



Stabilization of Pb and As in soils by applying combined treatment with phosphates and ferrous iron

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ABSTRACT

The chemical immobilization of Pb and As in contaminated soil from Lavrion, Greece, using monocalcium phosphate and ferrous sulfate as stabilizing agents was investigated. Monocalcium phosphate was added to contaminated soil at PO₄ to Pb molar ratios equal to 0, 0.5, 1, 1.5 and 2.5, whereas ferrous sulfate was added at Fe to As molar ratios equal to 0, 2.5, 5, 10 and 20. Phosphates addition to contaminated soil decreased Pb leachability, but resulted in significant mobilization of As. Simultaneous immobilization of Pb and As was obtained only when soil was treated with mixtures of phosphates and ferrous sulfate. Arsenic uptake by plants was also seen to increase when soil was treated only with phosphates, but co-addition of ferrous sulfate was efficient in maintaining As phytoaccumulation at low levels. The addition of at least 1.5 M/M phosphates and 10 M/M iron sulfate to soil reduced the dissolved levels of Pb and As in the water extracts to values in compliance with the EU drinking water standards. However, both additives contributed in the acidification of soil, decreasing pH from 7.8 to values as low as 5.6 and induced the mobilization of pH sensitive elements, such as Zn and Cd.

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1. Introduction

Mining, beneficiation and smelting activities may lead to the contamination of soil and water resources with heavy metals and metalloids. Apart from dust emission from smelting plants and deposition on soils pathway, geochemical weathering processes acting upon wastes and by-products may also initiate the process of transporting heavy metals and metalloids from contaminated areas and redistributing them to surrounding soils, surface and groundwater. Pb, As, Zn and Cd are of specific concern due to their relative abundance at mining sites and their toxicity and phytotoxicity. Several remedial technologies have been proposed and investigated for treating heavy metal contaminated soils including chemical stabilization techniques which aim to convert contaminants to their low leachability and bioavailability forms by adding solid or liquid stabilizing agents. Kumpiene et al. [1] have reviewed the type of stabilizing agents used and the mechanisms taking place for the immobilization of a number of heavy metals and metalloids.

It is well known that phosphorus reacts with many heavy metals, metalloids and radionuclides to form secondary phosphate precipitates that are considered stable over a wide range of environmental conditions, regarding pH, redox values and geochemical composition of natural waters. As seen in Table 1, Pb phosphates

present low solubility, generally several orders of magnitude lower than the analogous oxides, hydroxides, carbonates and sulfates. Therefore, the application of phosphate amendments has been identified as a potentially efficient *in situ* chemical immobilization technique for heavy metal contaminated soils.

Lead phosphates have been demonstrated to be the most stable Pb form under a wide variety of environmental conditions. Furthermore, they can form rapidly in the presence of adequate Pb and phosphate. A detailed thermodynamic basis for the reaction of Pb and phosphates in aqueous solutions has been established by Nriagu [4–6]. Among all the Pb–P minerals, it was found that chloropyromorphite, Pb₅(PO₄)₃Cl, is the most stable under conditions representing a wide range of natural environments, regarding pH, redox conditions and geochemical background. It is also predicted that other solid phase Pb species would be converted to pyromorphite by a dissolution–precipitation mechanism. Several researchers identified chloropyromorphite as a common weathering product of Pb bearing compounds in mine wastes, as well as urban and motorway roadside soils at normal soil phosphorus concentrations [7].

Many natural or industrial materials including natural or synthetic apatites, phosphate rocks, phosphoric acid or phosphoric salts mainly of calcium and sodium were tested and used as sources of phosphates for immobilizing heavy metals in soils [8–20]. The role of phosphates for treating Pb contaminated soil and in particular firing range soils has been reviewed by Chrysochoou et al. [21]. Although phosphate addition to contaminated soil immobilizes

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Table 1
Solubility products (K_{sp}) of selected Pb compounds.

Name	Reaction	log K_{sp}
Anglesite	$PbSO_4 = Pb^{2+} + SO_4^{2-}$	-7.79 ^a
Galena	$PbS = Pb^{2+} + S^{2-}$	-27.51 ^b
Litharge	$PbO = Pb^{2+} + H_2O - 2H^+$	12.89 ^a
Cerrusite	$PbCO_3 = Pb^{2+} + CO_3^{2-}$	-13.1 ^b
Lead hydrogen phosphate	$PbHPO_4 = Pb^{2+} + HPO_4^{2-}$	-11.45 ^a
Lead phosphate	$Pb_3(PO_4)_2 = 3Pb^{2+} + 2PO_4^{3-}$	-44.36 ^a
Hydroxypyromorphite	$Pb_5(PO_4)_3OH = 5Pb^{2+} + 3PO_4^{3-} + OH^-$	-76.79 ^a
Chloropyromorphite	$Pb_5(PO_4)_3Cl = 5Pb^{2+} + 3PO_4^{3-} + Cl^-$	-83.70 ^a
Fluoropyromorphite	$Pb_5(PO_4)_3F = 5Pb^{2+} + 3PO_4^{3-} + F^-$	-71.63 ^a
Bromopyromorphite	$Pb_5(PO_4)_3Br = 5Pb^{2+} + 3PO_4^{3-} + Br^-$	-78.14 ^a
Corkite	$PbFe_3(PO_4)(SO_4)(OH)_6 = Pb^{2+} + 3Fe^{3+} + PO_4^{3-} + SO_4^{2-} + 6OH^-$	-112.6 ^c
Hinsdalite	$PbAl_3(PO_4)(SO_4)(OH)_6 = Pb^{2+} + 3Al^{3+} + PO_4^{3-} + SO_4^{2-} + 6OH^-$	-99.1 ^c
Plumbogummitte	$PbAl_3(PO_4)_2(OH)_5 \cdot H_2O = Pb^{2+} + 3Al^{3+} + 2PO_4^{3-} + 5OH^-$	-99.3 ^c

Obtained from: ^aLindsay [2], ^bStumm and Morgan [3], ^cNriagu [4].

heavy metals, many studies indicated that it has a negative effect on As, inducing its mobilization [9,10,15,22–24]. Therefore, in cases where soils are contaminated with both Pb and As, other additives should also be applied to eliminate the problem of As mobilization.

