REVIEW

Phosphates for Pb immobilization in soils: a review

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Abstract In its soluble ionic forms, lead (Pb) is a toxic element occurring in waters and soils mainly as the result of human activities. The bioavailability of lead ions can be decreased by complexation with various materials in order to decrease their toxicity. Pb chemical immobilization using phosphate addition is a widely accepted technique to immobilize Pb from aqueous solution and contaminated soils. The application of different P amendments cause Pb in soils to shift from forms with high availability to the most strongly bound Pb fractions. The increase of Pb in the residual or insoluble fraction results from formation of pyromorphite $Pb_5(PO_4)_3X$ where X = F, Cl, Br, OH, the most stable environmental Pb compounds under a wide range of pH and Eh natural conditions. Accidental pyromorphite ingestion does not yield bioavailable lead, because pyromorphite is insoluble in the intestinal tract. Numerous natural and synthetic phosphates materials have been used to immobilize Pb: apatite and hydroxyapatite, biological apatite, rock phosphate, soluble phosphate fertilizers such as monoammonium phosphate, diammonium phosphate, phosphoric acid, biosolids rich in P, phosphatic clay and mixtures. The identification of pyromorphite in phosphate amended soils has been carried out by different non destructive techniques such as X-ray diffraction, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy, X-ray absorption fine structure, transmission electron microscopy and electron microprobe analysis. The effectiveness of in situ Pb immobilization has also been evaluated by selective sequential extraction, by the toxicity leaching procedure and by a physiologically based extraction procedure simulating metal ingestion and gastrointestinal bioavailability to humans. Efficient Pb immobilization using P amendments requires increasing the solubility of the phosphate phase and of the Pb species phase by inducing acid conditions. Although phosphorus addition seems to be highly effective, excess P in soil and its potential effect on eutrophication of surface water, and the possibility of As enhanced leaching remains a concern. The use of mixed treatments may be a useful strategy to improve their effectiveness in reducing lead phyto- and bioavailability.

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Introduction

Lead reaches the soil environment through pedogenic, related to the origin and nature of the parent material, and anthropogenic processes. Anthropogenic activities, primarily associated with industrial processes, manufacturing and the disposal of domestic and industrial waste materials, are the major source of lead contamination of soils (Adriano 2001). It is not possible to consider the presence of lead and its compounds in the environment and its potential toxicity to the ecosystem and to the human population without considering its chemical speciation and mineral form. Knowing lead speciation is vital, not only to predict its mobility and bioavailability, but also in the assessment

of risk to living organisms because insoluble forms of lead cannot easily be absorbed by biota.

A critical variable in the risk from soil Pb is the bio-availability of the Pb. The form of Pb in soil directly influences its bioavailability as do soil properties. For humans, most concern stems from ingested Pb. This commonly occurs when Pb-containing soil particles are consumed. The Pb must be released as Pb^{2+} in the digestive fluids before it can be absorbed into the body. A review on in vivo studies dealing with Pb ingestion can be seen in Hettiarachchi and Pierzynski (2004).

Lead can be carried in water, either dissolved or as waterborne particles. However, few compounds of lead dissolve readily in water, though most of this lead is then precipitated as a solid and becomes incorporated in the sediments at the base of the watercourse or ocean. In most cases lead in soil is relatively insoluble and has a low mobility. Thus, soils contaminated with lead retain high lead contents for many hundreds, even thousands, of years. The half life of lead in soil has been estimated as 740–5,900 years (Alloway and Ayres 1997). Lead compounds are more mobile under acidic conditions, which can occur in mine wastes or from landfill leachate.

The presence of Pb in soils is affected by three principal processes: (1) precipitation as a slightly soluble mineral phase (2) adsorption on the clay fraction, the Fe and Mn oxides, the alkaline earth carbonates and silicate lattices and (3) formation of relatively stable complexes by inter-action with soil organic matter (Davis 1995; Bradl 2004). The mobility of lead depends upon many factors: Pb spe-ciation and total Pb soil content, the type of soil, soil pH, moisture content of the soil and water infiltration from rainfall or other drainage. In soils, Pb shows very low aqueous phase concentrations (1 to <0.01% of total Pb) being Pb^{2+} the principal dissolved specie (Sauvé et al. 2000).

Solubility is generally used in reference to the stability of a given Pb mineral, nevertheless, solubility is a ther-modynamic parameter, only defined when the system reaches equilibrium. Mechanisms of retention and release of soil contaminants are in most cases not instantaneous equilibria but rather time-dependant processes. In a dynamic system as soil, the mineral dissolution kinetics must be considered. Slow rates of Pb dissolution from different minerals results in a decreased Pb bioavailability and a minor risk of soil Pb movement into groundwater (Laperche et al. 1996). Thus, in addition to solubility, the dissolution rate must be taken into account in order to evaluate the stability of a Pb compound. Pb phosphates have low solubility, they are several orders of magnitude less soluble than the analogous carbonates and sulphates (Nriagu 1984).

Remediation of contaminated soils and disposal of metal contaminated soils is very expensive and arduous task. As an alternative, in situ chemical immobilization is less expensive than excavation and land filling and provides a long-term remediation solution through the formation of stable metal minerals and/or precipitates (Vangronsveld and Cunningham 1998). The decrease in metal solubility and therefore in mobility reduces the risk of heavy metal transport from contaminated soils to groundwater and surface waters. According to the USEPA, remediation action is considered when the total soil Pb content exceeds 400 mg kg^{-1} (USEPA 1996).

Lead chemical immobilization using phosphate addition is a widely accepted technique to immobilize Pb from aqueous solution and in contaminated soils (Ma et al. 1993, 1994a, b, 1995; Ryan et al. 2001), to reduce Pb plant uptake (Cotter-Howells and Caporn 1996; Laperche et al. 1997; Hettiarachchi et al. 2000), to mitigate acid mine drainage (Melamed et al. 2003) and to minimize leachable Pb in industrial wastes (Eighmy et al. 1997, 1998; Crannell et al. 2000). Phosphate treatment has been proposed as a Best Management Practice for firing ranges where P occurs in its metallic forms and several other phases (carbonates, oxides) (Chrysochoou et al. 2007).

There are several possible Pb-phosphate minerals that can be formed in P-amended soils (Lindsay 1979; Traina and Laperche 1999; Essington et al. 2004; Porter et al. 2004). In acidic soils Pb phosphates predominate over Pb oxides and carbonates, which form in alkaline soils (Lindsay 1979; Davis 1995). Numerous studies demon-strated that the members of the pyromorphite family $Pb_5(PO_4)_3X$ where X = F, Cl, Br, OH are the most stable environmental Pb compounds under a wide range of pH and Eh natural conditions. The presence of As in many contaminated soils must be taken in consideration, as competition between phosphate and arsenate for adsorption sites may cause As mobilization (Peryea and Kammereck 1997; Boisson et al. 1999).

