

## Effect of Phosphate and Iron Oxide on Mobility of Lead and Arsenic in Shooting Range Soils

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### Abstract

Soil pollution in shooting range soils is a public health concern due to the presence of toxic elements such as lead and arsenic. This study evaluated the effectiveness of phosphate and Fe-oxide amendments to reduce the mobility of Pb and As in six shooting range soils in Florida using leaching tests, mineralogical analysis, kinetic study and geochemical modeling with Visual MINTEQ. Phosphate (phosphate rock and phosphoric acid) was applied either singly or in combination with iron-oxide at different Fe/As molar ratios. TCLP-Pb concentrations were reduced from 19-2422 to 1.75-5.16 mg/L in P treated soils, indicating that TCLP-Pb was reduced below or close to the regulatory limit of 5 mg/L. Even though the SPLP-Pb also reduced in P-treated soils, it did not fall below regulatory limit of 15 µg/L. P treatment also reduced TCLP-As probably by formation of arsenate-phosphate phases. However, P treatment increased SPLP-As but addition of iron oxide reduced SPLP-As below sole P treatments. TCLP-As decreased by 60% to 80% in iron oxide treated soils. A kinetic study showed that Pb immobilization by P can occur during TCLP extraction. Hydroxypyromorphite and lead-phosphate were predicted by Visual MINTEQ as the principal solubility-controlling phase for soluble Pb in both TCLP and SPLP systems. Though, there was high leaching of P, addition of iron oxides to P treated soils also reduced leaching of P. Phosphate and iron oxide can be used to reduce mobility of Pb and As in contaminated shooting range soils.

**Keywords:** Visual MINTEQ, TCLP, SPLP, Pb weathering, Mobilization, Pb minerals, Leaching.

### Introduction

Recreational shooting is a popular sport as evidenced by the 9,000 shooting ranges present in the US<sup>1</sup>. It is not surprising then that total soil Pb concentrations up to 7% have been reported in shooting ranges<sup>2</sup>. The primary contaminant in Pb bullets is Pb since lead shot contains 95-97% Pb by weight. Other contaminants found in Pb shot are Sb (0.4-2.0 %), arsenic (0.2-0.8%); Sn, Se, Mn, Cd, Cr, Cu, and Ni (> 30 mg/kg)<sup>3</sup>. Traditionally lead shot in soil was believed to be stable but experimental evidence indicated that metallic lead is unstable under typical soil conditions<sup>4-6</sup>.

Once Pb bullets are deposited into soils, metallic Pb is oxidized to cationic Pb<sup>2+</sup> which forms secondary minerals such as litharge (PbO), cerussite [Pb(CO<sub>3</sub>)<sub>2</sub>], hydrocerussite [Pb(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>] with small amounts of anglesite (PbSO<sub>4</sub>)<sup>7-13</sup>. Weathering and transformation of metallic Pb may increase Pb bioavailability to organisms that are exposed to Pb contaminated shooting range soils<sup>12</sup>. It is imperative therefore to find ways to limit Pb migration in shooting range soils.

Phosphate treatment has been recommended by USEPA for application in shooting range soils because it can stabilize Pb in soils<sup>14</sup>. Phosphate reacts with Pb in the soil to form insoluble lead phosphates, or pyromorphites. However, the addition of

phosphates may have some limitations regarding its field application because of slow dissolution of Pb and P<sup>15-16</sup>. The addition of an acid is expected to accelerate the immobilization process by increasing dissolution of Pb and P minerals in the soil. Even though Pb has been widely studied and monitored at shooting ranges, it's not the only contaminant. Arsenic contamination of shooting range soils has also been reported in previous studies<sup>17,18</sup>. Arsenate and phosphate are analogs and both compete for exchange sites in the soil<sup>19</sup>.

To reduce potential phosphate-induced As release in P treated shooting range soils, a combination of phosphate and iron oxide could be a good option, since iron is effective in As sorption<sup>20</sup>. Addition of iron based amendments is a cost effective method of remediation of metal/metalloid contaminated soils, including lead and arsenic<sup>21-24</sup>.

