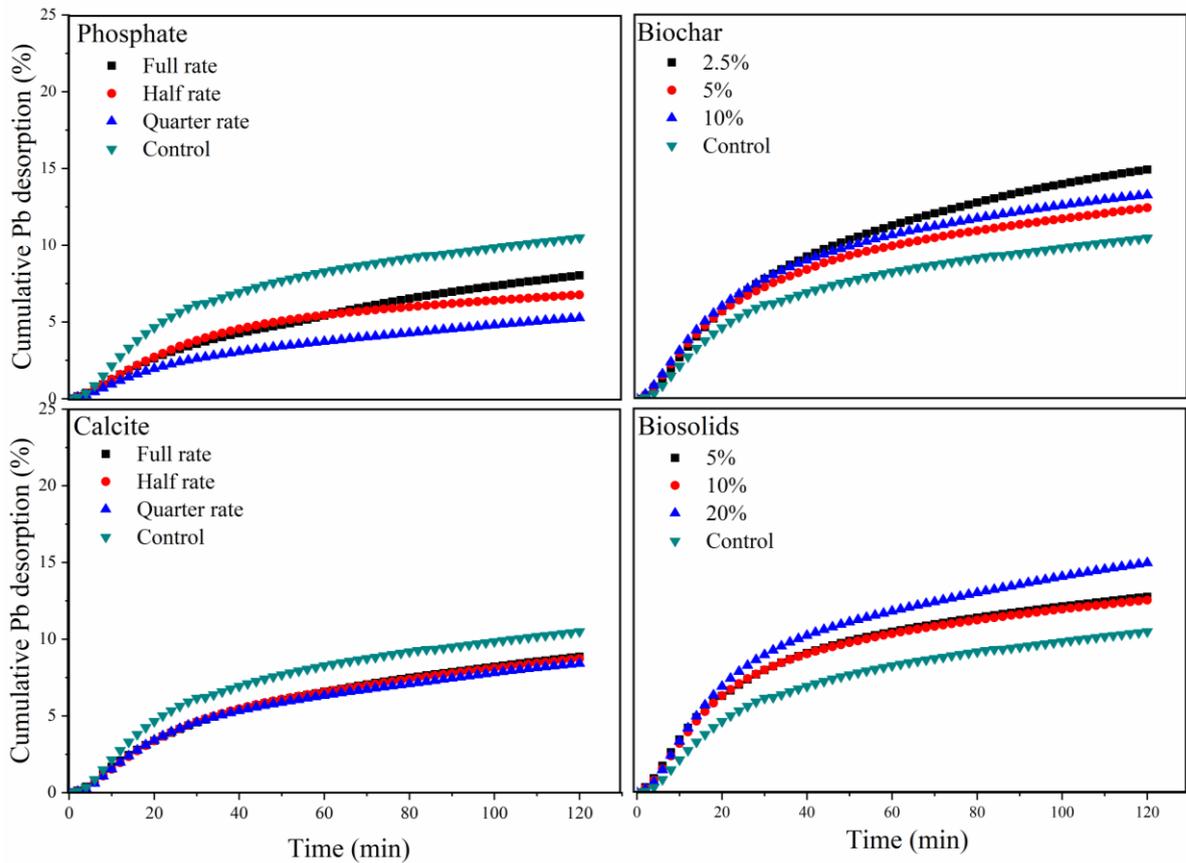


Figure 6. Cumulative Pb desorption (%) Mehlich-3 in the mining soil amended with rates of phosphate, calcite biochar and biosolids.

3.3.4 Sequential Extraction

The sequential extractions of Pb after amendment application with rates of phosphate, calcite, biosolids and biochar are given in Figure 7. No exchangeable fraction - F1 - (extracted

with 0.1 M CaCl_2) was detected in both non-amended and amended soils. The soil amended with rates of P and the highest rate of calcite and biochar did not release appreciable amounts of Pb when extracted with NaOAC (pH 5) (F2 treatment) designed to extract the species associated with carbonates. Biochar and biosolids were the only amendments that increased the Pb in the F3 treatment (extracted with 5% NaOCl (pH 8.5)) designed to extract species associated with organic matter.

In the non-amended soil and amended with calcite and phosphate, we did not detect a measurable amount of Pb in the F3 treatment. In the F4 treatment (extracted with 0.2M oxalic acid + 0.2M NH_4 oxalate (pH 3)), to extract the Pb bound to iron oxides, all rates of biosolids and the half rate and quarter rate of calcite decreased the exchangeable Pb. The biochar did not change and the half rate of phosphate decreased the Pb in the F4 treatment. The soil amended with rates of calcite and phosphate increased the Pb in the residual fraction (F5) while the biochar and biosolids had an opposite effect.

Sanderson et al 49 evaluated the effect of P in a shooting range soils contaminated by Pb and observed by sequential extraction a decrease in the Pb extracted in the F1 (exchangeable) and an increase in the residual fraction due to P treatment. A similar outcome was reported by Su et al. ⁴⁸ for P addition to an anthropogenic contaminated soil

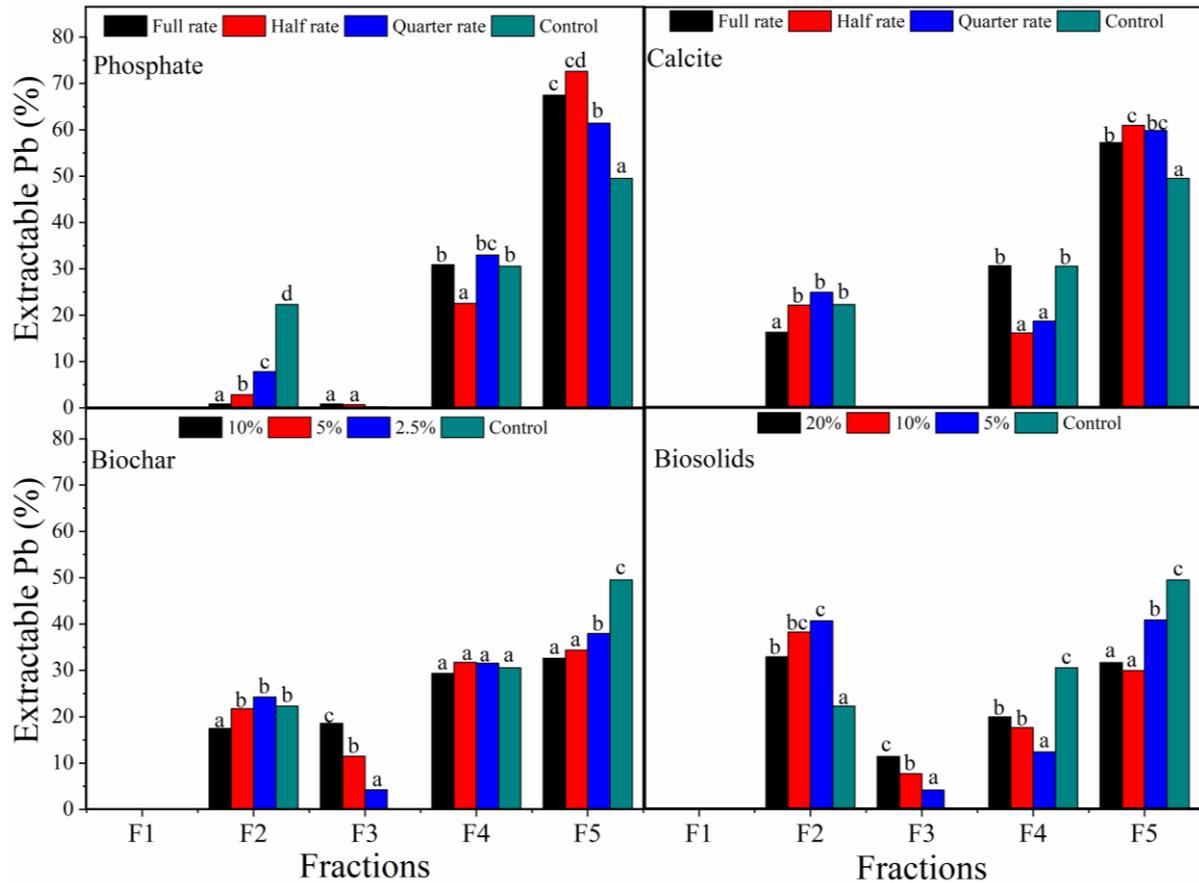


Figure 7. Relative distributions of Pb among the soil fractions as a function of treatments and rates. F1= exchangeable, F2= carbonate-associated, F3 = organic-matter associated. F4 = oxide, and F5 = residual (most strongly bound). Columns followed by the same letter in each fraction do not differ ($p < 0.05$) by Tukey test.

3.3.5 Leaching Column

The concentration of Pb (μmol) and the pH of the leachate varied as a function of the rate of phosphate (Figure 8). The first pore volume of leachate that passed through the column started with an acidic pH for all rates of phosphate applied. However, as more water passed through the column the pH began to increase before decreasing. The highest rate of P had more buffering capacity than the other rates as well as the non-amended soil.