Different P sources with different solubilities may impact the effectiveness of Pb immobilization. Numerous natural and synthetic phosphates materials have been used, apatite and hydroxyapatite, rock phosphate, soluble phos-phate fertilizers such as monoammonium phosphate (MAP), diammonium phosphate (DAP), phosphoric acid, etc (Ma et al. 1993, 1995; Ruby et al. 1994; Cotter-Howells and Caporn 1996; Basta et al. 2001; McGowen et al. 2001; Ryan et al. 2001; Yang et al. 2001; Mavropoulos et al. 2002; Cao et al. 2004; Hettiarachchi and Pierzynski 2004). We provide a review of the literature concerning the Pb immobilization in soil by phosphate natural and synthetic materials with focus on the role of complexation and chemical speciation in the geochemical process.

Pb geochemistry in P amended soils

Application of different P amendments caused Pb in soils to shift from forms with high availability: exchangeable, carbonate, Fe–Mn oxide, organic matter bound, to the most strongly bound Pb fractions: sulphide or residual (Berti and Cunningham 1997; Ma and Rao 1999; Ryan et al. 2001; Cao et al. 2002, 2003; Chen et al. 2003; Knox et al. 2003; Melamed et al. 2003; Tang et al. 2004; Chen et al. 2007). The increase of Pb in the residual fraction results from formation of pyromorphite.

Cao et al. (2002) and Melamed et al. (2003) reported a decrease in the carbonate-bound Pb soil fraction up to 40%, and 10% of the Fe–Mn oxide bound fraction while the residual fraction increased up to 60%. The more effective treatments should convert greater amount of Pb from the non residual to the residual fraction. It has been reported that some of the Pb transformation from the non residual to residual forms occurred during the extraction process (Ryan et al. 2001; Scheckel et al. 2003), however the fact that residual Pb soil fraction increases with time strongly demonstrated that conversion of soil Pb to more stable forms actually occurs in the field (Cao et al. 2002; Scheckel and Ryan 2002). This redistribution of Pb resulted in less phytotoxiciy as indicated by greater plant growth and lower metal concentration in plant tissue (Laperche et al. 1997; Boisson et al. 1999; Zhu et al. 2004; Chen et al. 2007; Deydier et al. 2007).

The interaction of Pb and P through the formation of pyromorphite is an important buffer mechanism controlling the migration and fixation of Pb in water, soils and wastes, reducing Pb solubility as well as bioavailability (Bolan et al. 2003). Phosphorus amendment could be an effective means of immobilizing lead in drinking or sewage, since accidental pyromorphite ingestion does not yield bio-available lead (Arnich et al. 2003). Pyromorphite is highly stable even in low pH and will not dissolve appreciably in the human digestive system (Cheng and Hseu 2002).

The solubility products of pyromorphites are extremely low, $10^{-71.6}$, $10^{-76.8}$, $10^{-78.1}$ and $10^{-84.4}$ for fluoro, hydroxyl, bromo and chloro pryromorphites respectively (Chen et al. 1997b). Chloropyromorphyte is several orders of magnitude less soluble than hydroxyl, bromo and fluoro pyromorphytes, and due to the ubiquity of chloride in nature, chloropyromorphite is the dominant form of pyromorphites (Ryan et al. 2001). The chemical and physical attributes of chloropyromorphite (low entropy state with aging) suggested that its persistence would endure most environmental conditions, thus making Pb immobilization via phosphorus and ideal remediation mechanism (Scheckel and Ryan 2002).

Because pyromorphites are the most stable Pb phosphate minerals under natural environmental conditions, thermodynamics predict that other solid phase would be converted to pyromorphite by a dissolution-precipitation process. Experimental evidence shows that various Pb compounds as cerrusite, anglesite, galena and also lead in contaminated soil are partly transformed to chloropyromorphite after reaction with hydroxyapatite, being the rate limiting step, the dissolution/oxidation of Pb in the bearing solid. (Laperche et al. 1996; Zhang et al. 1998; Zhang and Ryan 1999a, b; Ryan et al. 2001; Yang and Mosby 2006). Nevertheless, efficient Pb immobilization using P amendments requires enhanced solubility of metals by inducing acid conditions (Cao et al. 2003).

As mentioned before, thermodynamic considerations show that of the several lead phosphate minerals and salts chloropyromorphite is the most stable in soils environments. To convert all other forms of lead in this mineral, it is necessary to change all the calcium in the soil into hydroxyapatite $[Ca_{10} (PO_4)_6 (OH)_2]$. Since calcium is always 10–20 times more abundant than phosphate in soils, very large amounts of phosphate need to be added to increase the amount of phosphorus in the soil up to 400 μmol g^{-1} (PO$_4$/Ca ratio = 3/5) (Porter et al. 2004). This large input of P (>4% relative to soil Pb concentration) could be a concern for nearby water environments and also could alter the soil structure, as virtually all the calcium in soil will be precipitated as apatite, decreasing the soil friability (Scheckel and Ryan 2004).

The identification of pyromorphite in phosphate amended soils has been carried out by different non destructive techniques (Table 1) such as X-ray diffraction (XRD) (Ma et al. 1993, 1994a, b; Zhang and Ryan 1999b; Mavropoulos et al. 2002), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) (Laperche et al. 1997; Chen et al. 1997b; Zhang and Ryan 1999a; Ryan et al. 2001; Arnich et al. 2003), X-ray absorption fine structure (XAFS) (Cotter-Howells et al. 1994; Ryan et al. 2001), transmission electron microscopy (TEM) (Zhang et al. 1998; Zhang and Ryan 1999a; Mavropoulos et al. 2004; Srinivasan et al. 2006) and electron microprobe analysis (EMPA) (Yang et al. 2001).