Arsenic and phosphorous are both Group 5A elements of the periodic table and their respective pentavalent oxoanions, arsenate and phosphate, have very similar structure and chemical reactivity; they form similar minerals and their sorption behavior follows alike patterns. Due to their chemical similarity, phosphates can replace sorbed or even structurally bound arsenate anions and this has been proposed as one of the most important mechanisms contributing in the mobilization of arsenic and the subsequent pollution of water resources. Several laboratory and field scale studies have demonstrated the ability of phosphates to displace adsorbed arsenic or inhibit arsenic adsorption [25–30].

The ability of phosphate to displace As has been exploited by some researchers in an effort to develop appropriate techniques for the remediation of As contaminated soils [31,32]. In these works the soil was treated with an aqueous solution containing soluble phosphate compounds and the main objective was to obtain the removal of As from the soil and its recovery in the aqueous solution. In another work phosphates are added in the soil in order to obtain the stabilization of heavy metals and the simultaneous mobilization of As for subsequent phytoextraction [33].

The mobility of As in soil is mainly controlled by adsorption/desorption processes and co-precipitation with metal oxides [1]. Several agents were investigated for the stabilization of As bearing soils. Among them, iron compounds mainly in the form of Fe(II) or Fe(III) sulfates and zero valent iron, and, to a lesser extent, Al and Mn compounds were proven efficient for the stabilization of As in contaminated soils [34–41,56].

Previous studies indicated that ferrous or ferric sulfate applied in contaminated soil effectively reduced As mobility and phytoavailability [34–36]. Zero valent iron or iron oxides and hydroxides, such as goethite, were also examined as stabilizing agents for As contaminated soils [37–41]. It was reported that Fe(II)/Fe(III) salts combined with lime were more efficient stabilizing agents for As compared to zero valent iron, Fe(0), and goethite [36], with Fe(III) sulfate being more efficient than Fe(II) sulfate [34,36]. However, although zero valent iron oxidation and As stabilization reactions are not as fast as those of iron salts, it is more beneficial in a long-term perspective, since it is oxidized slowly releasing Fe(II) continuously, thus providing ideal conditions for the oxidation of As(III) to As(V), which is easily adsorbed to newly formed iron hydroxides [1,37].

In the present study, monocalcium phosphate and ferrous sulfate were used as stabilizing additives to contaminated soil from Lavrion, Greece, polluted by former mining and metallurgical activities, in order to immobilize both Pb and As. The effectiveness

of these additives as stabilizing agents was evaluated by applying leaching tests, according to the US EPA Toxicity Characteristic Leaching Procedure (TCLP) [42] or using de-ionized water, and by determining the phytoavailability of contaminants using *Phaseolus Vulgaris Starazagorski gw* (dwarf beans) as plant indicators.

2. Materials and methods

2.1. Materials

A soil sample was collected from a location called “Neraki” in Lavrion, Greece where the recent mining and metallurgical activities started in the end of 19th century and ceased in 1990 [43]. The soil sample was air-dried and sieved to remove the coarse fraction (>2.0 mm), whereas the fine fraction (<2.0 mm) was used as working sample for conducting characterization tests, analyses and stabilization experiments. Analytical grade monobasic calcium phosphate monohydrate ($Ca(H_2PO_4)_2 \cdot H_2O$, Sigma–Aldrich) and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, Fluka chemicals) were used as stabilizing agents.

2.2. Environmental characterization

Chemical analysis was carried out in duplicate on ground dry samples. Samples were digested with aqua regia for total elemental analysis. Measurement of the ions concentration in solution was conducted by Flame Atomic Absorption Spectrophotometry (AAS, PerkinElmer 2100). Loss on ignition was measured by ignition of the sample at 1000 °C for 1 h whereas total organic carbon (TOC) was determined by heating at 500 °C. Cation Exchange Capacity (CEC) measurements were performed by equilibrating 0.5 g of a dry sample with 10 mL of 1 M CH_3COONH_4 at pH 7 for 24 h. Paste pH measurements were conducted at water-to-solid ratio equal to 5 according to the EPA/600/2-78/054 guideline. Particle size distribution of the soil sample was determined by a combination of screening for particle size coarser than 0.063 mm and laser particle size analyses using a Master Sizer/E, Malvern Instruments for fractions finer than 0.063 down to 0.001 μm .

Mineralogical analysis was conducted by X-ray diffraction (XRD, Siemens D5000) and Scanning Electron Microscopy techniques with Energy Dispersive Spectroscopy using X-rays (SEM/EDS system, JEOL 6100/NORAN TN 5500) for elemental microanalysis of the solid phases.

2.3. Stabilization

To evaluate the effectiveness of the additives as stabilizing agents for contaminated soil, pot experiments were performed. 550 g of soil sample was thoroughly mixed with a calculated dose

Table 2
Stabilizing agents addition rates.

(a) Phosphates		(b) Iron		
PO ₄ /Pb ⁽¹⁾ (M/M)	Ca(H ₂ PO ₄) ₂ ·H ₂ O (g/100 g soil)	Fe/As ⁽²⁾ (M/M)	V ⁽³⁾ (mL/550 g soil)	FeSO ₄ ·7H ₂ O added (g/100 g soil)
0	0	0	0	0.00
0.5	0.212	2.5	25	0.77
1	0.424	5	50	1.54
1.5	0.636	10	100	3.08
2.5	1.061	20	200	6.16

(1) Pb in soil: 33.7 mmole kg⁻¹; (2) As in soil: 11.2 mmole kg⁻¹; (3) V: volume from a solution containing 0.61 M Fe(II) added in 550 g soil.

of Ca(H₂PO₄)₂·H₂O and FeSO₄ solution and placed in a 1 L pot. The Ca(H₂PO₄)₂·H₂O dose was determined based on the stoichiometric ratio of PO₄ ions to total Pb content in the soil sample. Five molar ratios of PO₄/Pb were tested: 0 (no addition), 0.5, 1.0, 1.5 and 2.5; the 1 M/M ratio corresponds to the addition of 0.424 g monocalcium phosphate hydrate to 100 g of soil (Table 2). Iron sulfate solution was prepared by dissolving 169.04 g of FeSO₄·7H₂O in 1 L de-ionized water resulting in 0.61 M FeSO₄ solution. The iron sulfate addition ratio was determined based on the stoichiometric ratio of Fe ions to total As content in the soil. Again, five molar ratios of Fe/As were tested: 0 (no addition), 2.5, 5, 10 and 20. Based on the total As content in the soil sample examined the 10 M/M ratio corresponds to the addition of 100 mL FeSO₄ solution to a pot containing 550 g of soil, which is equivalent to the addition of 3.08 g FeSO₄·7H₂O per 100 g of soil (Table 2). All the tests were performed in duplicate. Therefore, the total number of pot experiments performed was 50.