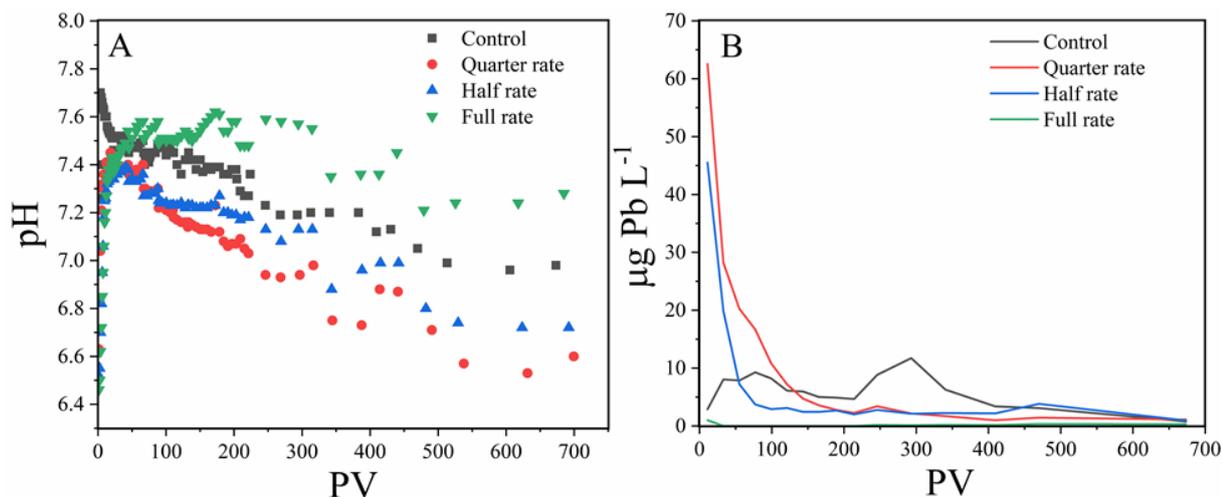


Figure 8. pH of the leachate (A) and the concentration of Pb on the leachate (B) for the rates of phosphate applied in the mining soil.

The full rate of P, we detected a low Pb concentration in all collected outflow samples. The half rate and quarter rate of P had less buffering capacity than the non-amended soil. These phosphate rates had more Pb leached during the initial period of leaching. However, after 150 pore volumes, these P rates had less Pb leached than the non-amended soil.

3.4 Discussion

The LCF included the Pb-bentonite (75%), the major species in the non-amended soil, followed by Anglesite (25%). The abundance of Pb-bentonite in the LCF is in agreement with XRD results (Figure 1). Clay minerals such as montmorillonite can be effective in binding heavy metals because they have large specific surface area and high CEC. The adsorption of heavy metals in this mineral can occur by outer-sphere adsorption, which occurs primarily on the basal planes existing in the interlayer of the clay minerals; and inner-sphere adsorption, which occurs at the amphoteric ligand sites existing on the edges of clay minerals.⁴⁷

Lead ions in bentonite may be incorporated in the positions of the inner-sphere complex by replacing some aluminum ions in the octahedral sites.⁴⁸ Lead adsorbed to bentonite and the anglesite may have been formed due to the oxidation of galena that was present in the soil environment. The formation of anglesite due to galena oxidation has already been well documented in the literature⁴⁹⁻⁵⁰, and its presence in the soil of the Vazante region has already been reported.⁵¹⁻⁵²

The LCF in the samples amended with phosphate showed that a substantial part of the Pb-bentonite was transformed in pyromorphite with a smaller amount converted to anglesite (Table 3). These results are important because pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) has at least 44 orders of magnitude smaller solubility than galena (PbS), anglesite (PbSO_4), cerrusite (PbCO_3), and litharge (PbO), which are common Pb minerals in contaminated soils.^{53,54} The presence of pyromorphite in the amended soil as detected by LCF was expected due to the high phosphate exchangeable and the decrease of the pH of the soil (Table 1).

The formation of pyromorphite is thermodynamically favored when H_3PO_4^0 and H_2PO_4^- are present; therefore, a lower soil pH is necessary to be established to support the conversion of soil Pb to pyromorphite.⁵⁵ According to Sanderson et al.⁹ for the pyromorphite formation it is necessary to have solubilization of Pb from an existing source and sufficient amount of chloride. However, when P and Cl are not in sufficient amount other species such as Pb phosphate ($\text{Pb}_3(\text{PO}_4)_2$ or PbHPO_4) and hydroxylpyromorphite are expected to form.

The LCF of the soil amended with calcite included Pb-bentonite (54%), Anglesite (16%) and Pyromorphite (30%), and the soil amended with phosphate the treatment with calcite also had substantial amount of pyromorphite formation (Table 3). This treatment resulted in a minor change in pH because our soil was already alkaline. On the other hand, the ionic strength of the soil solution increased and favored to increase the exchangeable P (Table 1) probably because of the competition for binding sites with CO_3^{2-} . However, Pb that was adsorbed to the outer-sphere complex may have been desorbed from the bentonite into the soil solution because of the excess of Ca^{2+} . Lead can exchange on the basal planes and form inner-sphere surface complexation at the edge sites on 2:1 phyllosilicate depending on the ionic strength and pH.⁵⁶ High ionic strength inhibits the outer-sphere adsorption of Pb on the basal planes of montmorillonite.⁵⁶ As we previously discussed, the presence of P and Pb in the soil solution facilitates the formation of pyromorphite. High pH of the soil may favor the precipitation of Pb as phosphate, hydroxides and carbonates, as well.⁵⁷

The results of sequential extraction and desorption kinetics give some useful insight into the immobilization of Pb in the soil and confirm their effectiveness (Figures 6 and 7). Pb extracted in the carbonate fraction decreased and was transferred to the residual fraction, indicating the presence of more recalcitrant species that is an evidence of the pyromorphite formation. Cao et al.¹¹ also reported a decrease in the Pb extracted in the carbonate fraction and an increase in the residual fraction in a soil amended with phosphate. Sanderson et al.⁵⁸ evaluated the effect of P in a shooting range soils contaminated by Pb and observed a decrease in the Pb extracted in the exchangeable and an increase in the residual fraction due to

P treatment. A similar outcome was reported by Su et al.⁵⁹ after P addition in an anthropogenic contaminated soil. In the calcite treatment, more Pb was found in the residual fractions.

The immobilization of Pb due the formation of pyromorphite is supported by the desorption kinetics results where the desorption of Pb decreased in all rates of phosphate and calcite. It is important to note that the rates of calcite did not have an appreciable impact on the desorption kinetics. On the other hand, the soil amended with phosphate had different amounts of Pb desorbed between the rates applied. This information is important to evaluate low-cost remediation strategies.

The phosphate treatment decreased the pH of the outflow (leachate) initially, but the leachate pH began to increase as more water passed through the column before decreasing again (Figure 8). The initial decrease of pH probably happened because of the dissociation of NH_4^+ and H_2PO_4^- in the solution provided by the $\text{NH}_4\text{H}_2\text{PO}_4$ that was used as a source of phosphate. The pH increased when these components began to be leached.

The highest rate of P had a higher buffer capacity probably because not all of the $\text{NH}_4\text{H}_2\text{PO}_4$ had reacted with soil. The half rate and quarter rates increased the leaching of Pb in the initial leaching probably due to the mineral solubilization. The acidity generated by the phosphate may cause the dissolution of the compounds of Fe, Al, Mn, organic matter and carbonates.⁶⁰ The use of soluble P source for amending soils increases the soil dissolved organic carbon concentration, thereby increasing Pb mobility.⁶¹ Although the half and quarter rates resulted in a higher initial leaching, these treatments in long-term may be effective to decrease the Pb mobility. Su et al.⁵⁹ evaluated the effect of the addition of sources of P with oxalic acid in different incubation times in a soil contaminated anthropogenically by Pb. The authors observed a decrease in the Pb leaching in all treatments with P and less Pb was leached in the highest times of incubation.

Conversely to the inorganic amendments (phosphate and calcite), the organic amendments (biochar and biosolids) made the Pb more available in the soil. The effectiveness of biochar and biosolids to immobilize Pb in contaminated soil is well documented⁶²⁻⁶⁷. These amendments can increase immobilization of heavy metals due to different chemical process, such as adsorption, complexation and precipitation.¹⁷ However, in our study, these amendments increased the desorption kinetics of Pb for all rates of biochar and biosolids, and we also verified a decrease in the residual fraction (F5) that is responsible for the most stable species in the soil.

Biochar and biosolids had a LCF with Pb-citrate indicating that part of Pb might be bound with organic groups. This result agrees with the sequential extraction in which the Pb extracted in the fraction 3 (organic matter bound) increased for both treatments. Scheckel et al.⁶⁸ evaluated the effect of amendments on the Pb speciation in a soil contaminated by smelter activities. They observed that the treatment with 10% of biosolids decreased the LCF with anglesite (32 to 12%) and galena (21 to 0%), and increased the LCF with Pb bound to organic matter (37 to 60%). They also reported that the treatment with rock phosphate and triple superphosphate used as source of P increased the LCF with Pyromorphite.