There have been several studies on P induced Pb immobilization but none has studied the simultaneous immobilization of Pb and As by phosphate and iron oxide in contaminated shooting range soils to our knowledge.

Hence, the objective of this study is i. to examine the effectiveness of phosphate sources on Pb immobilization in the presence of iron oxide ii. to investigate the effect of iron oxide on Pb and As mobility in shooting range soils of Florida.

## Materials and Methods

**Experimental Set Up:** The effect of phosphate (P) and iron oxide (Fe-oxide) on the immobilization of Pb and As was studied. Six surface soils (0-20 cm) were collected from the berm of three shooting ranges designated as O, OS, and G (Table-1). The collected soils were air-dried, gently ground, and passed through 2mm sieve. Soil characteristics such as total Pb, total Ca, water-soluble Pb, soil pH, particle size distribution, cation exchange capacity (CEC), organic matter content, oxalate extractable Fe and Al were determined in sieved soils before experimentation<sup>25-29</sup>. Detailed methods of analysis are described in another paper<sup>2</sup>. P was added to the soil at a P/Pb molar ratio (MR) of 4:1. About 33% of the added P was added as phosphoric acid (PA, more soluble form) and 67% was from phosphate rock (PR, less soluble form). The PR used in this study was obtained from Potash Corporation Saskatchewan, Inc. (White Springs, Florida). Both iron oxide and PA were obtained from Fisher Scientific Inc. (Pittsburgh, PA). Fe-oxide was added at 9 different Fe/As molar ratios (3 – 900) in O-1 and 7 different Fe/As molar ratios (3 - 180) in O-2. The soil was thoroughly mixed with PR and Fe-oxide before PA was added and mixed again. Each treatment was replicated four times. 400 g of soil was incubated in glass jars and kept under room temperature at 60% field capacity for 21 days. In the second incubation experiment, four soils, OS-1, OS-3, G-1, and G-2, were used. All the experimental details were same as described for the first incubation experiment except that only two levels of iron oxide treatments (Fe/As MR 20 and 100) were used in the second study.

**Leaching Test and Geochemical Modelling:** After the 21 d incubation, toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP) extractions were carried out. Batch TCLP extraction was performed using a modified EPA Method 1311<sup>30</sup>. Batch SPLP extraction was performed by a modified USEPA Method 1312 using the extraction fluid No 1 at a soil: solution ratio of 1:20<sup>30,31</sup>. The concentrations of Pb, As, Ca and P in the extracts were analyzed. Arsenic content in the extracts was analyzed on a graphite furnace atomic absorption spectrometer (AA240Z, Varian Inc., Walnut Creek, CA) following EPA Method 7060<sup>28</sup>. P analysis was done colorimetrically using a modified molybdenum blue method on a UV-vis spectrometer (UV 160U visible spectrometer, Shimadzu Corporation, Japan)<sup>32</sup>. The contents of Pb and Ca were determined using a flame atomic absorption spectrophotometer (FAAS; Varian 220, Walnut Creek, CA). NELAC quality assurance and control procedures were followed during analysis<sup>33</sup>. Wherever available, standard soil reference materials and spikes were used to determine accuracy. Duplicate preparation and analyses on selected samples were performed to assess the precision of each run (with  $\leq 10\%$  relative percentage difference). The concentrations from TCLP and SPLP extractions were entered into the Visual MINTEQ model, version 2.51<sup>34</sup>. Total metal analyses from Table-1, P, Ca and Fe from the soil plus amendments, H from

the amendments, and Na and  $\text{CH}_3\text{COO}^-$  from the TCLP fluid were used as inputs.

**Pb release and P-induced Pb immobilization during TCLP extraction:** A study was conducted using soil O-1, which had the highest Pb content of 70,350 mg/kg to determine Pb release and P-induced Pb immobilization during TCLP extraction. The soil was treated with P at P/Pb molar ratio of 4.0 with two-third of P from PR and one-third of P from PA. A 250-mL aliquot of the TCLP fluid was added to 12.5 g of soil without incubation for TCLP extraction. The suspensions were tumbled at 30 rpm. Several samples were withdrawn during the 18 h period and analyzed for Pb. Separate TCLP bottles were used for each time-based sampling. The leachates collected at different time periods were filtered with a 0.2  $\mu\text{m}$  membrane filter and concentration of Pb in the filtrates was determined on FAAS.