In order to promote the chemical reactions between the elements in soil and the additives introduced in the mixture, pots were systematically hydrated and the mixtures were kept saturated in water for approximately one month. The equilibration time was selected based on preliminary stabilization experiments of contaminated soil with phosphates which involved measurement of pH, redox potential and determination of elements leachability vs. time.

2.4. Evaluation of stabilization

Following the one-month stabilization period, the pH of saturated soil samples was measured at soil to water ratio equal to 2:1. Then, the stabilization efficiency was evaluated by conducting (a) chemical extraction tests with de-ionized water and by applying the US EPA Toxicity Characteristic Leaching Procedure and (b) biological tests, in order to evaluate directly the effect of phosphate

treatment on the accumulation of metal contaminants in plant tissues using dwarf beans (*Phaseolus Vulgaris Starazagorski gw*) as plant “indicator”.

Leaching tests with de-ionized water were carried out at liquid to solid (L/S) ratio equal to 1 L kg⁻¹ and after equilibrating for 1 day. The US regulatory Toxicity Characteristics Leaching Procedure (TCLP) involved leaching of the sample with the TCLP extraction fluid 1 corresponding to a solution of acetic acid/sodium hydroxide with pH 4.93 ± 0.05, for 24 h at 5% pulp density (L/S = 20 L kg⁻¹). If the dissolved metals exceed the specified limits the material is characterized as toxic and cannot be accepted for disposal in a municipal wastes landfill.

Concerning the biological tests, the seeds were sown after 24 h imbibition in de-ionized water. The seedlings were grown under artificial light (for 15 h per day) in the laboratory environment and watering with de-ionized water was adjusted to the needs of plants. The plants were harvested after a period of 30 days, when it was clear that their development was due to the nutrients uptake exclusively from soil and not from the initial germ. The shoot height was measured and the aerial parts of the plants were collected and analyzed for their Pb, Zn, Cd and As content. A wet digestion procedure was followed for the analysis of plant tissues (Theodoratos et al. [10]). The dried and ground plant tissue was placed in a small beaker with 10 mL of concentrated HNO₃ and the mixture was allowed to stay overnight. The beaker was heated gently on a hot plate until the production of red NO₂ fumes was ceased. After that the beaker was allowed to cool and a small amount (2–4 mL) of 70% HClO₄ was added. Finally, the sample was heated again, allowed to evaporate to a small volume, transferred to a volumetric flask and diluted with distilled water.

Metal concentrations in the aqueous solutions were analyzed by flame AAS. A graphite furnace (GF-AAS) and a hydride generator (HG-AAS) were also used for low concentrations.

Table 3
Chemical analysis and physicochemical properties of soil used.

Major elements	mg/kg ^a	Contaminants	mg/kg ^a	Dutch intervention values (mg/kg)
Ca	51725 ± 4278	Pb	6973 ± 336	530
Mg	8675 ± 318	As	840 ± 71	55
Fe	41875 ± 1025	Zn	5775 ± 35	720
Al	32535 ± 870	Cd	43 ± 4	12
Mn	2573 ± 74	Cu	115 ± 7	190
K	8650 ± 212			
Na	1275 ± 247			
Other properties		Texture		
Ins. (%)	63.19	Sand (2–0.063 mm)		24.2%
LOI (%)	9.55	Silt (0.063–0.002 mm)		52.4%
TOC (%)	4.82	Clay (<0.002 mm)		23.4%
CEC (meq/g)	0.13			
pH	7.8			
EC (mS/cm)	1.08			

^a Mean value ± deviation of duplicate measurements.

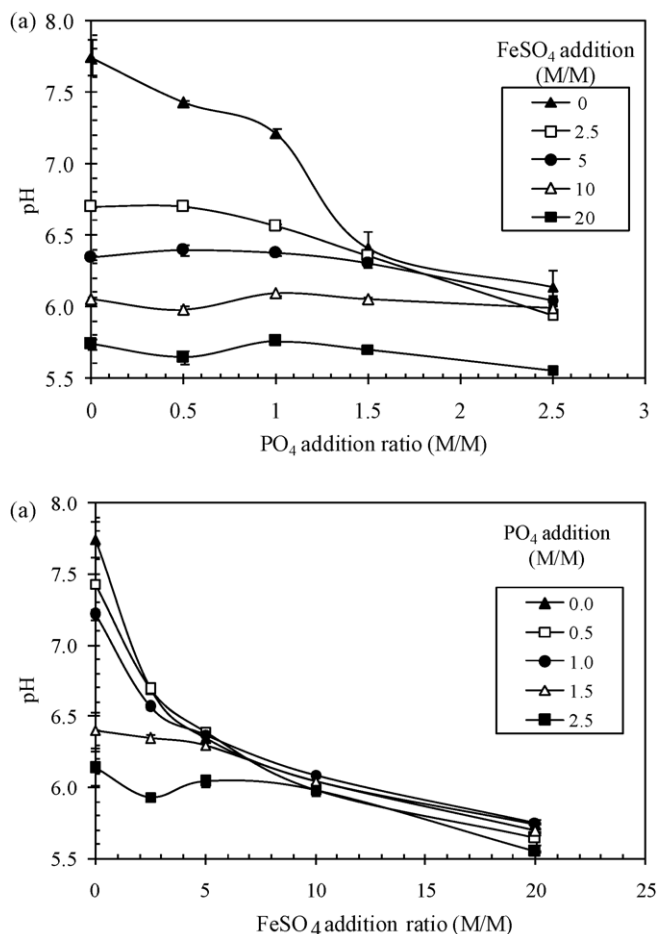


Fig. 1. Effect of PO₄ and FeSO₄ addition ratio on soil pH.