Lead may have been complexed by the soluble organic ligands originating from the biochar and biosolids and this may have increased your desorption. Lead has the ability to form a complex compound with the dissolved organic carbon.⁶⁹ The formation of soluble complexes with oxygen-containing functional groups of dissolved organic matter can increase the mobility of metals like Pb and Cu.⁷⁰ Strawn and Sparks⁶² evaluated the kinetic adsorption of Pb in a soil in which organic matter (SOM) was removed. They observed that the soil without SOM sorbed more Pb than the untreated soil. The SOM consists of a large polymer, and the diffusion to the sites on the interior of the SOM molecule limit the sorption process.⁶²

3.5 Environmental Recommendations

Application of P and calcite for chemical stabilization of Pb in a contaminated soil resulted in a significant formation of pyromorphite. These amendments decreased the desorption kinetics and formed more recalcitrant species of Pb. The highest rate of each treatment did not always result in more Pb immobilized. Thus, for remediation, a better option may be to start with the lowest rate, which may provide a more cost-effective and sustainable solution. In our study, biochar and biosolids increased the mobilization of Pb. However, the chemical characteristics and the production of these amendments can affect their effectiveness. The soil characteristics and the incubation time also should be considered. In future studies, it is important to verify the long-term effects of these amendments.

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4 RELEASE KINETICS OF CADMIUM IN A MINE-WASTE IMPACTED SOIL AMENDED WITH BIOCHAR, PHOSPHATE, CALCITE AND BIOSOLIDS

Abstract

Cadmium (Cd) is a hazardous heavy metal that may cause several problems in human health, and new remediation technologies to decrease its environmental risks are necessary. In situ remediation is a promissory and low-cost strategy for immobilizing heavy metals in soil. This technique is based on the utilization of soil amendments designed to immobilize heavy metals in soil, thus decreasing their risks. In this study, Cd release kinetics (by the stirred flow method) and sequential extraction were performed in a soil under forest and in a soil near the forest from a mining area as a function of the application of rates of biochar, phosphate, calcite, and biosolids. Biochar and biosolids were more effective to decrease the desorption kinetics of Cd in the forest soil than in the mine soil. Both treatments increased the Cd associated to organic matter (OM), and it suggests that part of the Cd was immobilized on the organic compounds provided by these amendments. The desorption kinetics of Cd in both soils was also decreased in samples amended with phosphate. A decrease in the fraction associated to carbonate and an increase in the OM fraction were observed, suggesting that the P could increase the negative charge on the organic compounds. The leaching column performed in the mine showed that the quarter rate and a half rate of P increased the leaching of Cd, while the highest rate decreased Cd leaching when compared with the unamended soil. The treatment with calcite was more effective to decreased Cd desorption kinetics in the mine soil at the initial times (30 min), while the same was observed in the forest soil only at 120 min. In both soils, the Cd associated to OM increased after the addition of calcite as it could increase the negative charge on the organic matter.

Keywords: Desorption kinetics; In-situ remediation of soils; Soil pollution; Sequential extraction

4.1 Introduction

Between 1973 and 2016, the world mine production of Cd increased from 17,200 to 23,000 tonnages, an increase of ~34%.^{1,2} The contamination of soil by heavy metals due to mining activities is pretty common in different places in the world.³ High Cd contents up to 360 mg kg⁻¹ have been found in soils at Zn-Pb mine sites.⁴ In addition to mining activities, the soil can have an input of heavy metals by atmospheric deposition of aerosol particles,⁵ direct applications of agricultural fertilizers,⁶ agrichemical⁷ and organic materials, such as biosolids⁸ and livestock manures.⁹

The soil contamination by Cd is a global environmental concern that results in ecological hazards and human health and also implies huge economic costs with respect to reclamation and restoration.¹⁰ Cadmium is a heavy metal that can cause several problems in the human health, such as cancer,¹¹ damages on the kidney,¹² reproductive system,¹³ respiratory system,¹⁴ and skeletal system.¹⁵ The consumption of crops contaminated by Cd correspond with >90% of the human exposure in the general population and most of dietary Cd is derived from soil via uptake in main food items, i.e. potatoes or cereals.³ The other

paths to heavy metals exposure may be direct ingestion or contact with contaminated soil and drinking of contaminated ground water.¹⁶

The scientific community is focused to develop of soil remediation technologies because of the implications of the contaminated soils on animal and human health.¹⁷ Conventional technologies for soil remediation, i.e., landfilling and excavation, are often expansive and environmentally unfeasible, as compared to alternative options. The utilization of amendments for metal immobilization/solidification are cost effective and less environmentally disruptive.^{18,19} The advantage of immobilize heavy metals in soil by amendments are (i) it is low invasive, (ii) simplicity and rapidity, (iii) relatively inexpensive, (iv) small amount of wastes are produced, and (vi) covers a broad spectrum of inorganic pollutants.²⁰

Many amendments, such as phosphate,²¹ alkaline materials,²² biochar,²³ and biosolids²⁴ have been used to immobilize Cd in soil and decrease its environmental risks. The amendments may immobilize the heavy metals due to adsorption, complexation, and precipitation reactions, thus making them unavailable for human and plant uptake and leaching to groundwater.²⁵

Many soil chemical processes are time dependent, and evaluation of desorption kinetics is crucial for understanding the mobility and availability of metals in contaminated soils after the addition of amendments. By means of kinetics desorption it is possible to determine the quantities of metal available with greater and slower speed, as well as the content not available, and can, therefore, help in predicting its fate over the time.^{26–28} For example, Ren et al.²⁹ evaluated the desorption kinetics of Cd, Zn, and Pb in a soil from a mining area and observed that the desorption of Cd had already reached equilibrium after three days of reaction, while Pb and Zn only reached after twelve days. According to Ren et al.²⁹, Cd was associated with low-affinity binding sites, while Pb and Zn were mainly associated with more specific forms of binding.

Our research aim was to evaluate if the addition of phosphate, calcite, biochar, and biosolids were able to immobilize the Cd in a mine-waste impacted soil from Brazil. Leaching column, sequential extraction, and stirred-flow kinetic approaches were performed to evaluate the effect of these amendments on Cd mobility.

4.2 Materials and Methods

4.2.1 Characterization of Soil, Biochar and Biosolids

The soil samples were collected from the surface layer (0-20 cm) in a deactivated Zn mining area and a forest close to the mining area both located in Vazante Minas Gerais, Brazil (close to geographic coordinates 17°59'11''S, 46°54'27'' W). The samples were air dried at room temperature (~25°C) and passed through a 2-mm sieve. The content of soil organic carbon was determined with a Shimadzu TOC-5000 carbon analyzer. The total concentration of heavy metals in the soils were extracted following the EPA3051a³⁰ method using a 1:3 HCl/HNO₃, and the metal contents were quantified by inductive couple plasma optical emission spectroscopy (ICP-OES). The content of exchangeable ions and pH analyses followed the methods of Ingram and Anderson.³¹

The chemical characteristics of the biochar and biosolids are in the Table 1. The biochar was produced using sugarcane (*Saccharum officinarum*) straw at the temperature of pyrolysis of 450 °C. For more information about the production and characterization of biochar see Feola Conz et al.³². The biosolids was produced from the composting of wood chips (eucalyptus) and sewage sludge. The composting took place in aerated rows for 60 days and was sieving in mesh with 36 mm² holes. In the composting process, about 2% of dolomitic limestone was added to the sludge. The sewage sludge was collected at a sewage treatment station located in Jundiai, São Paulo, Brazil and was composed in the major part by domestic than industrial sludge. The pH of biosolids was determined in water extracts (1:5 v/v), CEC was determined following the method described by Sparks³³ and the organic C content was determined by the Walkley and Black method. The metal (Cd, Zn and Pb) and nutrients (P, K, Ca and Mg) concentration in the biochar and biosolids were determined following the EPA3051a³⁰ method.

4.2.2 Amendments and Incubation Time

In triplicate the soils were amended individually with rates of ammonium phosphate monobasic (NH₄H₂PO₄), calcite (CaCO₃), biochar and biosolids. The soils were amended with 2.5; 5 and 10% of biochar³⁴ and 5, 10 and 20% of biosolids.³⁵ The rate of NH₄H₂PO₄ and CaCO₃ were estimated by the concentration of Cd, Zn and Pb in the soil and was designed to promote the precipitation of stable forms. The NH₄H₂PO₄ was applied evenly to the soil at 0

(control); 0.5 (quarter rate); 1.0 (half rate) and 2:1 (full rate) molar ratio of P to the sum of Cd, Zn and Pb. These rates were based on the stoichiometry ($P:M = 3:5$) form of the follow precipitate $M_5(PO_4)_3OH$ ($M =$ sum of Zn, Pb and Cd).³⁶ Calcite ($CaCO_3$) was applied evenly to the soil at 0 (control); 0.25 (quarter rate); 0.5 (half rate) and 1:1 (full rate) molar ratio of $CaCO_3$ to the sum of Cd, Zn and Pb.³⁷ The amendments were added and mixed homogeneously with the soil and incubated with deionized water at 70% of the maximum water retention at $25 \pm 2^\circ C$ in the lab for 60 days. To maintain the humidity, water was added every 3 days based on the mass loss of water.