**X-ray diffraction:** Soil samples from three ranges (O-1, OS-1 and G-1) were analyzed by X-ray diffraction (XRD; Philips Electronic Instruments, Inc., Mahwah, NJ). In addition, soil O-1 treated with P was analyzed by XRD before and after TCLP extraction to identify potential P minerals formed during the extraction. The samples were prepared by wet sieving to  $<53\mu\text{m}$  followed by air drying and gentle grinding to powder in an agate mortar. The mount of fine powder was prepared on a glass slide, which was then placed in a quartz sample holder. The X-ray diffraction patterns were analyzed and interpreted using databases<sup>35,36</sup>.

**Statistical analyses:** All statistical analyses were performed based on the generalized linear model using SAS software, version 8.02<sup>37</sup>.

## Results and Discussion

**Soil properties:** Selected physicochemical properties of the six soils tested in this research are given in Table-1. The soils were sandy with sand content ranging from 78 to 94%; the clay content was invariably under 5%. Organic matter content was low ( $<1\%$ ) in all six soils. CEC of the soils ranged from 6 to 25  $\text{cmol/kg}$  and was apparently related to clay and organic matter contents. The four soils from O and G shooting facilities had pretty similar pH in the range of 6.5-7.0, while the other two soils from OS shooting facility were more acidic with pHs of 5.1 and 5.6. Total and available Ca in the soil followed the order of  $\text{G} > \text{O} > \text{OS}$ . The total Pb concentration of the soils ranged from 1538 mg/kg in G-2 to as high as 7% in O-1. The soil with the highest total lead concentration also had the highest soil pH measured. This is in agreement with another study which suggested that weathering of Pb increases soil pH<sup>10</sup>. Water soluble Pb contents in OS-1 and OS-3 soils (16 and 12 mg/kg) were remarkably higher than other four soils, which may be attributable to their lower pH, lower oxalate Fe and lower Ca content. Total As content was highest (257 mg/kg) in O-2 while other soils had less than 12 mg/kg As. G-1 had the highest oxalate Fe and Al in the soil while the lowest oxalate Fe was recorded in OS-3.

**Table-1**  
**Selected properties of shooting range soils**

Characteristics	Soil/Range					
	O-1	O-2	OS-1	OS-3	G-1	G-2
Range characteristics						
Range type	Rifle	Shot-gun	Rifle	Rifle	Rifle	Pistol
Range size	100	30	50	200	100	25
Years of operation	18	18	43	43	9	9
Soil properties						
pH	7.04	6.63	5.10	5.55	6.84	6.53
CEC (cmol <sub>c</sub> /kg)	6.33	6.64	21.5	8.34	24.8	14.8
Total Pb (mg/g)	70.4	8.15	12.4	3.26	11.5	1.54
Total Ca (mg/g)	0.90	0.86	0.19	0.15	1.83	1.54
Total As (mg/kg)	11.6	257	1.7	0.9	4.3	1.0
Total P (mg/kg)	32.8	41.8	35.9	51.1	49.9	32.6
Water-soluble Pb (mg/kg)	0.69	0.78	15.82	12.14	4.34	2.19
Available P (mg/kg)	5.0	8.1	12.2	10.0	12.4	9.8
Available Ca (mg/kg)	171	198	85	119	723	659
Ox-Fe (mg/kg)	838	658	489	379	959	738
Ox-Al (mg/kg)	162	185	259	219	278	219
Organic matter (%)	0.22	0.73	0.72	0.71	0.90	0.66
% Sand	86.6	93.3	78.3	89.4	88	93.8
% Silt	9.5	4.2	17.2	7.9	7.1	2.9
% Clay	3.9	2.5	4.5	2.7	4.9	3.3