3. Results and discussion

3.1. Soil sample characterization

The chemical analysis results of the soil sample tested as compared to the Dutch soil intervention values [44] are presented in Table 3. It is seen that the Pb, Zn, Cd, and As content was well above the Dutch soil standards. The organic matter content of the soil sample was 4.82% (w/w). Mineralogical analyses indicated that the main minerals in soil were quartz, illite, muscovite, chlorite and calcite. Minor quantities of albite, biotite, ilmenite, rutile and antigorite were also observed. Lead was found mainly associated with limonite, whereas minor quantities of lead carbonates, sulfates and arsenates were also identified. In the upper horizons of soils, where oxic conditions prevail, arsenic occurs mainly in the form of arsenate anions, which are retained by sorption mechanisms on the surface of soil oxides and hydroxides. For the particular case of Lavrion soils, due to the high levels of both As and heavy metals, As was found to occur not only associated with the Fe-oxides but also in the form of a wide variety of arsenate minerals, such as scorodite, FeAsO₄·2H₂O, mimetite, Pb₅(AsO₄)₃Cl, beudanticite PbFe₃(AsO₄)(SO₄)(OH)₆, PbFe₂(AsO₄)₂(OH)₂, etc.

3.2. Change of soil pH

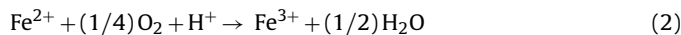
pH measurements of the stabilized mixtures were performed to evaluate the degree of acidification and subsequent adverse effects. As seen in Fig. 1, phosphate addition resulted in a decrease of soil pH. When only Ca(H₂PO₄)₂ was used for stabilization, without any

FeSO₄ addition, the pH of soil decreased from the initial value of 7.8 down to 6.1 at the maximum dose of phosphates, 2.5 M/M PO₄/Pb. The generation of acidity is due to the acidic character of monocalcium phosphate salt that was used during this experimental work. In the pH range between 7 and 11, the preponderant specie of phosphate anions, is the monoprotonated form, i.e. HPO₄²⁻. As a consequence, when Ca(H₂PO₄)₂ is added to the soil, the diprotonated anions tend to release H⁺ according to reaction (1):



At the maximum dose of 2.5 M/M PO₄/Pb, the acidity introduced in the soil corresponds to approximately 84 mmole of H⁺ per kg soil.

Ferrous sulfate addition also resulted in pH decrease and the effect was more pronounced compared to the addition of phosphates (Fig. 1b). This can be attributed to the hydrolysis and precipitation of Fe(III)-hydroxides, following the oxidation of Fe(II) to Fe(III) by air, according to reactions (2) and (3):



As seen in reaction (2) oxidation of ferrous iron to the ferric state consumes H⁺, but due to the hydrolysis and precipitation of Fe(III)-hydroxides (reaction (3)), there is net generation of acidity, corresponding to 2 moles of H⁺ per mole of Fe(II). The dose of 5 M/M Fe/As corresponds to 55.2 mmole kg⁻¹ of Fe(II) and this generates approximately 110 mmole of H⁺ per kg soil. This amount of acidity exceeds, almost by 30%, the acidity generated by the highest dose of phosphates. As seen in Fig. 1a, soil pH is close to 6.35 at the dose of 5 M/M FeSO₄ and remains constant regardless of the addition of phosphates. Only at the most elevated phosphate dose, 2.5 M/M, there is a significant decrease of soil pH to the value of 6.0 (Fig. 1b). At the higher doses of FeSO₄, soil pH is mainly determined by iron (II) addition and varies between 6.0 and 6.1 at the dose of 10 M/M and 5.6–5.8 at the dose of 20 M/M.

Due to the slightly alkaline pH of the initial soil, i.e. pH 7.8, it is probable that ferrous iron initially precipitates as Fe(OH)₂ and is subsequently oxidized to some form of Fe(III)-oxyhydroxide. Even in the form of solid ferrous hydroxide, Fe(II) is oxidized to the trivalent state with a relatively rapid kinetics. According to the study of Olwe and Genin [45], when a suspension of ferrous hydroxide is stirred in a vessel open to the atmospheric air, it is oxidized to some form of ferric oxyhydroxide in less than 6 h. It is noted that during the current experimental work the soils were left under aerated conditions for more than 1 month after the addition of stabilizing agents, it is thus expected that all ferrous iron will have been oxidized. It should also be noticed that the generation of acidity due to the addition of ferrous sulfate is not affected by the sequence of reactions, i.e. oxidation followed by hydroxide precipitation or vice versa. In both cases each mole of ferrous iron results in the generation of 2 moles of H⁺.

3.3. Leaching test results

3.3.1. Lead leachability

Lead concentrations in the TCLP leachates and the water extracts vs. phosphates addition ratios are given in Figs. 2 and 3, respectively. As seen in Fig. 2, Pb concentration in the TCLP leachate of the untreated soil is equal to 6.7 mg L⁻¹, i.e. above the regulatory limit of 5 mg L⁻¹. Addition of monocalcium phosphate reduces the leachability below this limit, even at the low dose of 0.5 M/M of phosphates. Increasing the dose of phosphates from 0.5 to 2.5 M/M (without FeSO₄ addition) decreases Pb leachability from 4.2 to 2.3 mg L⁻¹. Further decrease is obtained when there is simultaneous addition of FeSO₄. A dose of 10 M/M FeSO₄, combined with

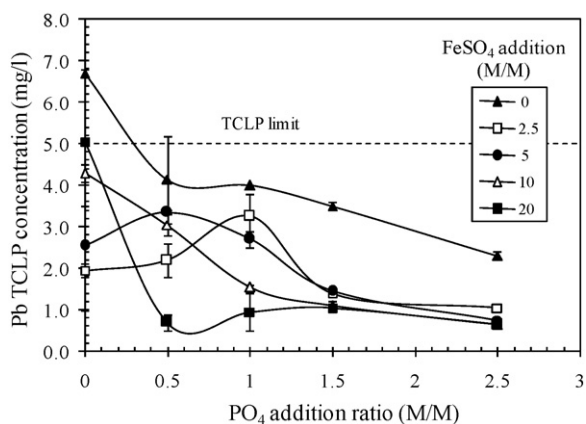


Fig. 2. Effect of PO_4 and FeSO_4 addition ratios on Pb concentration in the TCLP leachate (TCLP limit for Pb 5 mg L^{-1}). Bars represent deviations of duplicate measurements from mean values.