4.2.3 Desorption Kinetics

The desorption kinetics of Cd was performed using a stirred-flow reactor equipped with a piston displacement pump designed for use in a HPLC system. The stirred-flow chamber was 12 mL of volume and 200 mg of mass of amended soil was used to perform the desorption (Figure 1). The solution used was Mehlich-3 ($0.2M CH_3COOH + 0.25M NH_4NO_3 + 0.013M HNO_3 + 0.015M NH_4F + 0.001M EDTA$) as a desorption agent. In the reactor chamber was used a 25-mm diameter cellulose filter membrane with $0.45 \mu m$ pore size. The suspension in the reactor was stirred at 300 rpm and the liquid portion of it was flowed through the filter in the chamber at a rate of $1 mL min^{-1}$. The effluent was collected by a fraction collector at 2 min intervals and the concentration of Cd was quantified by ICP-OES. The amount of Cd desorbed was calculated according to Yin et al.³⁸ and plotted in cumulative Cd desorption percentages.

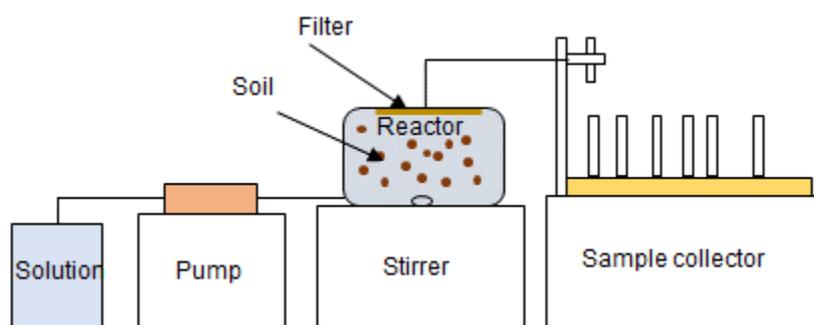


Figure 1. Schematic diagram of operation for stirred flow method

4.2.4 Sequential Extraction

The sequential extraction of the amended soils was done according to the procedure developed by Silveira et al.³⁹. The original method counts on seven fractions, but in the present study we extracted sequentially with 0.1 M CaCl₂ for readily exchangeable (F1); 1 M NaOAc (pH 5) for carbonates forms (F2); NaOCl (pH 8.5) for organic-matter bound (F3); 0.2M oxalic acid + 0.2M NH₄ oxalate (pH 3) for iron-oxides bound (F4); the residual (F5) was determined by digestion according to EPA3051a method using a 1:3 HCl/HNO₃³⁰. The Cd in each fraction was quantified by ICP-OES.

4.2.5 Leaching Column

The leaching experiment was conducted using only the soil from the mine area amended it with different rates of P. For this study, we used four 5.05-cm diameter (20 cm² cross sectional area) columns made from polycarbonate that was previously washed with acid and rinsed with distilled water. Twenty-six g of air-dried soil was packed at a bulk density of 1.3 g cm⁻³ (1 cm thick) between a 3-cm thick layer of washed sand on the top and on the bottom (Figure 2). One pore volume for the soil columns was approximately 10.1 cm³, assuming a particle density of 2.65 g cm⁻³. Deionized water, adjusted to pH of 4.3 with 0.001 M HNO₃, was pumped through the column at a rate of approximately 10 mL h⁻¹. The pH of the solution was based on a previous study that determined the chemical characteristics of the rainwater at a southeastern part of Brazil.⁴⁰ A total of 670 pore volumes of the solution was passed through each column and the outflow was collected on a fraction collector in 14-15 mL increments. We determined the concentration of Cd by ICP-MS and measured the pH in the outflow samples to establish breakthrough curves.

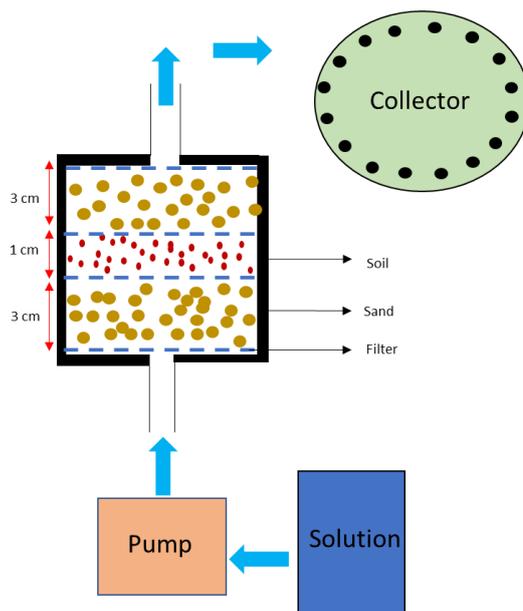


Figure 2. Diagram of the leaching column apparatus.

4.3 Results and Discussion

4.3.1 Effects of the Amendments on the Soil Properties

The concentration of Cd, Zn and Cd in the non-amended and amended soils were considered hazardous because their amount exceeded the intervention values adopted by the Environmental Agency of the State of São Paulo (Brazil)⁴¹ for residential and industrial areas (Table 1 and 2). However, the amendments did not affect the heavy metal concentration but affected the others chemical properties of the soils.

The treatment with rates of P decreased the pH and increased the exchangeable P of the soils. These changes, were more evident in the mine soil because the amount of P applied was higher. According to Sposito⁴² ammonium-based fertilizers can result in soil acidification. The phosphoric acid released by P fertilizers also could decrease the soil pH.⁴³ The decreasing in the pH due to MAP application already was reported in the literature.⁴⁴ Calcite treatment caused a slight increase in the soil pH and also increased the amount of Ca exchangeable. The calcite increases the pH due to the neutralization of H^+ by the OH^- released in the reaction of the calcite on the soil (equation 1, 2 and 3).

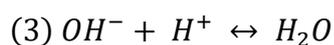
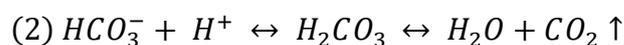
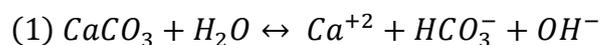


Table 1. Selected chemical properties of soils from the forest for all treatments (and non-amended control) of phosphate, calcite, biosolids and biochar.

Treatments	pH		C	P	K	Ca	Mg	H+Al	Al	Cd	Pb	Zn
	H ₂ O	CaCl ₂	g kg ⁻¹	mg kg ⁻¹	mmol _c kg ⁻¹					mg kg ⁻¹		
Control	6.9	6.1	43	19	4.6	49	29	18.0	0.2	13.1 ± 2	270 ± 34	858 ± 72
Phosphate												
Full rate	6.4	5.7	40	648	4.6	55	28	29.0	2.2	11.3 ± 2	270 ± 18	820 ± 41
Half rate	6.9	6.0	42	246	4.7	50	27	20.0	0.7	12.3 ± 2	215 ± 35	858 ± 90
Quarter rate	6.9	6.1	41	96	4.1	46	24	20.0	0.7	11.5 ± 2	223 ± 38	823 ± 91
Calcite												
Full rate	7.1	6.6	42	26	4.8	82	24	13.0	0.2	11.5 ± 2	200 ± 34	836 ± 30
Half rate	7.1	6.5	36	22	4.7	70	27	15.0	0.2	13.0 ± 3	220 ± 15	915 ± 98
Quarter rate	7.0	6.2	36	20	3.5	58	25	17.0	0.2	10.4 ± 2	214 ± 13	834 ± 55
Biosolids												
5%	7.1	6.5	39	97	8.3	94	59	15.0	0.2	13.8 ± 3	222 ± 23	812 ± 70
10%	7.0	6.6	59	196	13.5	93	58	14.0	0.1	13.5 ± 3	198 ± 28	821 ± 52
20%	7.1	6.8	71	278	19.9	118	67	13.0	0.1	12.1 ± 2	201 ± 14	840 ± 60
Biochar												
2.5%	6.8	6.2	51	29	12.8	50	35	17.0	0.3	11.7 ± 3	232 ± 40	770 ± 58
5%	6.5	6.0	67	37	20.4	46	25	18.0	0.2	12.2 ± 3	215 ± 25	810 ± 75
10%	6.2	5.9	95	45	23.8	48	26	18.0	0.3	13.5 ± 3	230 ± 23	816 ± 85

Table 2. Selected chemical properties of soils from the mining area for all treatments (and non-treated control) of phosphate, calcite, biosolids and biochar.