The effectiveness of in situ Pb immobilization has also been evaluated by selective sequential extraction (SSE) (Berti and Cunningham 1997; Ryan et al. 2001; Chen et al. 2007), by the toxicity leaching procedure were leaching concentration is compared against the USEPA limit of 5 mg L^{-1} (Hettiarachchi et al. 2000; Cao et al. 2001; Wilson et al. 2006) and also by a physiologically based extraction procedure simulating metal ingestion and gastrointestinal bioavailability to humans (PBET) (Ruby et al. 1996; Basta et al. 2001). Scheckel et al. (2003) reported

Table 1 Selected references on Pb immobilization by different P sources

Amendment material	Pb	Mineral characterization	Reference
Hydroxyapatite			
Synthetic hydroxyapatite and CaHPO4	Aqueous Pb	XRD	Ma et al. (1993)
Synthetic hydroxyapatite	$PbCl_2$; PbF_2, $Pb(NO_3)_2$	XRD, SEM	Ma et al. (1994a)
Synthetic hydroxyapatite	$Pb(NO_3)_2$	XRD, SEM	Ma et al. (1994b)
Synthetic hydroxyapatite	$Pb(NO_3)_3$	XRD, SEM	Xu and Schwartz (1994)
Synthetic hydroxyapatite	PbO, $PbCO_3$ and soil Pb	XRD, SEM	Laperche et al. (1996)
Synthetic hydroxyapatite	Soil Pb	XRD; TEM	Zhang et al. (1998)
Synthetic hydroxyapatite	Aqueous Pb	AFM	Lower et al. (1998)
Synthetic hydroxyapatite	Soil Pb	Chemical extraction	Boisson et al. (1999)
Synthetic hydroxyapatite	Galena	XRD, SEM/EDX, TEM	Zhang and Ryan (1999a)
Synthetic hydroxyapatite	Cerrusite	XRD	Zhang and Ryan (1999b)
Synthetic hydroxyapatite	Soil Pb	SEM-EDX, TEM,TCLP	Seaman et al. (2001)
Synthetic hydroxyapatite	Soil Pb	XRD, SEM/EDX, XAFS SSE	Ryan et al. (2001)
Synthetic hydroxyapatite	$Pb (NO_3)_2 \cdot 4H_2O$	XRD	Mavropoulus et al. (2002)
Synthetic hydroxyapatite	$PbCl_2$	SEM, EDX, in vivo	Arnich et al. (2003)
Synthetic hydroxyapatite	Aqueous $Pb(NO_3)_2 \cdot 4H_2O$	XRD, SEM, TEM	Mavropoulos et al. (2004)
Synthetic hydroxyapatite (3DOM)	Aqueous $Pb(NO_3)_2 \cdot 4H_2O$	XRD, SEM-EDX, TEM	Srinivasan et al. (2006)
Natural and synthetic apatite	Soil Pb	SEM-EDX, XRD	Laperche et al. (1997)
Natural apatite	$Pb(NO_3)_2$	XRD, SEM	Chen et al. (1997a)
Natural apatite	$Pb(NO_3)_2$ and soil Pb	XRD, SEM-EDX, TCLP	Chen et al. (1997b)
Natural apatite	Soil Pb	XRD- EDX	Knox et al. (2003)
Natural and biological apatite	Soil Pb	TCLP	Wilson et al. (2006)
Soluble phosphate			
Na_2HPO_4	Soil Pb	XRD, TEM, XAFS	Cotter-Howells et al. (1994)
Na_2HPO_4	Soil Pb	XRD, SEM-EDX	Cotter-Howells and Caporn (1996)
KH_2PO_4	Soil Pb	SSE, PBET	Berti and Cunningham (1997)
K_2HPO_4 (soil P-goethite)	Aqueous $Pb(NO_3)_2 \cdot 4H_2O$	SEM-EDX, XRD	Manecki et al. (2000)
H_3PO_4	Soil Pb	SEM-EDX; PBET, EPMA	Yang et al. (2001)
DAP	Soil Pb		McGowen et al. (2001)
H_3PO_4	Aqueous $PbCl_2$	XRD, XAFS; HRGTA	Scheckel and Ryan (2002)
$Ca_3(PO_4)_2$, $CaH(PO_4)$, $Ca(H_2PO_4)_2$	Aqueous $Pb(NO_3)_2 \cdot 4H_2O$	XRD-SEM , EPMA	Sugiyama et al. (2003)
H_3PO_4; STP	Soil Pb	LCF-XAFS	Scheckel and Ryan (2004)
H_3PO_4; STP	Soil Pb	LCF-XAFS, SSE, PBET	Scheckel et al. (2005)
H_3PO_4	Soil Pb	SEM-EDX	Yang and Mosby (2006)
H_3PO_4	Wetland soil Pb	XRD-EDX, EPMA	Strawn et al. (2007)
Phosphate rock			
PR	Aqueous Pb and soil Pb	XRD; SEM	Ma et al. (1995)
PR	Soil Pb	XRD	Ma and Rao (1999)
PR	Soil Pb	SSE, TCLP; PBET	Basta et al. (2001)
PR	Aqueous $Pb(NO_3)_2 \cdot 4H_2O$	TCLP; XRD, SEM	Cao et al. (2004)
PR	Soil Pb	SSE	Lin et al. (2005)
PR	Soil Pb	SSE, XRD, SEM-EDX	Garrido et al. (2006)
PR	Soil Pb	SSE	Chen et al. (2006)
PR	Aqueous Pb	XRD	Mouflih et al. (2006)
PR + H_3PO_4	Soil Pb	TCLP; PBET	Yoon et al. (2007)
Other phosphorous materials			
Bone meal	Soil Pb	XRD, SEM	Hodson et al. (2001)
Bone meal	Soil Pb	XRD	Sneddon et al. (2006)

Table 1 continued

Amendment material	Pb	Mineral characterization	Reference
Bone meal	Soil Pb and aqueous Pb	XRD	Deydier et al. (2007)
Fishbone	Soil Pb		Admassu and Breese (2007)
Peat	Soil Pb	TEM, XAFS, SEM-EDX	Cotter-Howells et al. (1999)
Biosolids	Soil Pb	In vivo, in vitro tests	Brown et al. (2003)
High P biosolid compost	Soil Pb	Extraction tests	Farfel et al. (2005)
Phosphatic clay	Aqueous Pb	XRD, SEM, TCLP	Singh et al. (2001)
Iron phosphate nano particles	Soil Pb	TCLP; PBET; SSE	Liu and Zhao (2007)
Mixed phosphates			
TSP and H_3PO_4 and RP	Soil Pb	XRD, PBET	Hettiarachchi et al. (2001)
H_3PO_4; H_3PO_4 + $Ca(H_2PO_4)_2$ and H_3PO_4 + PR	Soil Pb	XRD-SEM; SSE	Cao et al. (2002)
H_3PO_4; H_3PO_4 + $Ca(H_2PO_4)_2$ and H_3PO_4 + PR	Soil Pb	SEM-EDX, XRD SSE	Cao et al. (2003)
H_3PO_4; H_3PO_4 + $Ca(H_2PO_4)_2$ and H_3PO_4 + PR	Soil Pb	XRD, SEM-EDX, TCLP	Melamed et al. (2003)
H_3PO_4; H_3PO_4 + $Ca(H_2PO_4)_2$ and H_3PO_4 + PR	Soil Pb	XRD, TCLP	Chen et al. (2003)
HA, PR, SSP, HA + SSP	Soil Pb	SSE	Zhu et al. (2004)
HA, PR, SSP, HA + SSP	Soil Pb	SSE	Tang et al. (2004)
TSP, PR, H_3PO_4, compost + TSP	Soil Pb	PBET	Brown et al. (2004)
TSP, PR, H_3PO_4	Soil Pb	PBET	Brown et al. (2005)
Natural HA, PR, TSP, DAP	Soil Pb	XRD, SEM-EDX, SSE	Chen et al. (2007)

that during the extraction steps of SSE and because the kinetics of pyromorphite precipitation are fast, the solubilized P from the amended soils reacted with Pb released by the extractant to form pyromorphite-type minerals in a secondary precipitation. Thus, the resulting residual fraction Pb values were greater than those from spectroscopic studies. Scheckel et al. (2005) discussed the limitations of these methods and concluded that appropriate application of advanced, molecular level spectroscopic methods provides more conclusive and accurate results than the use of sequential extraction analysis.