**Mineralogy:** XRD results (Figure-1) shows metallic lead present in both G-1 and O-1 soils confirming the possibility of fine fractions of Pb fragments in the soil. A previous study reported the significant presence of metallic lead (2.2%) in a shooting range soil with no cerussite peaks detected<sup>38</sup>. They suggested that this indicated a lower rate of weathering in the soil. Thus, the absence of metallic lead in OS-1 soil may

indicate a higher rate of weathering of the metallic lead in the soil. It has been reported that transformation of all metallic lead to secondary minerals such as litharge and hydrocerrussite occurred after five days of incubation<sup>12</sup>. A previous study showed that crust materials on weathered bullet was composed of a mixture of litharge ( $\alpha$ -PbO), hydrocerrussite [ $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ] and cerrussite ( $\text{PbCO}_3$ )<sup>39</sup>. All of these three

minerals were detected by XRD for O-1 soil (Figure 1). The absence of such peaks in G-1 and OS-1 soils may be due to their lower total Pb contents and carbonate content. However, calcite was identified as one of the minerals in G-1 soil which is consistent with its high calcium content (Table-1).

**Effects of Phosphate and Iron Oxide on Leachability of Pb and As:** In agreement with past research, this study showed that phosphate treatment effectively stabilized Pb and reduced its mobility in Pb contaminated soils through formation of insoluble pyromorphite in the soil<sup>40,41</sup>. Phosphate treatment reduced Pb concentrations in TCLP extracts of soil O-1 from 2,422 mg/L to below 2.7 mg/L which corresponds to 897 times reduction in TCLP-Pb (Figure-2). In O-2 soil, Pb concentrations in TCLP-Pb concentration decreased from 202 mg/L to below 3.8 mg/L in P-treated soils (Figure-2). Similarly, P-treatment resulted in drastic reduction of TCLP-Pb in OS-1, OS-3, G-1, and G-2 with percentage reduction of TCLP-Pb ranging from 94 to 99%. All the P-treated soils passed the regulatory limit of TCLP test (5 mg/L) except soil OS-3 with the value of 5.14 mg/L. Addition of Fe-oxide to the P treatment resulted in increased reduction of TCLP-Pb at molar ratio (MR) greater than 9 in O-1; MR of 180 in O-2, MR of 100 in OS-1; MR of 20 & 100 in OS-3. Addition of Fe-oxide to the P treatment had no significant effect in G-1 and G-2 probably because of their high Ca content (1.54-1.83mg/g). The presence of Ca enhances the amount of phosphate adsorbed on Fe-oxide which reduces the amount of P available for Pb immobilization<sup>42</sup>.

Unlike TCLP-Pb concentrations in the control soils, the SPLP-Pb concentrations in all six untreated soils were manifolds lower and ranged from only 0.34 to 3.8 mg/L (Figure-3) showing that most of the Pb in the soil was insoluble in water. P-treatment significantly reduced SPLP-Pb concentrations in all soils except G-2. Both sole P and mixed P/ Fe-oxide treatments did not reduce SPLP-Pb below the regulatory limit of 15µg/L for all six soils. Addition of Fe-oxide to the P treated soils further reduced SPLP-Pb in OS-3 and O-2 at MR 180; had no significant effect in OS-1 and G-2 while it increased SPLP-Pb in O-1 at MR 3, 18, 30; O-2 at MR<180; and G-1 at MR 20. In a similar experiment, the iron sulphate added to a P treated (Calcium magnesium phosphate, PR, SSP) Pb/Zn mine soil reduced concentration of water soluble As but increased concentration of CaCl<sub>2</sub> extractable Pb<sup>43</sup>. As suggested earlier, P may be adsorbed by iron oxide thereby reducing the amount of P available for Pb immobilization. The adsorption of the phosphate oxyanion by Fe-oxide has been reported in literature<sup>44,45</sup>.