Treatments	pH		C	P	K	Ca	Mg	H+Al	Al	Cd	Pb	Zn
	H ₂ O		g kg ⁻¹	mg kg ⁻¹		mmol _c kg ⁻¹				mg kg ⁻¹	g kg ⁻¹	g kg ⁻¹
Control	8.3		15	90	0.9	183	215	0.0	0.0	111 ± 11	4.1 ± 0.4	13.1 ± 0.7
Phosphate												
Full rate	6.3		16	8991	0.4	79	186	166.0	119.5	98 ± 7	4.3 ± 0.3	13.0 ± 0.6
Half rate	6.4		14	6185	0.5	104	156	142.0	64.0	86 ± 9	4.3 ± 0.4	13.2 ± 0.7
quarter rate	6.7		13	3870	0.8	116	165	64.0	20.0	91 ± 8	4.2 ± 0.5	13.1 ± 0.9
Calcite												
Full rate	8.5		21	125	0.6	356	198	0.0	0.0	110 ± 10	4.3 ± 0.4	13.3 ± 0.8
Half rate	8.3		17	54	1	354	155	0.0	0.0	98 ± 10	4.0 ± 0.3	13.5 ± 0.7
Quarter rate	8.5		15	46	0.7	298	152	0.0	0.0	95 ± 9	4.2 ± 0.3	13.3 ± 0.9
Biosolids												
5%	7.7		23	148	5.8	190	198	0.0	0.0	102 ± 10	4.0 ± 0.3	12.9 ± 0.6
10%	7.8		31	259	11.3	208	180	0.0	0.0	95 ± 9	4.0 ± 0.5	13.1 ± 0.9
20%	7.7		32	344	18.2	194	166	0.0	0.9	98 ± 10	3.4 ± 0.5	12.0 ± 1.1
Biochar												
2.5%	8.1		49	47	9.6	146	171	0.0	0.0	97 ± 9	3.9 ± 0.4	13.2 ± 0.9
5%	8.2		52	40	17.4	164	188	0.0	0.0	93 ± 10	3.9 ± 0.5	13.1 ± 1.1
10%	8.4		85	65	24.5	115	115	0.0	0.0	104 ± 13	3.7 ± 0.6	12.4 ± 1.0

Both organic amendments (biochar and biosolids) increased the amount of C on the soils. Biochar had ~4.5 times more C than biosolids. Although the biochar and biosolids were alkaline (Table 3) they had different behavior on the pH in the soil from the forest and from mine area. The Biochar decreased the pH of the forest soil and did not have a significant effect on the mine soil. On the other hand, biosolids increased a little the pH of the forest and decreased the pH of the mine probably because your pH was smaller than mine soil. The pH may decreased due to the oxidation of C to form acidic carboxyl groups.⁴⁵ The forest soil probably had more microbial activities and it could favor the biochar degradation resulting in the decreasing the soil pH. The application of biochar in soil increase the microbial population and microbial activity in soils^{46,47} and biochar may accelerate the decomposition of soil native C by improving microbial populations.^{48,49}

Table 1. Chemical properties of biochar and biosolids.

Amendments	pH	CEC	C	P	K	Ca	Mg	Cd	Pb	Zn
	H ₂ O	mmol _c kg ⁻¹	g kg ⁻¹					mg kg ⁻¹		
Biosolids	7.4	270	150	6.99	8.1	38	13.2	< 0.1	19.1	314
Biochar	8.8	200	650	1.67	9.87	2.6	3.01	0.0	0.0	0.03

4.3.2 Effects of the Amendments in the Immobilization of Cadmium

4.3.2.1 Phosphate

The behavior of Cd differed among the rates of P and soils. The results of desorption kinetics, sequential extraction, and leaching columns are presented in Fig 3 to 7. The results of desorption kinetics showed us that the desorption of Cd decreased due to rates of Phosphate. This decrease was more pronounced in the first 30 min for the mine soil whereas the forest soil was after 120 min (Figure 3 and 4). In the first 30 minutes, the amount of Cd desorbed in the mine soil ranged from 9.2 to 8.3% for rates of P, while the untreated soil was 11.5%. However, this difference decreased after 120 minutes for some rates of P.

At 120 min, the amount desorbed in the forest soil ranged from 9.8 to 8.1% for rates of P while it was 9.5% in the untreated soil. The efficiency of phosphate compounds to immobilize Cd in soils is well documented in the literature.^{37,50,51} Basta et al.³⁷ investigated the effect of P in the immobilization of Cd in a soil collected in a smelter site in Northeastern Oklahoma, USA. They observed a reduction of 53% and 94% on the elution of Cd due to the treatment with rock phosphate and diammonium phosphate, respectively. Based on the use of geochemical computer speciation modeling, Basta et al.³⁷ concluded that the Cd phosphate was the most probable solid phase formed after diammonium phosphate treatment.

Phosphate increase the immobilization in soils through various chemical process such as direct adsorption/substitution by P compounds, P anion-induced metal adsorption and precipitation.⁵² The P may improve the soil negative surface charge, and it increases Cd sorption.⁵³ Adhikori and Singh⁵⁴ suggested the following sorption mechanisms resulted from P application: (i) precipitation of Cd as Cd₃(PO₄)₂, (ii) sorption of Cd-P complexes, (iii) surface complex formation of Cd onto sorbed P, and (iv) P-induced Cd sorption. Cadmium phosphate [Cd₃(PO₄)₂] may control Cd solubility in soils before immobilization treatments.⁵⁵

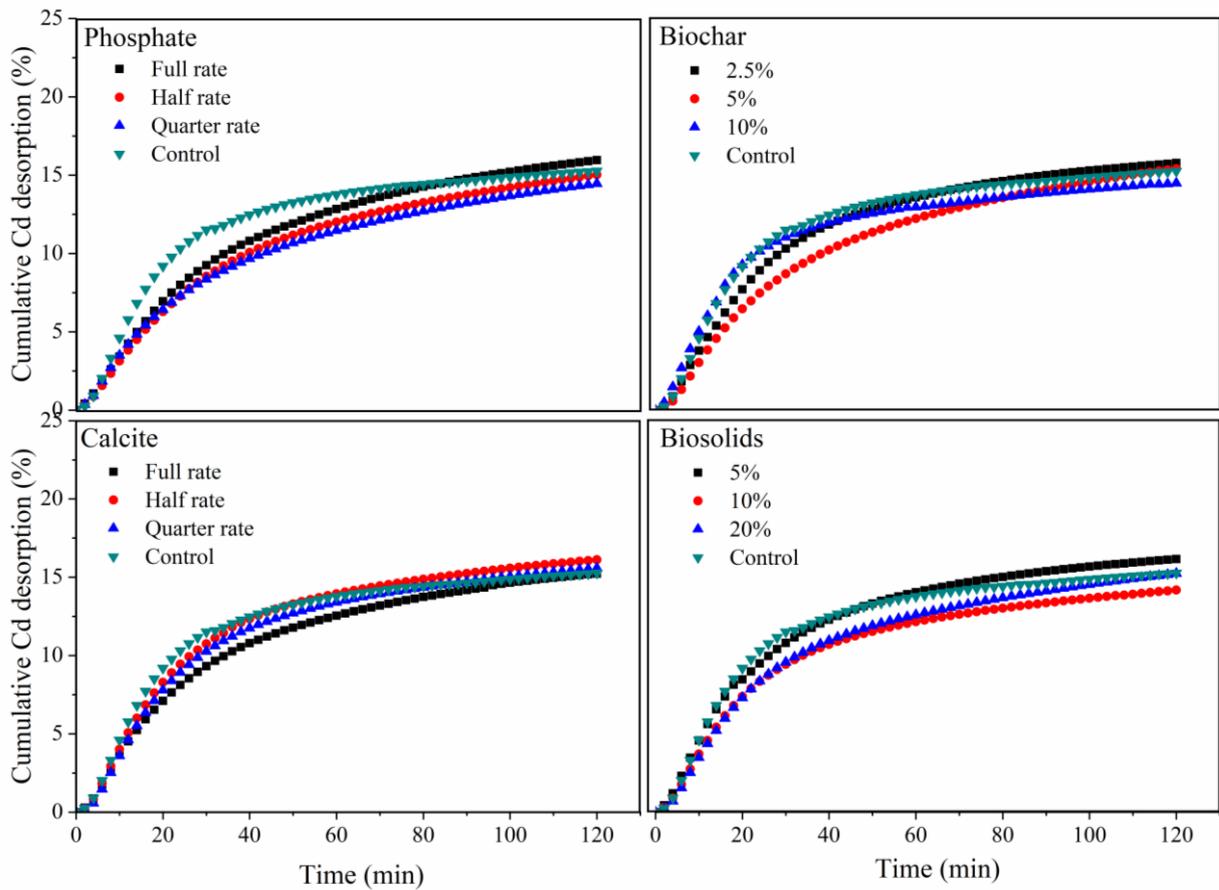


Figure 3. Cumulative Cd desorption (%) Mehlich-3 in the mining area amended with phosphate, calcite, biochar and biosolids in different rates.

Cadmium in the forest soil was distributed almost 100% in the F4 (bounded to iron oxides) while the most part the mine soil was in the F2 (carbonate forms) and F3 (organic matter bound) (Figure 5 and 6). The treatment with rates of P did not have a significant effect ($p < 0.05$) in the forest, but this treatment decreased the Cd in the F2 and increased in the F3 in the mine soil. The increase of the Cd in the F3 could be due to the increase in the negative charge in the minerals or organic compounds.

The adsorption of specifically ligands such as H_2PO_4^- and HPO_4^{2-} in strongly weathered and variable charge soils can induce Cd (II) adsorption through increased negative surface charge.^{56,57} On the other hand, Wang et al.⁵⁸ evaluated the effectiveness of amendments to immobilize heavy metals in a contaminated soil from a crop land in the vicinity of a galvanized factory in Fuyang district, China, and observed that the soil amended with triple superphosphate increased the Cd bound to iron-manganese oxides fraction and decreased in the exchangeable fraction. The different results were probably because of differences in the sequential extraction methods, the sources of contamination, the soil characteristics and the source of P used as amendments.