2.5 M/M phosphates, reduces Pb extractability in the TCLP buffer solution to the value of 0.65 mg L^{-1} .

The reduction of Pb availability due to monocalcium phosphate and iron sulfate addition is more pronounced when water is used as leaching agent (Fig. 3). As seen in this figure, monocalcium phosphate addition to contaminated soil reduced Pb concentration in the water extract from $140 \text{ } \mu\text{g L}^{-1}$ (no addition) to levels below the value of $10 \text{ } \mu\text{g L}^{-1}$, which is the upper permitted level for drinking water (DW) according to the European Directive 98/83/EC. Without FeSO_4 addition, concentrations lower than $10 \text{ } \mu\text{g L}^{-1}$ were obtained when the PO_4 dose was higher than 1.5 M/M. Addition of FeSO_4 at doses 2.5, 5 and 10 M/M were also very effective in maintaining the extractability of Pb in water below the DW limit, regardless of the PO_4 dose. However, stabilization was less efficient, at the highest FeSO_4 dose of 20 M/M. In this case, co-addition of phosphate at a dose greater than 1.5 M/M was required in order to obtain Pb solubility lower than $10 \text{ } \mu\text{g L}^{-1}$.

The role of phosphates in the stabilization of Pb is more or less well understood. As previously mentioned Pb phosphates, and more particularly pyromorphites, are the thermodynamically most stable Pb bearing minerals, exhibiting very low solubility between pH 3 and 11 [4–6]. It is thus reasonable to assume that in the presence of phosphates and in the long term, all lead species will be transformed to the form of pyromorphites. However, Hashimoto et al. [46] presented evidence that pyromorphite formation may not be always kinetically favored. The researchers examined a series of soils stabilized with several phosphate amendments, 380 days

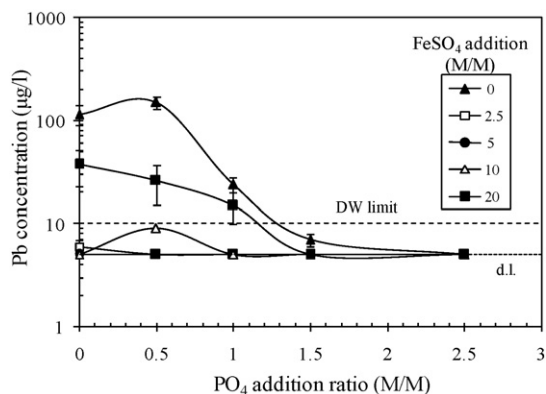


Fig. 3. Effect of PO_4 and FeSO_4 addition ratios on Pb concentration in the water extract. Drinking water (DW) limit: $10 \text{ } \mu\text{g L}^{-1}$ (according to the EU Directive 98/83/EC); detection limit (d.l.) $5 \text{ } \mu\text{g L}^{-1}$ with GF-AAS. Bars represent deviations of duplicate measurements from mean values.

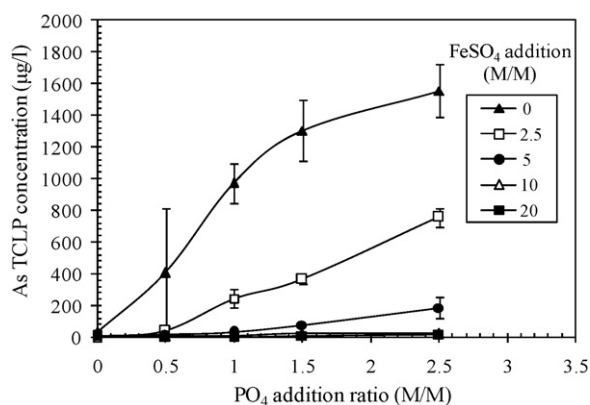


Fig. 4. Effect of PO_4 and FeSO_4 addition ratios on As concentration in the TCLP leachate. (TCLP limit for As 5 mg L^{-1}). Bars represent deviations of duplicate measurements from mean values.

after their treatment. They used extended X-ray absorption fine structure (EXAFS) spectroscopy and found out that transformation of initial Pb species of soil in the form of chloropyromorphite was no more than 31% of total Pb, despite the long incubation period.

Moreover, the exact mechanism and the kinetics of pyromorphite formation are not clear and remain still a subject of debate, particularly when the main source of phosphates are compounds of limited solubility, such as the hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, or other natural phosphate rocks [1,17,21]. In our case, the phosphate source is soluble, therefore the main constrain is the limited solubility of Pb compounds in the contaminated soil, e.g. PbCO_3 , PbSO_4 , etc. Decrease of soil pH can increase the concentration of lead in pore water, and this can favor the formation of pyromorphite type minerals. In this experimental work both soil amendments, i.e. $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and FeSO_4 , contribute in the acidification of soil and this can explain the synergetic effect of the admixture on Pb stabilization. However the highest dose of FeSO_4 , 20 M/M, reduces soil pH to rather low values, i.e. 5.6–5.8, which seems to affect adversely Pb solubility in water, particularly at low PO_4 doses.

Ferrous sulfate addition was found to stabilize Pb even without phosphate addition (Fig. 3). In this case, the preponderant mechanism is most probably the retention of mobile Pb species in the freshly produced ferrihydrite. The stabilizing potential of ferrous sulfate has been exploited by Lundtorp et al. [47], who developed a method called Ferrox process for the stabilization of toxic elements in several industrial residues. The Ferrox process is carried out by mixing the waste material with a ferrous sulfate solution and subsequently aerating the suspension to promote oxidation of Fe(II) to Fe(III) and formation of ferrihydrite. They have applied this method for the stabilization of a residue produced from the air pollution control equipment of a municipal solid waste incinerator. The amount of water-soluble elements was reduced from the initial values of $990 \text{ mg Pb per kg solid}$ and $0.29 \text{ mg Cd per kg solid}$ to the values of $0.28 \text{ mg Pb kg}^{-1}$ and $0.0092 \text{ mg Cd kg}^{-1}$ solid after the treatment.