Addition of P not only had significant effect on Pb mobility, but also on As mobility. Addition of P alone effectively reduced the TCLP-As concentrations in all soils except O-1 (Tables-2 and 3). A recent study reported that a calcium-phosphate treatment helped immobilize arsenic in arsenic contaminated soils probably due to precipitation of arsenic-phosphate phases<sup>46</sup>. They suggested that the added ortho-phosphoric acid flushed out

the arsenic which co-precipitated as Ca-phosphate-arsenate phases. Arsenic did not co-precipitate with P in the absence of additional calcium. Adding Fe-oxide further increased the reduction of TCLP-As in the soils. The addition of Fe-oxide led to increasing reduction of TCLP-As with increasing Fe/As MR in O-1 and O-2. Iron oxide treatment at Fe/As molar ratio of 20 significantly reduced TCLP-As over sole P treatment in OS-1, OS-3, and G-1 (Table-3). The Fe/As ratio of 100 resulted in significant reduction of TCLP-As in OS-1 and G-1 but not in OS-3 and G-2 (Table-3).

Different from the effect on TCLP-As, after adding P alone SPLP-As increased over control (untreated soils) for all six soils (Tables-2 and 3), suggesting P-induced As mobilization. The addition of phosphoric acid may also reduce soil pH which may solubilize arsenate thereby increasing its mobility in the soil. Lowering of soil pH may be much more evident in SPLP extractions because of its low buffering capacity. It is also possible that the higher concentration of phosphate anion in the soil solution led to displacement of the arsenate anion on exchange sites in the soils since they are both group V elements with similar chemical properties. The mobilization of arsenic in contaminated soils is not desirable because of its health effects. The addition of Fe-oxide to the P treatment may be able to reduce arsenic mobility. Results show that the addition of Fe-oxide resulted in lower SPLP-As concentrations than sole P treatments in all soils except OS-3. In O-2 soil, addition of Fe-oxide reduced the SPLP-As concentrations below the untreated at Fe/As molar ratios greater than 30 (Table-2). The reduction in As mobility after addition of Fe-oxide may be due to adsorption and formation of arsenate surface complexes on Fe-oxide<sup>47</sup>.

**Soil Chemistry and Mineralogy: Kinetics of P-induced Pb immobilization during TCLP extraction:** Kinetics of Pb release from untreated and P-treated (at P/Pb=4) O-1 soil during 18 h TCLP extraction was studied. The P-treated soil with no incubation was used to determine P-induced Pb immobilization during TCLP extraction. TCLP-Pb in untreated soils (Figure-4) increased steadily with time and reached the maximum of 2,025 mg/L after 18 h. Release of Pb from P-treated soil (Figure-4) also increased with time, peaked at 16 h (1.41 mg/L), and then showed a decrease. Interestingly, release of Pb at different extraction durations from the P-treated soil during TCLP extraction was around 1400 to 7200 times lower than from untreated soil. This suggests that P-induced Pb-immobilization could have occurred simultaneously during TCLP extraction. Similar results were obtained when linear combinations fittings of X-ray absorption near edge structure (LCF-XANES) spectra was used to show the transformation of Pb into pyromorphite precipitate during the TCLP extraction<sup>48</sup>. Another study also reported dissolution of metallic Pb and re-precipitation as cerussite (PbCO<sub>3</sub>) during TCLP leaching test which prevented the system from reaching equilibrium at the end of the extraction (after 18h)<sup>49</sup>.

**Table-2**  
**Effect of P and Fe-oxide treatment on TCLP and SPLP As for the two soils included in the first batch of experiment**

Treatments	TCLP As <sup>c</sup>		SPLP As <sup>c</sup>	
	O-1	O-2	O-1	O-2
Untreated	8.2±0.8	761±30.1	3.8±0.9	47.5±2.6
Treated with P	21.5±2.0	107±3.8	19.3±0.4	103.3±28.9
Fe/As MR <sup>a</sup> (P+Fe-oxide)				
3	18.6±2.9	92.7±3.8	18.9±2.5	82.8±9.4
9	17.6±1.7	78.9±4.9	18.8±0.1	71.2±3.1
18	17.5±1.8	63.1±7.5	16.2±1.5	58.9±6.1
30	13.1±2.0	46.4±7.6	16.2±1.7	41.3±4.6
60	NT <sup>b</sup>	43.2±3.7	NT	35.3±4.2
90	14.8±3.5	39.4±1.3	13.1±1.8	41.8±2.4
180	14.8±3.2	27.1±1.6	12.5±2.7	22.1±1.5
300	9.6±1.7	NT	10.6±1.7	NT
600	10.3±2.6	NT	8.2±1.6	NT
900	7.6±1.9	NT	6.4±2.1	NT

<sup>a</sup>MR=molar ratio <sup>b</sup>NT=not tested <sup>c</sup>Mean ± standard error.