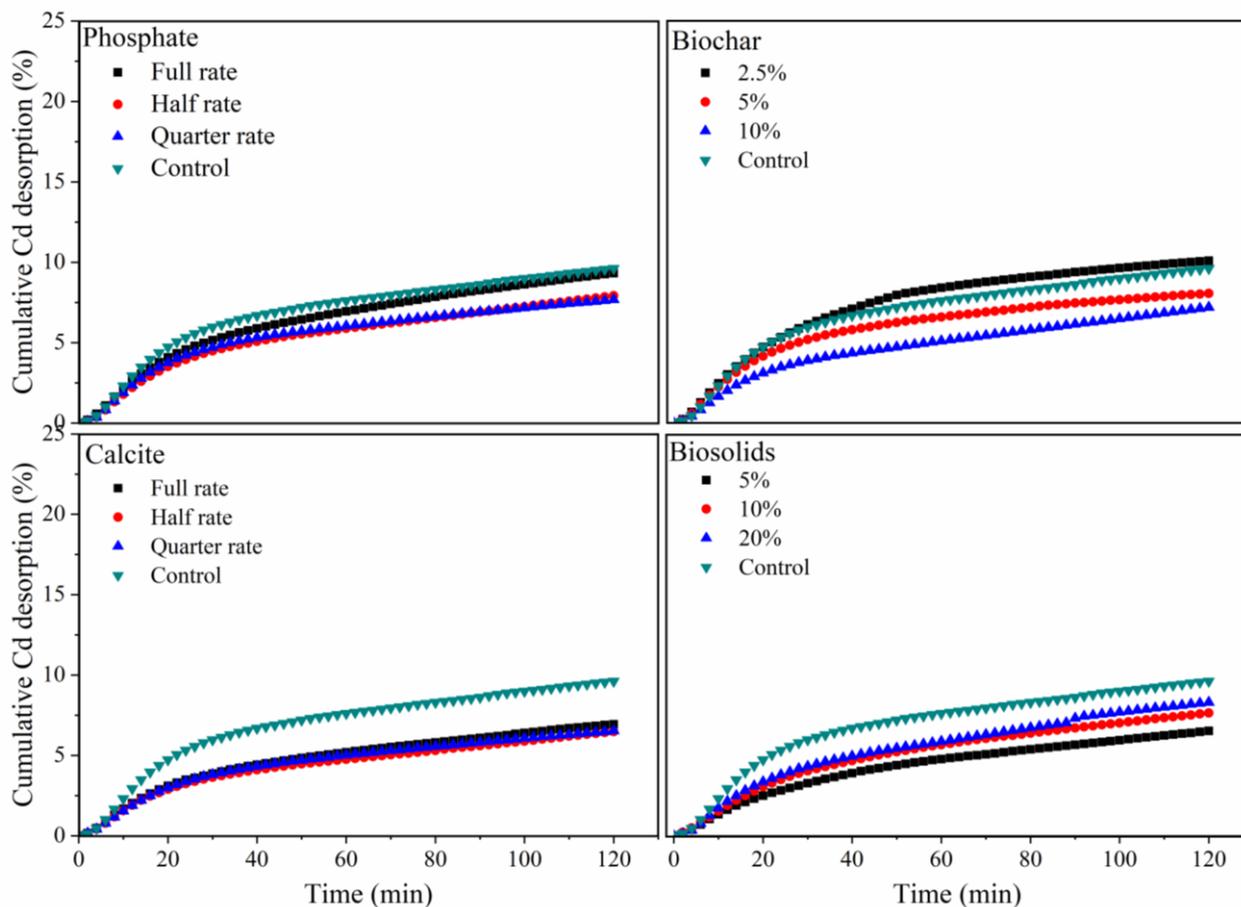


Figure 4. Cumulative Cd desorption after extraction with Mehlich-3 solution in the forest amended with phosphate, calcite, biochar and biosolids at different rates.

The amount of Cd in the leached increased in the quarter rate and half rate of P (Figure 7). However, the full rate leached less Cd than unamended soil. The reduction of Cd adsorption in presence of P in soils is attributed to the formation of Cd-P complexes in solution.⁵⁹ The pH of the leached in the all rates of P started around 6.5 and increased until 7.4 when more water passed through the column. The low pH in the initial leaching was probably due to the dissociation of NH_4^+ and H_2PO_4^- in the solution provided by the $\text{NH}_4\text{H}_2\text{PO}_4$ used as a source of P. Fertilizers with high NH_4^+ amounts reduce the soil pH⁴² and may increase the content of Cd on the soil solution.⁵³ The treatments that the faster pH decreases were the same with the highest Cd releases. In other words, the rate of quarter of P decreased more the pH and increased Cd release in comparison with the other rates. The increase of Cd concentration on the solution could be associated with the decrease in the soil pH and presumably with the desorption of Cd from exchange sites on soil colloids.⁶⁰

4.3.2.2 Calcite

Calcite was more effective to immobilize Cd in the forest soil than in the mine soil. In the mine soil the rates of calcite decreased the Cd release in the initial times (0 to 30 min) (Figure 3). In the first 30 min the cumulative desorption in the mine soil amended with rates of calcite ranged from 9.3 to 10.7%, while in the unamended soil it was 11.5%. However, after 120 min, the cumulative desorption of the amended soil was bigger or equal to the unamended soil. The amount desorbed was 15.2, 16.1, 15.5 and, 15.2% for the full rate, half rate, quarter rate and unamended soil, respectively. The decrease of the release of Cd during the first 30 min could be due to the buffering capacity caused by the calcite. Considering that the mine soil was already alkaline (Table 3), this favored so that calcite remained without reacting on the soil.

The treatment with calcite increased the Cd extracted in the F3 (organic matter bound) (Figure 5). The other fractions did not have significant changes. Calcite reduces the H^+ concentration and increases the negative charges sites⁵², and this could increase the adsorption of Cd in the organic matter. Soil organic matter is one of the most important soil components controlling the heavy metal adsorption and desorption in the soil. It has two important binding sites that are carboxylic and phenolic groups that control metal binding, and each type of binding site formed through various combinations of those two types of sites have distinct thermodynamic properties, such as the proton and metal binding constants.^{62–64} Organic matter of the soil sorbs the Cd at negatively charged carboxylic and phenolic groups or directly with these and other groups forming monodentate or multidentate bonding (chelation).⁶¹

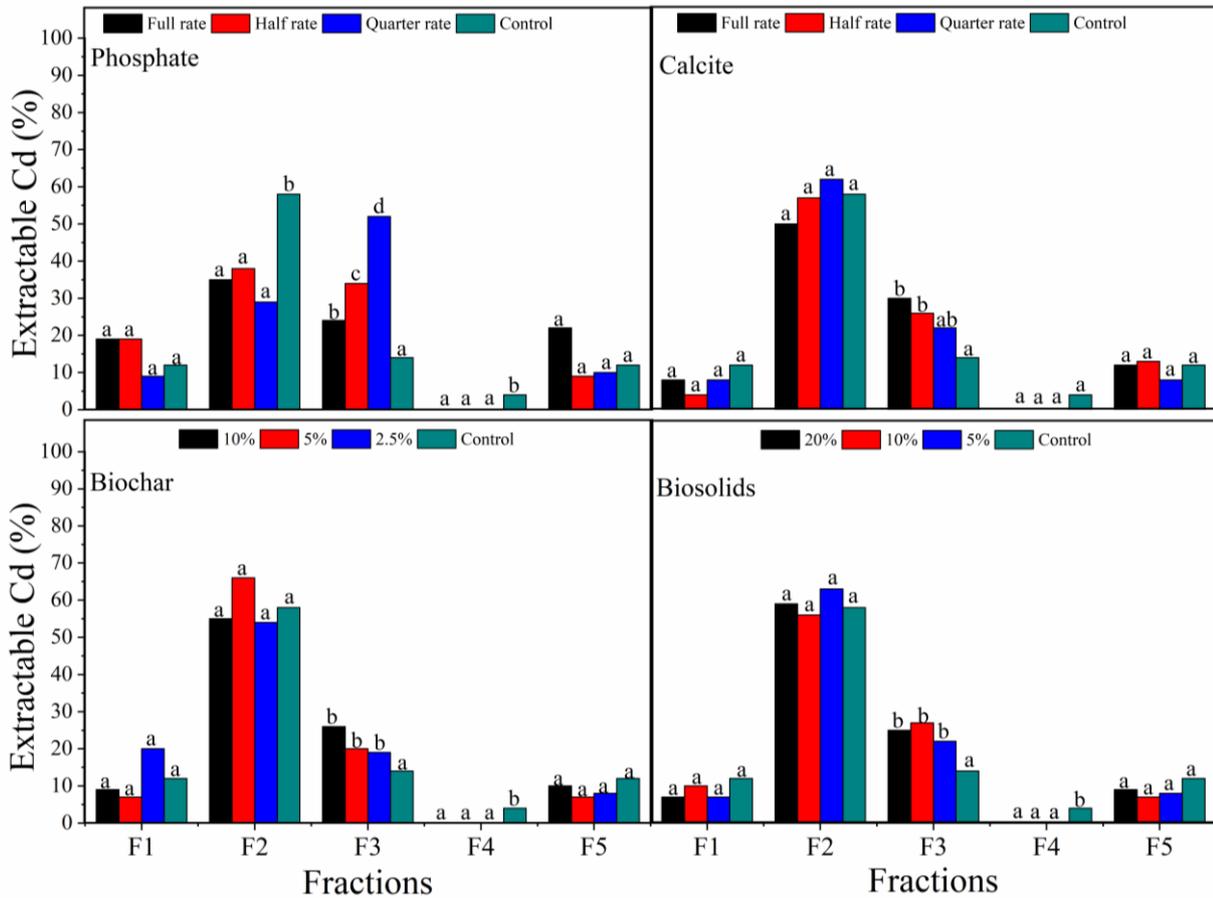


Figure 5. Relative distributions of Cd in the mining area among the various soil fractions in different treatments and rates. F1= exchangeable, F2= carbonate-associated, F3 = organic-matter associated. F4 = oxide, and F5 = residual (most strongly bound). Columns followed by the same letter do not differ at 0.05 (Tukey test).