3.3.2. Arsenic leachability

Arsenic concentrations in the TCLP leachates and the water extracts are presented in Figs. 4 and 5, respectively. As seen in both figures, As was mobilized by adding monocalcium phosphate in contaminated soil. The concentration of As in the TCLP leachate increased from $31 \text{ } \mu\text{g L}^{-1}$ (untreated soil) to $1555 \text{ } \mu\text{g L}^{-1}$ at the maximum phosphates addition ratio applied. Furthermore, the concentration of As in the water extract increased from $135 \text{ } \mu\text{g L}^{-1}$ (untreated sample) to as high as $16,000 \text{ } \mu\text{g L}^{-1}$ at the maximum phosphate addition ratio (Fig. 5). This mobilization strongly depends on the phosphates addition ratio and is explained

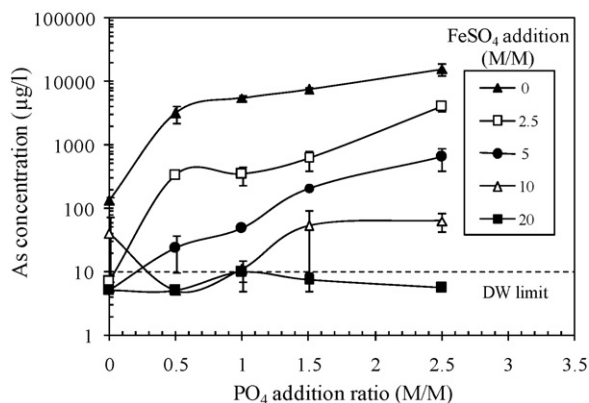


Fig. 5. Effect of PO_4 and FeSO_4 addition ratio on As concentration in the water extract. Drinking water (DW) limit: $10 \mu\text{g L}^{-1}$ (according to the EU Directive 98/83/EC); detection limit (d.l.) $5 \mu\text{g L}^{-1}$ with HG-AAS. Bars represent deviations of duplicate measurements from mean values.

considering the close chemical similarity between the phosphate and arsenate ions that leads to the partial substitution of the latter by phosphates during this intense phosphate treatment [9,10,15,22–24].

Ferrous sulfate addition to soil counterbalanced the adverse effect of As mobilization due to phosphates addition. It is clearly seen that by increasing the amount of FeSO_4 in the soil–phosphates mixture, As concentration in both the TCLP leachate and the water extract is decreased. At the maximum phosphate addition ratio (2.5 M/M), As TCLP concentration progressively decreased from 1720 to $20 \mu\text{g L}^{-1}$ by increasing the FeSO_4 addition ratio from 0 to 20 M/M (Fig. 4). At the phosphate addition ratio of 2.5 M/M, the concentration of As in the water extract decreased from 16,000 to $6 \mu\text{g L}^{-1}$ by increasing the amount of FeSO_4 added from 0 to 20 M/M (Fig. 5). As seen in Fig. 5, the leachability of As in water remains below the drinking water limit of $10 \mu\text{g L}^{-1}$ at all phosphate doses, only at the highest FeSO_4 addition of 20 M/M.

The immobilization of As by iron compounds is a well known process, which has been widely applied for the treatment of contaminated industrial effluents, natural surface and underground waters, as well as soils and sediments. The stabilization of As with iron is achieved via the formation of amorphous or crystalline iron(III) arsenate compounds or through its adsorption on the surface of iron oxyhydroxides. The amorphous ferric arsenates with stoichiometric ratio $\text{Fe}/\text{As} = 1 \text{ M/M}$ and approximate formulas $\text{FeAsO}_4 \cdot \text{H}_2\text{O}$ or $\text{FeAsO}_4(\text{OH}) \cdot x\text{H}_2\text{O}$ [48] have very high solubility and cannot immobilize effectively arsenic. On the other hand crystalline scorodite $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$, is formed only at higher temperatures or following a long ageing period. It has a considerably higher stability compared to the amorphous stoichiometric compounds, but is mainly stable in slightly acidic pHs. Solubility calculations, carried out with VMinteq software [49] and using the compiled thermodynamic data by Drahotka and Filipi [50], indicated that the solubility of As at pH 7.0 corresponds to 31.5 mg L^{-1} for the amorphous ferric arsenate and 0.25 mg L^{-1} for crystalline scorodite. Solubilities in the order of ppb can be achieved using high stoichiometric ratios between Fe and As, e.g. $\text{Fe}/\text{As} > 4 \text{ M/M}$, and in this case the preponderant mechanism is adsorption on the surface of Fe(III) hydroxides, and more particularly the poorly crystalline ferrihydrite. The common industrial practice to stabilize arsenic in metallurgical circuit is to form precipitates having Fe/As molar ratios greater than 3 or 4. Although of major practical importance the meaning of this ratio remained unknown. Paktunc et al. [48] demonstrated that due to structural constraints, As concentration on ferrihydrite surfaces cannot exceed the value corresponding to Fe/As molar ratio of 4. At lower Fe/As ratios the resulting product

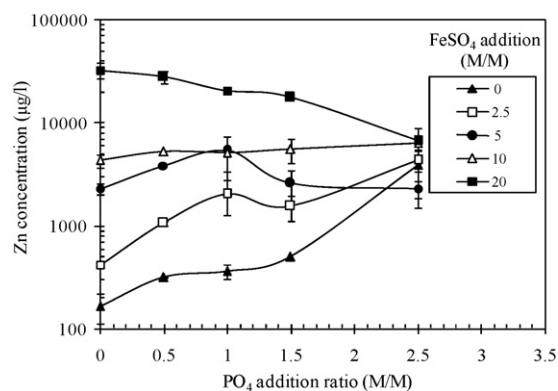


Fig. 6. Effect of PO_4 and FeSO_4 addition ratio on Zn concentration in the water extract. Bars represent deviations of duplicate measurements from mean values.

is a mixture of ferric arsenate and ferrihydrite and the mobility of arsenic is primarily dictated by the unstable ferric arsenate. Current study confirms the necessity to use a rather high molar excess of Fe in order to maintain the solubility of As at low levels, particularly in the presence of phosphates.

3.3.3. Zinc and cadmium leachability

Zinc and cadmium concentrations in the water extracts are given in Figs. 6 and 7, respectively. Both additions of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and FeSO_4 had a negative effect on the stability of Zn and Cd. Water leachability of these elements in the initial soil were 165 and $< 40 \mu\text{g L}^{-1}$ for Zn and Cd, respectively. The addition of phosphates (at 0 M/M FeSO_4) increased the solubility of Zn up to the value of $3900 \mu\text{g L}^{-1}$ and that of Cd up to $60 \mu\text{g L}^{-1}$. More important mobilization was observed during the addition of FeSO_4 . At the highest dose of FeSO_4 20 M/M (without phosphate addition) the concentration of Zn in the water extract was as high as $32,000 \mu\text{g L}^{-1}$ and that of Cd $790 \mu\text{g L}^{-1}$. The observed mobilization of Zn and Cd during the addition of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ or FeSO_4 can be attributed to the acidification of soil. As previously mentioned the addition of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ decreased soil pH from 7.8 to 6.1 and that of FeSO_4 from 7.8 to 5.7.