**Table-3**  
**Effect of P and Fe-oxide treatment on TCLP and SPLP As in four soils with P/Pb MR=4.0 and different Fe/As MR**

Shooting range	Control	0	Fe/As MR of Fe-oxide treatment	
			20	100
TCLP As (µg/L) <sup>§</sup>				
OS-1	41.0±5.4	12.7±0.5	10.4±0.3	8.7±0.4
OS-3	15.8±1.6	5.4±0.4	4.6±0.2	6.1±0.8
G-1	41.5±2.1	14.7±0.6	10.1±0.5	7.4±0.5
G-2	30.7±4.1	8.0±0.5	8.5±1.4	7.2±0.8
SPLP As (µg/L)				
OS-1	3.4±0.3	12.2±0.6	10.9±0.6	7.3±0.3
OS-3	5.9±0.4	6.6±0.6	8.9±1.2	7.6±0.4
G-1	3.3±0.5	16.7±1.0	15.7±0.2	11.6±0.7
G-2	7.3±0.8	9.5±0.6	7.8±0.5	8.1±1.6

<sup>§</sup>MR=molar ratio <sup>§</sup>Mean±standard error

**Table-4**  
**Geochemical modeling results for TCLP and SPLP Pb (mg/L) in the six soils treated with phosphate rock at P/Pb molar ratio of 4.0 (no Fe-oxide) and incubated for 21 days**

Parameter	O-1	O-2	OS-1	OS-3	G-1	G-2
TCLP						
Model	144	6.05	7.26	2.29	11.6	0.49
Actual	2.69	3.79	2.07	5.16	2.67	2.80
SPLP						
Model	1.43	0.56	0.46	0.34	1.44	0.13
Actual	0.56	0.54	0.39	0.81	2.87	0.30

**Mineralogical analysis of O-1soil:** Dissolution and formation of Pb-bearing minerals as a consequence of P-treatment was investigated on <53  $\mu\text{m}$  size fraction of O-1 soil using X-ray diffraction under various conditions. The results show that O-1 soil contains Pb predominantly as cerussite, a crystalline  $\text{PbCO}_3$  mineral (Figure-5). The cerussite peaks in the untreated soil disappeared after TCLP extraction, suggesting that the TCLP fluid dissolved  $\text{PbCO}_3$  to below the detection limit of XRD. In sharp contrast, in the P-treated soil, cerussite peaks was present after TCLP extraction, with reduced intensities. Thus the results confirmed that P-treatment stabilized the cerussite as well as formed new Pb-phosphate crystalline solid phases, resistant to TCLP extraction. The low solubility of lead phosphate or pyromorphite reduces its mobility in Pb contaminated shooting range soils<sup>50</sup>.

**Geochemical modeling:** The TCLP and SPLP leaching data from all six soils were modeled using Visual MINTEQ for the treatment with P at P/Pb molar ratio (MR) of 4.0 without any Fe-oxide. However, only the TCLP leaching data for the treatments with P at P/Pb MR of 4.0 plus Fe-oxide at Fe/As MR of 90 and 900 for O-1 and O-2 soils were modeled with Visual MINTEQ to identify the formation of potential solid phases involving Fe. Modeling results on pH, Ca, and P for both TCLP and SPLP data of all six shooting range soils were in good agreement with the respective measured values. On the contrary, the predicted TCLP-Pb values were not in close agreement with actual TCLP-Pb showing an overestimation for O-1, O-2, OS-1 and G-1, and underestimation for OS-3 and G-2 soils (Tables 4). The overestimation of TCLP-Pb was especially large for O-1 soil treated with P (Table 4) probably because of its high Pb concentration (7%).