Different sources of P for Pb immobilization in soils

Amendments with apatite

Apatite $Ca_{10}(PO_4)_6(OH, F, Cl)_2$ is a promising candidate for heavy metal stabilization as its crystal structure is tolerant to many ionic substitutions and complete replacement of Ca^{2+} by Ba^{2+}, Sr^{2+}, Cd^{2+} and Pb^{2+} and P^{5+} by V^{5+}, Cr^{5+} and As^{5+} (Srinivasan et al. 2006).

Most of the studies on Pb immobilization by apatite (Table 1) were carried out with Pb^{2+} aqueous solutions or Pb from contaminated soils and solid apatite (Ma et al. 1993, 1994a, b; Xu and Schwartz 1994; Laperche et al. 1996, 1997; Chen et al. 1997a, b; Zhang and Ryan 1999a, b; Zhang et al. 1998; Ryan et al. 2001; Seaman et al. 2001; Mavropoulos et al. 2002, 2004; Knox et al.
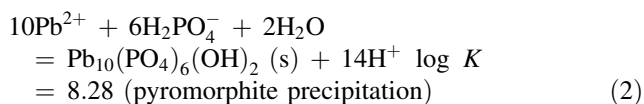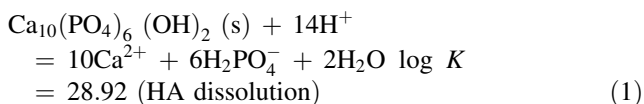
2003; Srinivasan et al. 2006) etc, although previously dissolved hydroxyapatite Ca_{10} $(PO_4)_6$ $(OH)_2$ also was used (Manecki et al. 2000; Arnich et al. 2003). Synthetic hydroxyapatite was used by Ma et al. (1993, 1994a, b); Xu et al. (1994); Laperche et al. (1996); Boisson et al. (1999); Mavropoulos et al. (2002, 2004) and natural apatite by Chen et al. (1997a, b); Laperche et al. (1997); Knox et al. (2003).

Application of hydroxyapatite to aqueous Pb or Pb contaminated soils at a P/Pb molar ratio 3/5 (the same molar ratio than in chloropyromorphite) has been suggested (Ma et al. 1993; Laperche et al. 1996), but higher ratios had been used for soluble P (Zhang et al. 1998; Basta et al. 2001; Hettiarachchi et al. 2001). When hydroxyapatite is added to soil mainly as a source of P, also has a liming value in addition to supplying Ca. The liming action of apatite is due to the presence of free $CaCO_3$ as an impurity and to the fact that consumes H^+ in the dissolution process reducing soil acidity (Knox et al. 2003).

Two main different mechanisms have been proposed for the immobilization of lead by hydroxyapatite:

(1) The first mechanism involves hydroxyapatite dissolution, followed by phosphate reaction with dissolved Pb and precipitation of pure hydroxypyromorphite (Ma et al. 1993; Xu and Schwartz 1994; Chen et al. 1997a, b; Zhang and Ryan 1999a, b; Zhang et al. 1998; Lower et al. 1998).

The chemical equations involved are:

$$Ca_{10}(PO_4)_6 (OH)_2 (s) + 14H^+$$
$$= 10Ca^{2+} + 6H_2PO_4^- + 2H_2O \quad \log K$$
$$= 28.92 \text{ (HA dissolution)} \tag{1}$$

$$10Pb^{2+} + 6H_2PO_4^- + 2H_2O$$
$$= Pb_{10}(PO_4)_6(OH)_2 (s) + 14H^+ \quad \log K$$
$$= 8.28 \text{ (pyromorphite precipitation)} \tag{2}$$

Several authors have reported that the overall reaction is fast, hydroxyapatite reduced initial aqueous Pb concentration from 100 mg L^{-1} to <1 μg L^{-1} in less than 10 min (Ma et al. 1993; Xu and Schwartz 1994). As reaction rate is controlled by hydroxyapatite dissolution and availability of soluble P, lowering soil pH was found to significantly enhance dissolution of soil Pb and favour the reaction towards pyromorphite formation (Laperche et al. 1996; Zhang et al. 1998). Although from a thermodynamic approach, pyromorphite has the potential to control Pb solubility, pyromorphite formation is kinetically controlled by pH, the solubility of the phosphate source and the solubility of the Pb species (Chrysochoou et al. 2007).

The composition of the solution influences the interaction of dissolved Pb with apatites. Ma et al. (1994a) reported that hydroxyapatite was transformed in hydroxypyromorphite in the presence of NO_3^-, Cl^-, F^-, SO_4^{2-} and CO_3^{2-}. The presence of other metal ions also influences the reaction of dissolved Pb with hydroxyapatite, especially when the ratio metal/Pb > 7 (M = Zn, Cd, Ni, Cu, Fe (II), Al) (Ma et al. 1994b).

Microscopic and spectroscopic studies showed that pyromorphite can precipitate either homogeneously from solution or heterogeneously on the surface of apatites which serve as a substrate for nucleation and as source of phosphate ions (Manecki et al. 2000). Evidence of homogeneous nucleation in the precipitation of hydroxypyromorphite was shown by Lower et al. (1998) using atomic in situ and ex situ force microscopy (AFM) technique. Diffusion of phosphate away from dissolving hydroxyapatite was the rate-limiting step.

The evidences for this hydroxyapatite dissolution/pyromorphite precipitation mechanism were based on XRD and on SEM studies performed on the solid phase (Table 1). Also analysis of solution pH and Ca^{2+} and $PO4^{3-}$ concentrations during Pb^{2+} immobilization was performed.

(2)   The second mechanism involves ion exchange between Pb^{2+} in solution and Ca^{2+} on hydroxyapatite lattice (Suzuki et al. 1981; Takeuchi and Arai 1990; Shashkova et al. 1999).