The amount of Cd released during all the time (0 to 120 min) in the forest soil was smaller in all rates of calcite compared to the unamended soil (Figure 4). The cumulative desorption after 120 min was 6.9, 6.4, 6.5 and 9.6% for the full rate, half rate, quarter rate and unamended soil, respectively. The decreasing in the Cd desorption in this soil amended with rates of calcite probably occurred due to the increase in the pH. This soil attribute is the most dominant factor influencing Cd sorption in soils.^{65,66}

The increase in the pH increase the negative surface charge in the iron oxides, organic matter and phyllosilicates.⁶⁷ Cd decreased in the F4 (iron oxides bound) and increased in the F3 (organic matter bound) (Figure 6), and this could happen because the pH increased the negative charge in the organic matter and favored the Cd bound as discussed before.

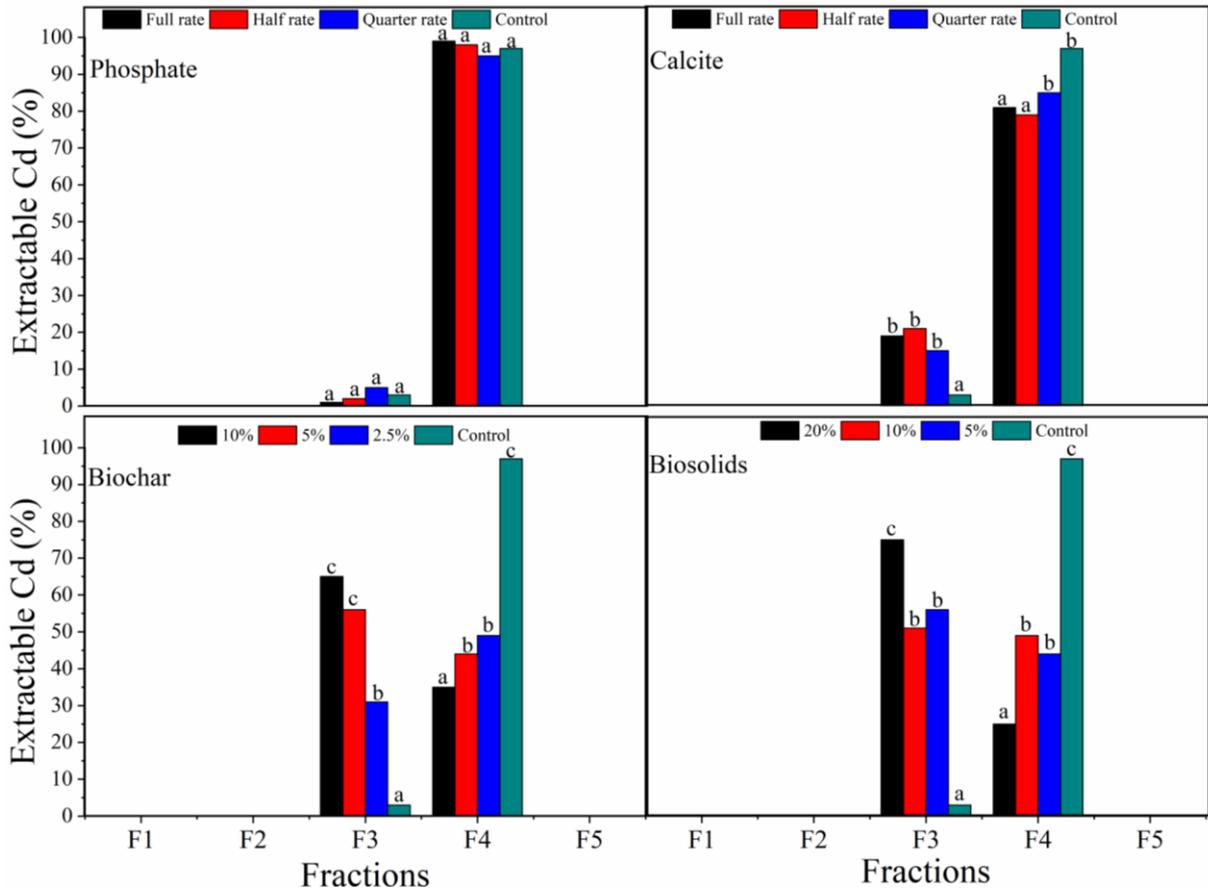


Figure 6. Relative distributions of Cd in the forest among the various soil fractions in different treatments and rates. F1= exchangeable, F2= carbonate-associated, F3 = organic-matter associated. F4 = oxide, and F5 = residual (most strongly bound). Columns followed by the same letter do not differ at 0.05 (Tukey test).

4.3.2.3 Biosolids

The treatment with biosolids was effective to immobilize Cd in both soils (Figure 3 and 4). However, the effectiveness was more evident in the forest soil than in the mine soil. In the first 30 min, the amount of Cd desorbed in the mine soil ranged from 10.8 to 9.4% while it was 11.5% in the unamended soil. After 120 min the amount desorbed was 16.1, 14.1, 15.3 and 15.2% for the 5%, 10%, 20%, and unamended soil, respectively. This showed that biosolids was effective to reduce the amount released in the initial times (30 min) but with a higher time of desorption (120 min) they were pretty similar to the unamended soil. On the other hand, the forest soil amended with rates of biosolids was effective to decrease Cd desorption in all time (0 to 120 min). The cumulative desorption after 120 min was 6.5, 7.6, 8.3 and 9.6% for the 5%, 10%, 20% and unamended soil, respectively.

The biosolids increased the amount of Cd extracted in the F3 (organic matter bound) for both soils (Figure 5 and 6). Nevertheless, in the forest soil, the Cd in the F3 increased 70% for the rate of 20% whereas this increase was only 10% in the mine soil. These results indicate that the biosolids increased the Cd bounded to organic compounds on the soil due to organic matter present in this amendment. The biosolids contains significant quantities of organic matter and nutrients such as nitrogen and phosphorus.⁶⁸⁻⁷⁰ Also, the organic matter from biosolids may increase the pH, cation exchange capacity and sorption sites might affect sorption of heavy metals in soils.⁷¹⁻⁷³

The forest soil had an increase in the pH due the biosolids application. This also may help to increase the immobilization of Cd. The biosolids also could increase the DOC on the soil and form Cd-DOC. These organic compounds may decrease, increase or have no effect on Cd sorption.⁶¹

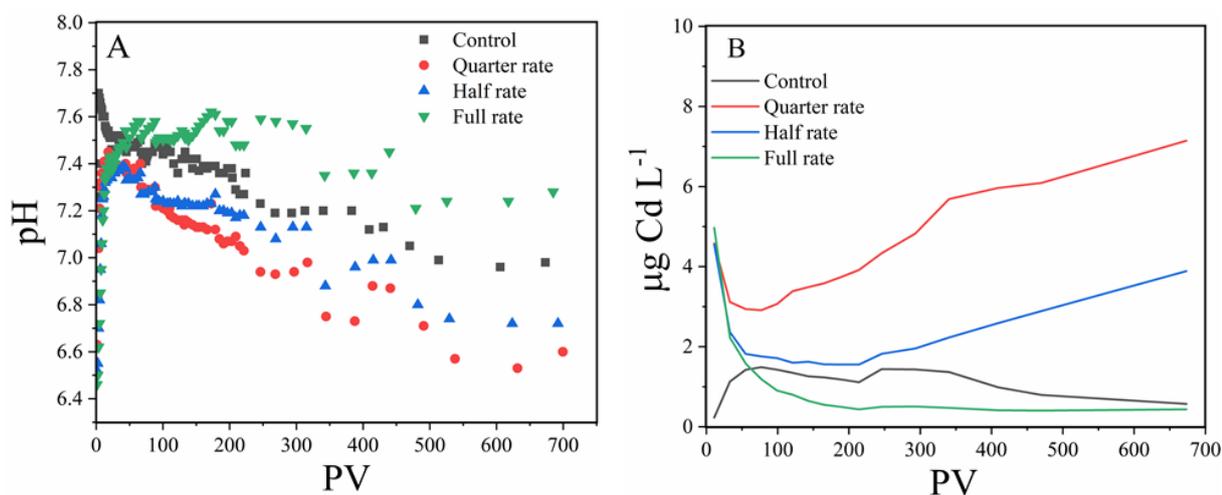


Figure 7. pH of the leachate (A) and the concentration of Cd on the leachate (B) for the rates of phosphate applied in the mine soil.