It is known that Zn and Cd are more easily mobilized due to soil acidification in comparison with Pb. A study by Covelo et al. [51] demonstrated that acidic soils, with pHs varying between 4.6 and 6.6, can retain much more effectively Pb than Zn or Cd. Another characteristic example is the behavior of these elements during

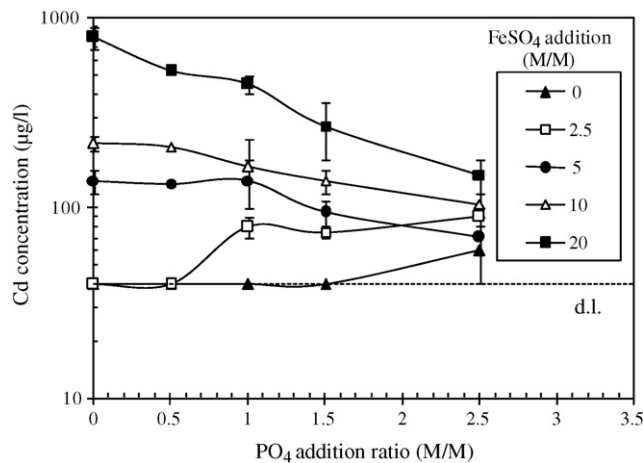


Fig. 7. Effect of PO_4 and FeSO_4 addition ratios on Cd concentration in the water extract. Detection limit (d.l.) in Atomic Absorption Spectroscopy-Flame Emission $40 \mu\text{g L}^{-1}$. Bars represent deviations of duplicate measurements from mean values.

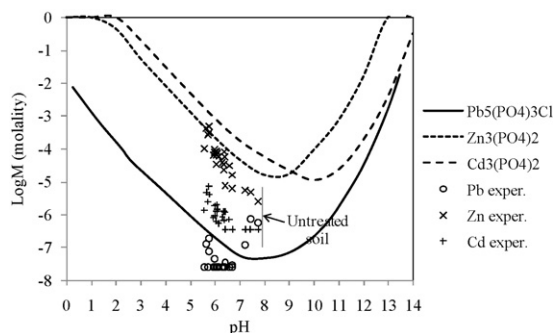


Fig. 8. Solubilities of $Zn_3(PO_4)_2$, $Cd_3(PO_4)_2$ and $Pb_5(PO_4)_3Cl$ vs. pH, as calculated using VMinteq software [49]. Measured Pb, Zn and Cd concentrations during the leaching tests with distilled water are also included in the chart.

their sorption on amorphous or crystalline Fe(III) oxyhydroxides [52–54]. According to the data compiled by Dzombak and Morel [52], the pH edge for Pb adsorption on amorphous hydrous ferric oxides (HFO) is located to relatively acidic pH values, i.e. between 3.5 and 6.0 (when total Fe = 1×10^{-3} M and total Pb = 5×10^{-6} M). The corresponding adsorption edges for Zn and Cd are located at pHs 5.5–7.0 and 6.0–7.5, respectively. The exact position of pH edge depends on the relative amounts of metals and Fe oxide, but the general trend does not change. A similar trend is also observed during the sorption of metals on more crystalline oxides, such as the ferrihydrite or the goethite [53,54]. The ability of Pb to be strongly retained by the Fe(III) oxyhydroxides at pHs as low as 6.0 can explain the positive effect of $FeSO_4$ additions on Pb stability (see Fig. 3), despite the acidification of soil. On the contrary the decrease of soil pH below the initial value of 7.8 mobilized Zn and Cd, without any secondary adsorption on the surface of Fe(III) hydroxides (Figs. 6 and 7 at PO_4 0 M/M).

At the highest ferrous sulfate addition ratio (20 M/M), Zn and Cd concentrations in the water extracts decrease from 32,000 to $6700 \mu g L^{-1}$ and from 790 to $150 \mu g L^{-1}$ respectively, with the increase of phosphate addition ratio from 0 to 2.5 M/M. This is an indication that Zn and Cd can form relatively insoluble phosphates, which can stabilize part of the mobilized Zn and Cd. It should be noted that Zn and Cd cannot form stable compounds similar to Pb-pyromorphite [17]. The simple Zn and Cd orthophosphates, i.e. $Zn_3(PO_4)_2$, $Cd_3(PO_4)_2$, are much more soluble compared to Pb-pyromorphite as seen in Fig. 8. However, in most studies Zn and Cd were found to be associated with other phosphate compounds, such as the hydroxylapatite, $Ca_5(PO_4)_3(OH)$. Panfili et al. [55] have identified Zn-rich hydroxylapatite phases in sediments treated with phosphates. On the other hand, Raicevic et al. [17] have demonstrated that Cd can be retained even inside the crystal lattice of the mineral with a combined mechanism of surface precipitation and ion diffusion.

The results indicate that due to the coexistence of Pb, As, Zn and Cd, the treatment scheme should be completed with an additional step aiming at increasing soil pH at the initial slightly alkaline values. Addition of lime or limestone is often applied to avoid the acidification of soil [56]. However, pH correction should be carried out at a later stage, because the initial acidification of soil was found to favor the stabilization of Pb, probably through the partial dissolution of existing Pb phases that makes more Pb available for precipitation in the form of pyromorphite.

3.4. Biological tests

The metal uptake results are presented in Figs. 9–12. As seen in Fig. 9 the results of Pb uptake present significant scatter, however as an overall trend it is observed that Pb uptake by plants decreases by

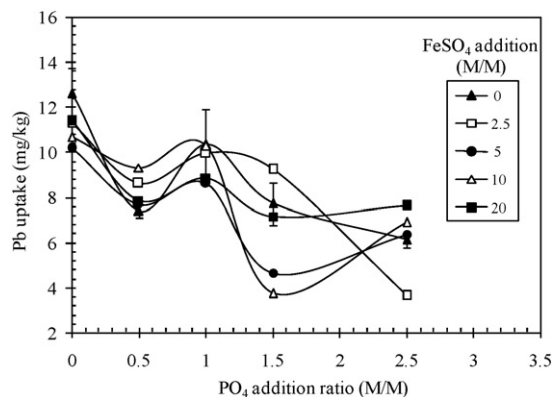


Fig. 9. Effect of PO_4 and $FeSO_4$ addition ratios on Pb uptake by plants.