The chemical equation involved is:

$$Ca_{10} (PO_4)_6 (OH)_2 (s) + xPb^{2+}$$
$$= Ca_{(10-x)} Pb_x (PO_4)_6 (OH)_2 (s) + xCa^{2+} \tag{3}$$
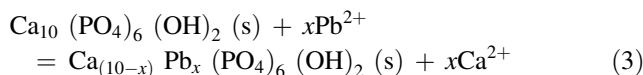
This mechanism could lead to the formation of mixed apatites by adsorption of Pb or by dissolution of hydroxyapatite followed by coprecipitation (Laperche and Traina 1998). However, these researchers showed using spectroscopic techniques and synthetic hydroxyapatite, that even at low Pb^{2+} concentration, the reaction product was pyromorphite and not (Pb–Ca) apatite. The principal mechanism involved was dissolution of apatite followed by precipitation of pyromorphite rather than adsorption of Pb in apatite particles.

Arnich et al. (2003) reported that the mechanism involved in the immobilization of lead as pyromorphite, identified by XRD, was ion exchange between Ca^{2+} ions in hydroxyapatite lattice and Pb^{2+} ions in solution.

Mavropoulos et al. (2002) demonstrated that reaction of Pb with hydroxyapatite was controlled by hydroxyapatite dissolution and the formation of a new lead and calcium solid solution, $Pb_{(10-x)} Ca_x (PO_4)_6 (OH)_2$ (PbCaHA) which transforms in hydroxypyromorphite with time, with Pb^{2+} ions occupying Ca^{2+} sites. The existence of PbCaHA as an intermediate phase was confirmed by XRD and the use of electron microscopy analysis (TEM) (Mavropoulos et al. 2004).

The capability of three dimensionally ordered macroporous hydroxyapatite (3DOM) to immobilize Pb was studied by Srinivasan et al. (2006). The macroporous product consisted primarily of hydroxyapatite (>80%) together with amorphous calcium phosphate. By using XRD and SEM, these researchers showed that Pb adsorption resulted in total destruction of the macroporous structure of hydroxyapatite and the accumulation of pyromorphite (30%) and lead carbonate (9%) among the disrupted network. As the hydroxyapatite content (61%) was high after exposure to Pb solution, the authors suggested that the amorphous apatite dissolved preferentially to release phosphate ions that rapidly precipitate pyromorphite, promoting further dissolution of the phosphate. The direct ion exchange process on the surface of hydroxyapatite was a slower process overwhelmed by the reactions mentioned before.

The theoretical studies on Pb immobilization by hydroxyapatite showed that two mechanisms, pyromorphite precipitation and Pb adsorption on hydroxyapatite lattice could be contributing mechanisms. The influence of each of them is strongly dependent on pH and pore solution chemistry (Chrysochoou et al. 2007).

Amendments with water-soluble phosphates

The dissolution-precipitation mechanism mentioned in the section before suggest that phosphates and hydrogen phosphates that can dissolve more easily than hydroxyapatite may be employed as Pb amendments (Table 2). Soluble phosphate sources could provide and abundance of solution P and increase the efficiency of metal-phosphate mineral formation (McGowen et al. 2001). Water soluble phosphates include potassium mono and dihydrogen phosphate (KH_2PO_4, K_2HPO_4); calcium monohydrogen ($CaHPO_4$) and calcium dihydrogen phosphate $Ca(H_2PO_4)_2$; phosphoric acid (H_3PO_4) and the phosphates used as fast-release fertilizers: single super phosphate (SSP), and triple superphosphate (TSP), MAP ($NH_4H_2PO_4$) and DAP [$(NH_4)_2HPO_4$], being calcium mono hydrogen phosphate ($CaHPO_4$) the principal component of super phosphates (Bolan et al. 2003). DAP is a major source of P fertilizer and represents approximately 70% of the total USA production (McGowen et al. 2001). The use of sodium phosphate is not recommended as it causes later problems in soils.

Application of hydroxyapatite or PR to calcareous soils could restrict the precipitation of Pb as pyromorphite or pyromorphite-like minerals because dissolution of the hydroxyapatite or PR is limited. Application of H_3PO_4 that would lower soil pH and provide highly soluble P constitutes an effective remedial treatment in calcareous Pb contaminated smelter soils by formation of pyromorphite (Yang et al. 2001).

$$5Pb^{2+} + 3H_2PO_4^- + Cl^- = Pb_5(PO_4)_3Cl_{(s)} + 6H^+$$
$$\log K = -25.5 \tag{4}$$
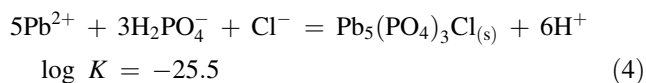
Neutralization of protons generated during pyromorphite precipitation showed in Eq. 4 favours the reaction towards the pyromorphite formation, thus initially acidifying soil followed by gradually increasing soil pH would enhance the transformation of Pb.

Statistical analysis by linear combination fitting applied to XAFS spectroscopic data were utilized by Scheckel and Ryan (2004) to obtain in situ evidence of principal Pb species in amended soils with H_3PO_4. They found that addition of H_3PO_4 promoted pyromorphite formation and that the rate of formation increased with increasing P concentration (up to 45%). Similar results were found by the above investigators using TSP enriched with Fe.

Yang and Mosby (2006) tested different methods of application of H_3PO_4 in Pb contaminated soils and reported that rototilling was the most effective in terms of the soluble P homogeneity and the reduction of Pb bioaccessibility in the treated soil zone. Strawn et al. (2007) also studied H_3PO_4 amendments on Pb contaminated soils by means of XRD and EMPA techniques and concluded that that after addition of P, distinct mineralogical changes occurred in soils, such as oxidation of siderite. In the original soil Pb was associated with poorly crystalline Fe and Mn oxides and the P added resulted primarily associated with Fe oxide phases. They also observed that soil pore waters were undersaturated with respect to chloropyromorphite and plumbogummite $PbAl_3(PO_4)_2(OH)_5$ H_2O, in contrast with control soil, indicating that P added diminished Pb solubility.

Phosphoric acid was regarded as the most effective amendment (USEPA 2001) because of its easy delivery and superior ability to dissolve Pb^{2+} form existing minerals and transform it in pyromorphites. The amendment dosage proposed by USEPA (2001) is 3% PO_4 by weight for soils.