4.3.2.4 Biochar

The results of desorption kinetics and sequential extraction varied between the rates of biochar applied (Figure 3 to 6). As biosolids, the biochar was more effective to reduce the Cd release in the forest soil than mine soil. The cumulative desorption in the first 30 min for the mine soil was 10.3, 8.7, 11.0 and 11.5% for the rate of 2.5%, 5%, 10% and unamended soil, respectively (Figure 3). For the forest soil, the cumulative desorption was 6.1, 5.1, 3.9 and 5.9 for the rate of 2.5%, 5%, 10% and unamended soil, respectively (Figure 4). In the

mine soil the cumulative Cd desorbed after 120 min was 15.7, 15.4, 14.5 and 15.2 for the rate of 2.5%, 5%, 10% and unamended soil, respectively, while for the forest soil, the cumulative desorption was 10.1, 8.0, 7.2 and 9.6% for the rates of 2.5%, 5%, 10% and unamended soil, respectively.

In the forest, the rate of 5% and 10% had a smaller cumulative desorption after 120 and only the rate of 2.5% had a higher release in comparison with the unamended soil. But, for the mine soil, only the rate of 10% had a smaller cumulative desorption of Cd after 120 min. Puga et al.⁷⁴ evaluated the effect of rates of biochar in a soil from a Zn mining area in Vazante. They also utilized biochar produced from sugar cane straw but different temperature of pyrolysis (700 °C) and incubation time (120 days). The authors⁷⁴ observed a linear reduction of the available Cd in soil extracted by EDTA due to the rates (1.5, 3.0 and 5.0%, w/w) of biochar applied. The immobilization of Cd by the biochar application have previously been reported.^{23,75–77}

The treatment with biochar in both soils decreased the Cd in the F4 (iron oxides bound) and increased in the F3 (organic matter bound) (Figure 5 and 6). The biochar increased the amount of C in both soils, and that is in agreement with the results of the sequential extraction where the amount of Cd in the F3 (organic matter bound) increased. Curiously, Wang et al.⁵⁸ did not observe increase in the Cd extracted in the organic matter fraction in a soil amended with pine biochar, but found a decrease in the exchangeable fraction. However, in their soil, almost 60% of the Cd was extracted in the exchangeable fraction, while in our soils they were between 10 for the mine soil and 0% for the forest soil. This shows that the species of Cd present in their soil probably were different from ours. Another explanation for these differences is that they incubated the soil only for 5 days, whereas we used 60 days, and probably the biochar did not have enough time to react with the soil. The chemical characteristics of the soil and biochar also could have influenced these differences.

Feedstock type and pyrolysis condition are the main factors influencing the sorption behavior of biochars.⁷⁸ Biochar has a high carbon content,⁷⁹ stable physical and chemical properties and large specific surface area with good adsorption capacity for heavy metals and ions.⁵⁸ Biochar may have high sorption ability from three reasons: (i) electrostatic interactions negatively charged carbon surface and metal cations; (ii) ionic exchange between ionizable protons at the surface of acidic carbon and metal cations and (iii) sorptive interaction involving delocalized electrons of carbon.⁸⁰

4.4 Summary and Conclusions

Some amendments were effective to immobilize Cd in the soil from mining area and adjacent forest. In the mining soil amended with phosphate, the desorption kinetics of Cd decreased more in the initial times (30 min) and the half rate and quarter rate of phosphate were more effective to decrease the desorption after 120 min of cumulative desorption. For the forest soil, the half rate and quarter rate of phosphate also were most effective to decrease Cd desorption. The results of sequential did not show different between the Cd extracted in each fraction for the forest soil. On the other hand, in the soil from mining area, the Cd contents decreased in the carbonate forms and increased in the organic matter bound forms. This is an evidence that the treatment with phosphate may have increased the negative charge in the organic matter, thus favoring the Cd bound and decreasing its desorption. Cd also may have precipitated with stable phosphate species. The half rate and the quarter rate of phosphate leached more Cd in the mining soil than the unamended soil. The amount leached followed the pH of the leached solution, indicating that this attribute may control Cd desorption. The increase in Cd leached in the half rate and quarter rate could be attributed to the formation of Cd-P complexes in the solution.

Calcite was more effective to reduce the cumulative Cd desorption in the forest than in the mine soil. In the mining soil, this treatment decreased the cumulative Cd desorbed in the first 30 min and was almost equal to the unamended soil after 120 min. In the forest soil, all rates of calcite had less cumulative desorption of Cd than in the unamended soil after 120 min. In both soils, the Cd extracted in the F3 (organic matter bound) increased, and it shows that addition of calcite increased the pH and increased the negative charges site on the organic matter. The calcite also could increase the buffering capacity in the mining soil because this soil already was alkaline.

The organic amendments (biochar and biosolids) were effective to decrease the amount of Cd desorbed in the kinetics experiment. However, the decrease in the Cd desorption was more pronounced in the forest than in the mine soil. In the mine soil the rate of 2.5 and 5% of biochar decreased the cumulative desorption in the initial time (30 min). However, after 120 min, the desorption was almost equal to the unamended soil. The same behavior was observed for the rate of 5 and 10% of biosolids. On the other hand, in the forest soil, except for the rate of 2.5% of biochar, the rates of biochar and biosolids decreased the cumulative desorption of Cd than unamended soil. Both amendments increased the Cd

extracted in the F3 (organic matter bound), and these results indicate that Cd was probably adsorbed on the organic matter compounds provided by the biochar and biosolids.

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5 FINAL REMARKS

The soil amendments had different behaviors in the immobilization of Zn, Pb, and Cd in soils. In general, phosphate was effective to decrease Zn, Pb, and Cd desorption. The decrease in Pb desorption was probably due to the formation of pyromorphite that was identified by the bulk XANES. The full rate of P increased Zn desorption probably because of the decrease in the pH thus causing the formation of ZnO (identified by the μ -XANES and bulk XANES) that is more soluble than the other species identified, such as Zn-kerolite. After phosphate addition, most parts of Zn species was changed to Zn-P. On the other hand, the quarter rate and the half rate were effective to decrease Zn desorption, suggesting either the formation of more stable species such as Zn-P or the adsorption to the soil constituents. Phosphate also was more effective to decrease Cd desorption in the half rate and quarter rate, thus suggesting the formation of Cd-P species, or due to an increase in the negative charge in the surface of mineral or organic compounds.

Calcite was effective to increase Zn, Pb, and Cd immobilization in the soil. Even though we did not observe differences in Zn species by the bulk XANES, the results of desorption kinetics showed that calcite decreased Zn desorption in all rates applied, but the quarter rate and half rate were most effective. The LCF of the Pb in the soil amended with calcite showed that some species (Pb-bentonite and anglesite) were changed to pyromorphite. All rates of calcite desorbed almost the same amount of Pb. Calcite decreased the Cd desorption kinetics in the initial times in the mining soil, and the full rate was the most effective, while all rates desorbed almost the same amount of Cd in the forest soil. The sequential extraction suggested that part of Cd was immobilized on the organic matter as a result of the calcite treatment.

Biochar was effective to decrease Zn desorption and was more effective in the rate of 5%. No differences were observed in the Zn bulk XANES spectra but, in the sequential extraction experiment, Zn increased in the F3 (organic matter- OM associated) and F4 (iron oxides associated) fractions, which suggests that these two fractions could have immobilized the element. Biochar increased the desorption kinetics of Pb in all rates utilized. Part of Pb species was modified to Pb-citrate, and this species could have caused the increase of Pb mobility. The results of sequential extraction showed an increase in the Pb extracted in the OM fraction, which is evidence that Pb could have associated with organic compounds. Different from Pb, the desorption kinetics of Cd decreased due to biochar applications, and

the results of sequential extraction suggested that Cd could have been immobilized on the organic matter.

Biosolids also decreased Zn desorption and was most effective in the rate of 10%. As occurred with biochar, no differences were found in the bulk XANES spectra of this treatment, but the sequential extraction showed an increase in the Zn associated to OM (F3). Biosolids increased Pb desorption in all rates. By LCF we identified Pb-citrate and PbCl_2 that could have been responsible for increasing Pb mobility. Biosolids also decreased the desorption kinetics of Cd for the mining and forest soil, and caused an increase in the Cd extracted in the OM fraction, thus suggesting that Cd was immobilized by organic compounds, as occurred with biochar.

The combination of synchrotron-based techniques, desorption kinetics and sequential extraction are powerful tools to evaluate the behavior of heavy metals in contaminated soils after the addition of amendments. Our results will may help to develop an/or improve modern and effective strategies to remediate mine waste contaminated soils. The heavy metals had different behaviors as affected by the addition of amendments. An interesting result is that the half rate and quarter rate were more effective to decrease the mobility of heavy metals than the full rate in some treatments, and this information is important to create some more cost-effective and sustainable solutions.

Future researches may focus on the effect of the mixing effect of different amendments. Soils contaminated with multiple elements such ours may need to be remediated with different amendments because one amendment could immobilize one element and mobilize another one. The effect of incubation time and other sources of amendments should also be detailed in future researches.