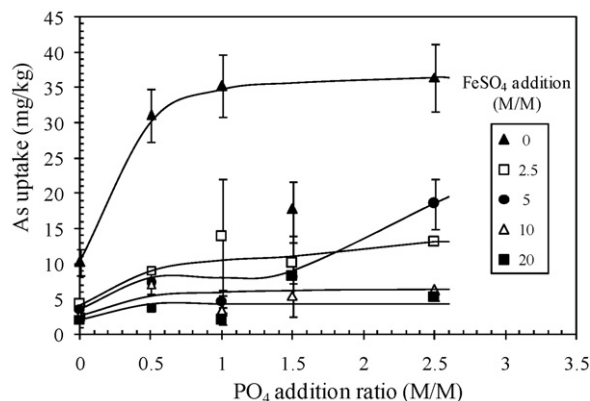


Fig. 10. Effect of PO_4 and $FeSO_4$ addition ratios on As uptake by plants.

increasing phosphates addition ratio from 0 to 2.5 M/M. The ferrous sulfate addition ratio has not any effect on Pb uptake by plants for almost all the phosphates addition ratios examined. When no phosphate is added in the soil Pb uptake varies between 10.2 and 12.6 mg kg^{-1} . At the highest dose of phosphate, 2.5 M/M, the uptake ranges between 3.6 and 7.6 mg kg^{-1} .

Arsenic uptake by plants increased from 10 mg kg^{-1} to approximately 35 mg kg^{-1} by increasing phosphates addition ratio from 0 to 2.5 M/M, respectively (Fig. 10), which is attributed to the increase of As mobility due to phosphates addition, as has been already observed during the leaching tests (Figs. 4 and 5). However, by increasing the quantity of $FeSO_4$ in the soil-phosphates mixture, the enhanced As uptake by plants was reduced to lower

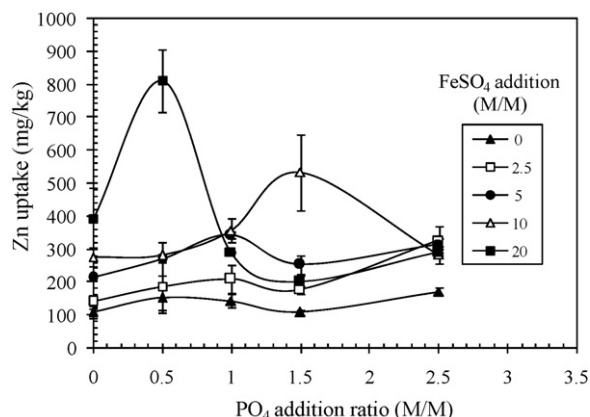


Fig. 11. Effect of PO_4 and $FeSO_4$ addition ratios on Zn uptake by plants.

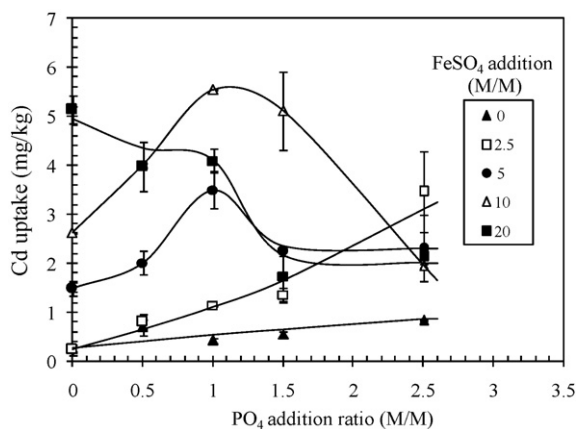


Fig. 12. Effect of PO₄ and FeSO₄ addition ratios on Cd uptake by plants.

values (Fig. 10). At the maximum FeSO₄ addition ratio applied the As uptake was not affected by the addition of phosphates and remained almost constant to less than 5 mg kg⁻¹.

The results of zinc and cadmium uptake by plants are presented in Figs. 11 and 12 respectively. It is seen as a general trend that Zn uptake increases by increasing FeSO₄ addition ratio from 0 to 20 M/M. The increase of Zn uptake by plants by increasing ferrous sulfate addition ratio is more abrupt at low phosphate addition ratios. At 0 M/M PO₄, concentration of Zn in the plant tissues increases from 108 mg kg⁻¹ in the untreated soil to 400 mg kg⁻¹ in the soil treated with 20 M/M FeSO₄. At the dose of 2.5 M/M PO₄ Zn uptake increase from 170 to 330 mg kg⁻¹, when the FeSO₄ dose increases from 0 to 20 M/M.

Cd uptake by plants increased by increasing the dose of FeSO₄, in agreement with the observed increase of Cd solubility in water due to the acidification of soil. At 0 M/M PO₄ phytoaccumulation of Cd increases from 0.25 to 5.2 mg kg⁻¹ when the dose of FeSO₄ increases from 0 to 20 M/M. At the maximum PO₄ dose, 2.5 M/M, Cd increases from 0.83 to 3.8 mg kg⁻¹.

In general, the pattern of Zn and Cd phytoaccumulation reflects the two antagonistic actions taking place by adding phosphates and ferrous iron in the soil mixture: (a) the decrease of pH due mainly to iron sulfate addition and partially to the addition of phosphates addition, and (b) the co-precipitation of Zn and Cd in the form of mixed metal phosphates. These two effects result in either increased or decreased total Zn or Cd solubility affecting their uptake by plants.

4. Conclusions

Based on the results of the present study, monocalcium phosphate and/or iron sulfate addition in contaminated soil had a positive effect on Pb immobilization. However, monocalcium phosphate addition resulted in a significant As mobilization. This adverse effect was restricted by adding ferrous iron sulfate. It was found that a phosphates addition ratio of 1.5 M/M or higher is required to effectively immobilize Pb in Lavrion soil sample tested and address the adverse effect of Pb mobilization observed at iron sulfate addition ratios higher than 5 M/M. Furthermore, it was found that the minimum phosphate and iron sulfates addition ratio that result in the reduction of Pb and As dissolved concentration in the water extracts below the EU drinking water values is 1.5 and 10 M/M, respectively. An undesirable side effect is that Ca(H₂PO₄)₂ and FeSO₄ additions decreased soil pH from the initial value 7.8 to values as low as 5.6, causing the mobilization of Zn and Cd. To avoid this effect the treatment scheme should be combined with the addition of lime or limestone, which is a common agricultural prac-

tice, to obtain the effective control of soil pH at neutral or slightly alkaline values.

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