Other different sources of soluble P in Pb immobilization in contaminated soils had been tested (Cao et al. 2002, 2003; Melamed et al. 2003; Sugiyama et al. 2003; Schwab

Table 2 Solubility of phosphate and Pb phosphate compounds

Mineral	Formula	Log Kps	Solubility (g per 100 g)	Reference
Fluoroapatite	$Ca_{10}(PO_4)_6F_2$	−55.9	Insoluble	Bolan et al. (2003)
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	−110.2	Insoluble	Bolan et al. (2004)
Carbonate apatite	$Ca_{10}(PO_4)_6(CO_3)_2$	−108.3	Insoluble	Bolan et al. (2005)
Tricalcium phosphate	$Ca_3(PO_4)_2$	−24	0.02	Bolan et al. (2006)
Calcium monohydrogen phosphate	$CaHPO_4.2H_2O$	−6.6	0.14	Bolan et al. (2007)
Calcium dihydrogen phosphate	$Ca(H_2PO_4)_2\ H_2O$	−1.14	18	Bolan et al. (2008)
Vivianite	$Fe_3(PO_4)_2.8\ H_2O$	−36		Liu and Zhao (2007)
Chloropyromorphite	$Pb_5(PO_4)_3Cl$	−18.69		(pH 0–2.12) Brown et al. (1994)
	$Pb_5(PO_4)_3Cl$	−25.05		(pH 2.12–7.21) Lindsay (1979)
	$Pb_5(PO_4)_3Cl$	−46.9		(pH 7.21–12.38) Brown et al. (1994)
	$Pb_5(PO_4)_3Cl$	−84.4		(pH 12.38–14) Brown et al. (1994)
Hydroxypyromorphite	$Pb_5(PO_4)_3OH$	−4.14		Lindsay (1979)

et al. 2006). A pilot scale field experiment was conducted by Cao et al. (2002, 2003) in a Pb contaminated site using three treatments (P/Pb molar ratio of 4.0): (1) 100% P from H_3PO_4; (2) 50% P from H_3PO_4 + 50% from $Ca(H_2PO_4)_2$ and (3) 50% P from H_3PO_4 + 50% from phosphate rock. The role of H_3PO_4 in the mixture was to solubilize the Pb bearing minerals and also the PR, increasing the readily available Pb in the soil. They concluded that although all the treatments immobilized Pb due to the formation in situ of insoluble pyromorphite-like minerals, the H_3PO_4 and phosphate rock treatment produced less impact on soil pH reduction and less leaching of soluble P, a potential eutrophication risk. Similar results were reported by Chen et al. (2003) and Melamed et al. (2003).
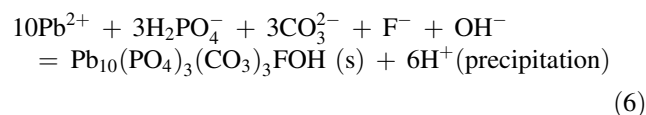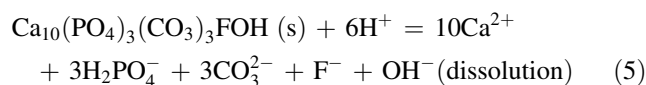
Lead immobilization in aqueous solution using calcium phosphate and calcium hydrogen phosphates proceeded through the P dissolution and pyromorphite precipitation mechanism (Sugiyama et al. 2003). Soluble phosphate as DAP at a rate of 2,300 mg P kg^{-1} provided effective immobilization of Pb in smelter contaminated soil (McGowen et al. 2001), however the contaminated soil had received limestone application previous to the amendment. Application of liming materials together with DAP may be necessary to reduce potential soil acidification in non alkaline soils. Berti and Cunningham (1997), immobilized Pb in soils in situ by using potassium dihydrogen phosphate. Phosphate added as low as 0.5% P was able to reduce leachable Pb to below the regulatory limit of 5 mg L^{-1} in soils with a Pb content of 1,200–3,500 Pb mg kg^{-1}. The authors mentioned before also reported promising results in the use of the physiologically based extraction test (PBET) that determines the soil Pb bio-accessibility, a chemically surrogate measurement for soil Pb bioavailability in animals as a result of soil ingestion.

The choice of amendment with soluble phosphate salts to remediate lead contaminated soils must be carefully studied, not only because of the material cost but the for secondary contaminant problems. Due to the high solubility of these phosphates and to the fact that phosphate is a nutrient, this technique can lead to eutrophication of groundwater and surface waters (Cotton-Howells and Caporn 1996). It has been reported that P adsorption decreases with increasing additions of phosphorous (Heredia and Fernández-Cirelli 2007).
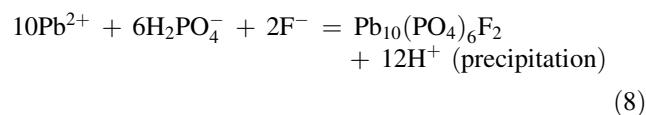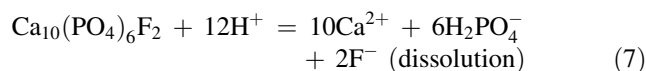
Amendments with phosphate rock

We have already mentioned that amendments with highly soluble P may increase the risk of P-induced eutrophication, therefore, the use of igneous or sedimentary phosphate rock phosphate rock, primarily fluoroapatite (FA) $Ca_{10}(PO_4)_5F_2$ to immobilize aqueous Pb or Pb from contaminated soils may reduce that risk. The structure of FA is similar to that of hydroxyapatite, F^- occupying the OH^- sites on the sixfold axis. However, hydroxyapatite is much more soluble than FA ($\log K_{ps} = -55.9$ and -110.2 respectively) (Table 2). In general, the solubility of PR increases with an increase in carbonate substitution (Ma et al. 1995). The following equations correspond to the dissolution of an apatite with carbonate substitution followed by precipitation of carbonated fluoro pyromorphite-like mineral.

$$Ca_{10}(PO_4)_3(CO_3)_3FOH\ (s) + 6H^+ = 10Ca^{2+}$$
$$+ 3H_2PO_4^- + 3CO_3^{2-} + F^- + OH^- (dissolution) \quad (5)$$

$$10Pb^{2+} + 3H_2PO_4^- + 3CO_3^{2-} + F^- + OH^-$$
$$= Pb_{10}(PO_4)_3(CO_3)_3FOH\ (s) + 6H^+ (precipitation)$$
$$(6)$$

The removal of Pb from aqueous solution using natural phosphate rock was investigated by Mouflih et al. (2006) reporting that the principal mechanism at low pH was dissolution of natural phosphate and precipitation of chloropyromorphite. The addition of phosphate rock to convert the soil Pb to the more stable pyromorphite was accomplished by several authors (Laperche et al. 1997; Ma and Rao 1999; Hettiarachchi et al. 2000; Basta et al. 2001; Cao et al. 2002; Lin et al. 2005). Ma et al. (1995) reported a reduction in dissolved Pb of 22–100% after addition of phosphate rocks to 13 contaminated soils.

The main mechanism of Pb immobilization is the dissolution of the phosphate rock followed by the precipitation of fluoropyromorphite $Pb_{10}(PO_4)_6F_2$ (Chen et al. 1997a, b; Cao et al. 2003, 2004). The formation of fluoropyromorphite $Pb_{10}(PO_4)_6F_2$ has been confirmed by XRD and SEM (Cao et al. 2004).

$$Ca_{10}(PO_4)_6F_2 + 12H^+ = 10Ca^{2+} + 6H_2PO_4^-$$
$$+ 2F^- \ (dissolution) \quad (7)$$

$$10Pb^{2+} + 6H_2PO_4^- + 2F^- = Pb_{10}(PO_4)_6F_2$$
$$+ 12H^+ \ (precipitation)$$
$$(8)$$

It has been suggested that Pb has a higher probability of being incorporated into the apatite structure by isomorphic substitution because of Pb^{2+} ionic radius = 0.133 nm being greater than Ca^{2+} radius = 0.094 nm. The isomorphic substitution for those metals with lower radius, Cu^{2+} (0.069 nm) or Zn^{2+}(0.074 nm) would be less favourable (Boisson et al. 1999).

As seen in Eqs. 7 and 8, although FA dissolution consumes H^+, the same amount of H^+ is liberated in the fluoropyromorphite precipitation, so there should not be a change in the solution pH (Mavropoulos et al. 2002). Cao

et al. (2004) reported that up to 78.3% of sorbed Pb was irreversibly chemisorbed onto the phosphate rock via fluoropyromorphite precipitation but they observed a reduction in pH and concluded that other surface mechanism besides phosphate rock dissolution and fluoropyromorphite precipitation may have contributed to the pH decrease. They proposed that complexation occurred on the phosphate rock surface sites, partially displacing H^+ ions as shown in the following equation

$$PR - OH + Pb^{2+} = PR - OPb^+ + H^+ \qquad (9)$$

Unlike soluble P fertilizers such as SSP, TSP and DAP, phosphate rocks neutralize soil acidity during dissolution process and present a liming effect. Also phosphate rocks usually contain some free calcium carbonate ($CaCO_3$) that is a liming agent per se.

It has been shown that the formation of pyromorphites decreases when using phosphates rocks of limited dissolution in alkaline soils (Laperche et al. 1997; Zhang et al. 1997). Soil acidic conditions play an important role in Pb immobilization using P amendments because in neutral or alkaline soils, the solubility of Pb and P minerals is low. Melamed et al. (2003) reported that when phosphate rock is used to immobilize Pb at pH 8.7, soluble P concentration is low, resulting in a relatively low soil Pb immobilization. However at pH 3.7, phosphate rock dissolves and Pb immobilization is instantaneous, forming a pyromorphite-type material.

Garrido et al. (2006) found that after soil amendment with PR, most of the Pb was associated to the Fe and Al oxyhydroxide fraction and that this distribution did not change during incubation for 1 year. Mixing both H_3PO_4 and phosphate rock with contaminated soil and application of PR as a layer in the soil column was effective in reducing Pb migration (73–79%), minimizing soil acidification and P eutrophication (Yoon et al. 2007).

A study of the grain size of phosphate rock and the effectiveness of Pb immobilization was performed by Chen et al. (2006). The results showed that phosphate rock of the smallest grain size (<35 μm) was superior to that with large grain size for in situ remediation technology. However, effectiveness of solid phosphate is hindered by the size of the particles. In fact, even fine-ground solid phosphate particles are not mobile in soils, fact which prevents solid phosphate from being delivered to the contaminated zone and reacting with Pb^{2+} sorbed in soils (Liu and Zhao 2007).

Amendments with other phosphorus materials

The application of biosolids may constitute an alternative method for Pb immobilization, due to the fact that biosolids often have high concentrations of Fe and P and >50% organic matter (Brown et al. 2003). High P biosolids compost had been used to reduce the bioavailability and bioaccessibility of urban soil Pb (Brown et al. 2004). Also, Farfel et al. (2005) reported that soils with >800 mg Pb kg^{-1} were successfully amended with 110–180 dry t/ha of biosolids compost rich in Fe and P.

The mechanisms responsible of the reduced Pb availability when using biosolids are not clear, although it is assumed that adsorption and posterior precipitation could be the principal ones (Li et al. 2000). As biosolids contain high concentrations of Fe and Mn combined with the high organic matter content, ferrihydrite formation is favoured. In the presence of Pb, ferrihydrite forms surface inner sphere complexes that with time lead to the precipitation of a more crystalline Pb-bearing Fe oxide (Scheinost et al. 2001).
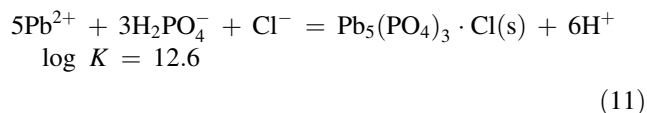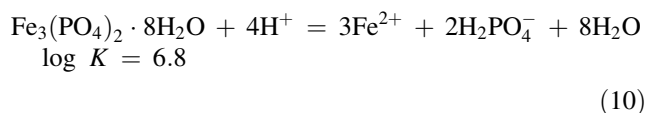
Bone meal, hydroxyapatite as the principal mineral constituent, has been identified as a potentially source of P due to the moderate solubility associated with its carbonate content and poorly crystalline structure. Hodson et al. (2001) and Sneddon et al. (2006) reported a significant decrease in solution Pb when bone meal was added to soil, although the Pb immobilization mechanism could not be determined. Due to bovine spongiform encephalopathy crisis, bone meal production can no longer be used to feed cattle and must be safely disposed and transformed. The commercial cost of bone meal is 25% that of the synthetic hydroxyapatite (Hodson et al. 2001) thus, bone meal could be a cost-effective natural phosphate source for P amendment.

The ashes produced as meat and bone meal combustion residue, a calcium-phosphate rich material, were use by Deydier et al. (2007) for in situ remediation of lead contaminated solutions and soils. These researchers determined by use of chemical kinetics and XRD analysis that lead was immobilized as pyromorphite and lead carbonate dehydrate ($PbCO_3 \cdot 2H_2O$).
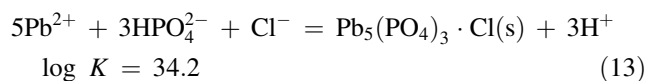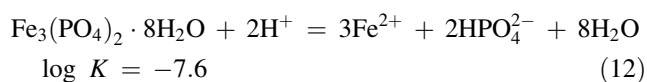
Fishbone, a natural apatite rich substance (70% apatite equivalent) was used to immobilize Pb^{2+} from aqueous solutions to below detectable levels (Admassu and Breese 1999). The effectiveness of phosphatic clay, a by-product of the phosphate mining industry for immobilizing Pb^{2+} from aqueous solutions was studied by Singh et al. (2001), being precipitation of fluoropyromorphite, the principal immobilization mechanism. The results were confirmed by XRD and SEM.

In recent's, environmental application of nanoscale zero-valent iron has attracted considerable interest, because of improved reactivity, especially when it is stabilized by cellulose to prevent agglomeration. Liu and Zhao (2007) tested a new class of cellulose stabilized iron phosphate $Fe_3(PO_4)_2 \cdot 8H_2O$ (vivianite) nanoparticles for immobilizing

Pb^{2+} in three representative soils (calcareous, neutral and acidic) and/or solid and hazardous wastes. The significant decrease of Pb^{2+} availability in the soils was attributed to the formation of pyromorphite minerals through the iron phosphate nanoparticle amendment. Under acidic conditions, the following reactions follow

$$Fe_3(PO_4)_2 \cdot 8H_2O + 4H^+ = 3Fe^{2+} + 2H_2PO_4^- + 8H_2O$$
$$\log K = 6.8 \tag{10}$$

$$5Pb^{2+} + 3H_2PO_4^- + Cl^- = Pb_5(PO_4)_3 \cdot Cl(s) + 6H^+$$
$$\log K = 12.6 \tag{11}$$

At pH >7.2, equations become

$$Fe_3(PO_4)_2 \cdot 8H_2O + 2H^+ = 3Fe^{2+} + 2HPO_4^{2-} + 8H_2O$$
$$\log K = -7.6 \tag{12}$$

$$5Pb^{2+} + 3HPO_4^{2-} + Cl^- = Pb_5(PO_4)_3 \cdot Cl(s) + 3H^+$$
$$\log K = 34.2 \tag{13}$$

The use of vivianite stabilized nanoparticles in Pb contaminated soil converted large fraction of water soluble/exchangeable and carbonate bound Pb^{2+} to highly stable pyromorphite minerals resulting in enhanced Pb^{2+} immobilization. The stabilized nanoparticles produced much less phosphate leachate in comparison to phosphate salts, reducing the risk of eutrophication.

Mixed phosphate amendments

Different P amendments on Pb contaminated soils were tested by Hettiarachchi et al. (2001): TSP, phosphate rock, acetic acid and TSP and H_3PO_4 in different doses. A significant reduction of bioavailable Pb was determined by PBET, resulting phosphate rock the most effective in the stomach phase and in intestinal phase. Similar results were reported by Cao et al. (2003) resulting a mixture of H_3PO_4 and phosphate rock the most efficient in immobilizing Pb with less impact in soil pH and less leaching of soluble P.

Zwonitzer et al. (2003) studied the effect of soluble P (KH_2PO_4) and PR in the immobilization of Pb, Cd and Zn from contaminated soil, resulting the soluble source more effective for decreasing Pb bioavailability. No conclusive results were found for Cd^{2+} and Zn^{2+}.

An international inter-laboratory study was performed to test the ability of different P amendments: phosphate rock, TSP and H_3PO_4 to reduce the availability of Pb in situ (Brown et al. 2005). P added as either TSP or H_3PO_4 resulted the most effective as it was shown by increased plant growth, reduced metal concentration in plant tissue,

reduced soil solution and extractable Pb and reduced bioavailability of soil Pb.

The effectiveness of the addition of different P amendments (hydroxyapatite, phosphate rock and SSP) in the bioaccessibility of Pb in soils to the human, using in vitro test was studied by Tang et al. (2004). These investigators found that SSP had the best performance in minimizing the Pb bioaccessibility in the gastric phase, and the hydroxyapatite in the small intestinal phase.

Zhu et al. (2004) also studied the effect of different P amendments (hydroxyapatite, phosphate rock, SSP and the combination hydroxyapatite and SSP) in a Pb polluted alkaline soil. The Pb bioavailability was determined by plant uptake and sequential extractions. Hydroxyapatite was effective in transforming Pb from non residual fractions to residual form, reducing the Pb bioavailabitiy in soil and also the Pb accumulation by vegetable crops. The low effectiveness of phosphate rock was due to soil alkalinity.

Chen et al. (2007), evaluated the efficiency of different phosphorus amendments: natural hydroxyapatite, phosphate rock, TSP and DAP in contaminated soils to reduce the bioavailability of lead concluding that phosphate rock and hydroxyapatite efficiently decreased the uptake of lead by plants due to the formation of pyromorphite in soils and roots. Although DAP resulted efficient to immobilize Pb, it decreased soil pH, causing leaching of heavy metals from soil. The immobilization and bioavailability of Pb was determined by plant uptake, SEM-EDX and SSE.

A mix treatment, the formation of pyromorphite by amendment of contaminated Pb soil with soluble phosphate Na_2HPO_4 and by the biochemical action of the roots of *Agrostis capillaris* proposed by Cotter-Howells and Caporn (1996) resulted to be more ecologically acceptable than the addition of large amounts of soluble phosphate. Also, the effects of combining two microbial and three different apatite amendments on the bioavailability of lead in a shooting range soil were studied by Wilson et al. (2006).

Conclusion

The main goal of in situ soil remediation techniques is to reduce mobility, bioavailability and toxicity of the metal contaminant although total metal concentration is not significantly reduced by amendment addition. The results of these studies demonstrate that pyromorphite formation can be accomplished by the reaction of Pb in a contaminated soil and different phosphorus sources, increasing the geochemical stability of soil Pb. The redistribution of lead from more chemically labile forms to residual phases resulted in less bioavailability and less phytotoxicity, indicated by greater plant growth and lower metal concentrations in the plant tissue (Knox et al. 2003; Brown

et al. 2004; Ryan et al. 2004). The chemical stability of chloropyromorphite under different environmental conditions (Scheckel and Ryan 2002) makes Pb immobilization by phosphorous amendments a very effective remediation technique, since accidental pyromorphite ingestion does not yield bioavailable lead, being pyromorphite insoluble in the intestinal tract (Zhang et al. 1998; Arnich et al. 2003).

We must take in consideration that the formation of pyromorphite as solubility controlling phase is kinetically controlled by pH, the solubility of the phosphate phase and the solubility of the Pb species, so soluble or acidic phosphates sources are necessary for in situ successful treatment (Chrysochoou et al. 2007). The use of lime to restore soil pH reduces pyromorphite formation.

Phosphoric acid was regarded as the most effective amendment (USEPA 2001) because of its easy delivery and superior ability to dissolve Pb^{2+} form existing minerals and transform it in pyromorphites. Although phosphorus addition seems to be highly effective, excess P in soil and its potential effect on eutrophication of surface water remains a concern. The use of mixed treatments could improve their effectiveness in reducing lead phyto and bioavailability, however inconsistencies in measurements make it difficult to assess their effectiveness (Brown et al. 2004, 2005).

The efficiency of the P amendment in Pb contaminated soil depends on the type of soil and the nature and extension of the contamination. The type and rate of the P source and also the application management to be used in the soil amendment should be carefully studied. Also the risk of primary P leaching and eutrophication of surface water sources, and the possibility of As enhanced leaching are of great concern.

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