In comparison to TCLP-Pb, the modeled SPLP-Pb for all six soils was in better agreement with the measured values (Table-4). This implies that the problem of over estimation and under estimation may be with the TCLP leaching test. The TCLP procedure is prone to over-estimate or under-estimate Pb

leachability because it did not produce stabilized results by standard time (18h)<sup>51</sup>. A past study reported similar results and suggested that an extended tumbling time beyond the standard 18 h may be required for the TCLP test to reach an equilibrium<sup>48</sup>. This inability to reach equilibrium was attributed to the presence of soluble Pb species in the solid residue of shooting range soils with pH 6-8<sup>48</sup>. Analytical SPLP results were consistent with those obtained from modeling because SPLP leaching was able to achieve equilibrium within the standard 18 h leaching period<sup>49</sup>. These results show that SPLP estimates leachability of Pb more accurately than TCLP in shooting range soils.

In both TCLP and SPLP systems without Fe-oxide treatment (Table 4), excess phosphate was precipitated predominantly as hydroxyapatite  $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ ,  $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$ , and tricalcium-phosphates (both amorphous and crystalline whitlockite) with some monetite ( $\text{CaHPO}_4$ ) and brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ). Hydroxypyromorphite  $[\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2]$  and lead-phosphate  $[\text{Pb}_3(\text{PO}_4)_2]$  were predicted as the principal solubility-controlling phase for soluble Pb in both TCLP and SPLP systems. Two other solid phases such as  $\text{Pb}(\text{OH})_2$  and  $\text{PbHPO}_4$  were also predicted with lower orders of saturation index for controlling soluble Pb. The model predicted  $\text{Pb}_3(\text{AsO}_4)_2$  in controlling soluble As in both TCLP and SPLP systems for O-1 soil and only in TCLP system for O-2 and G-1 soils. Both TCLP and SPLP systems of OS-1, OS-3, and G-2 soils were under-saturated with respect to the ion activity product for the formation of  $\text{Pb}_3(\text{AsO}_4)_2$  solid phase probably owing to the limitation of low As levels. The model predicted  $\text{Pb}_3(\text{AsO}_4)_2$  rather than  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$  as a precipitate controlling soluble As in the TCLP system of O-1 soil treated with P and Fe-oxide, probably due to very high Pb content of this soil. But in P and Fe-oxide treated O-2 soil (having higher As content), model prediction indicated undersaturation of the TCLP system with respect to the formation  $\text{Pb}_3(\text{AsO}_4)_2$ ; and  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$  was indeed predicted as the solid phase controlling soluble As.

**P leaching:** Phosphate concentrations were measured in both TCLP and SPLP leachates. Phosphate leaching was substantial in all P treated samples; the highest P concentrations of 585 mg/L in TCLP and 398 mg/L in SPLP leachates were observed for O-1 soil, while the lowest concentrations of 26 mg/L in TCLP and 20 mg/L in SPLP leachates were observed in G-2 which relates well with the P-dosing (P:Pb; 4:1) dictated by the Pb content (Table-1). The high P leaching may also be due to the low P adsorption capacity of sandy soils. Up to 90% of P applied to sandy soils may be lost through leaching and drainage<sup>52</sup>. This is confirmed in this study with greater leaching of TCLP-P in the two soils (O-2 and G-2) with highest sand content (Table-1). Leaching of P after phosphate induced Pb immobilization has been reported in a multi-metal contaminated

soil and shooting range soils<sup>16,53</sup>. The phosphate leaching potential was evaluated for all P-treated soils based on P-leachability ratios calculated similarly to the Pb leachability ratio. For the O-1 soil, phosphate leaching was relatively low at 28% for TCLP and 19% for SPLP. It was as high as 61% for TCLP leachate and 41% for SPLP leachate from O-2 soil. O-2 soil had the lowest clay content (Table-1) and the highest P leachability during TCLP extraction. Inclusion of Fe-oxide at Fe/As MR of 90 reduced the P-leachability ratio TCLP from 28% to 21% for O-1 and from 61% to 36% in O-2 soils probably due to formation of strengite. However, dosing of Fe-oxide at Fe/As MR of 900 for O-1 and of 180 for O-2 had hardly any additional benefit over the Fe/As MR of 90 in reducing P-leachability ratio.

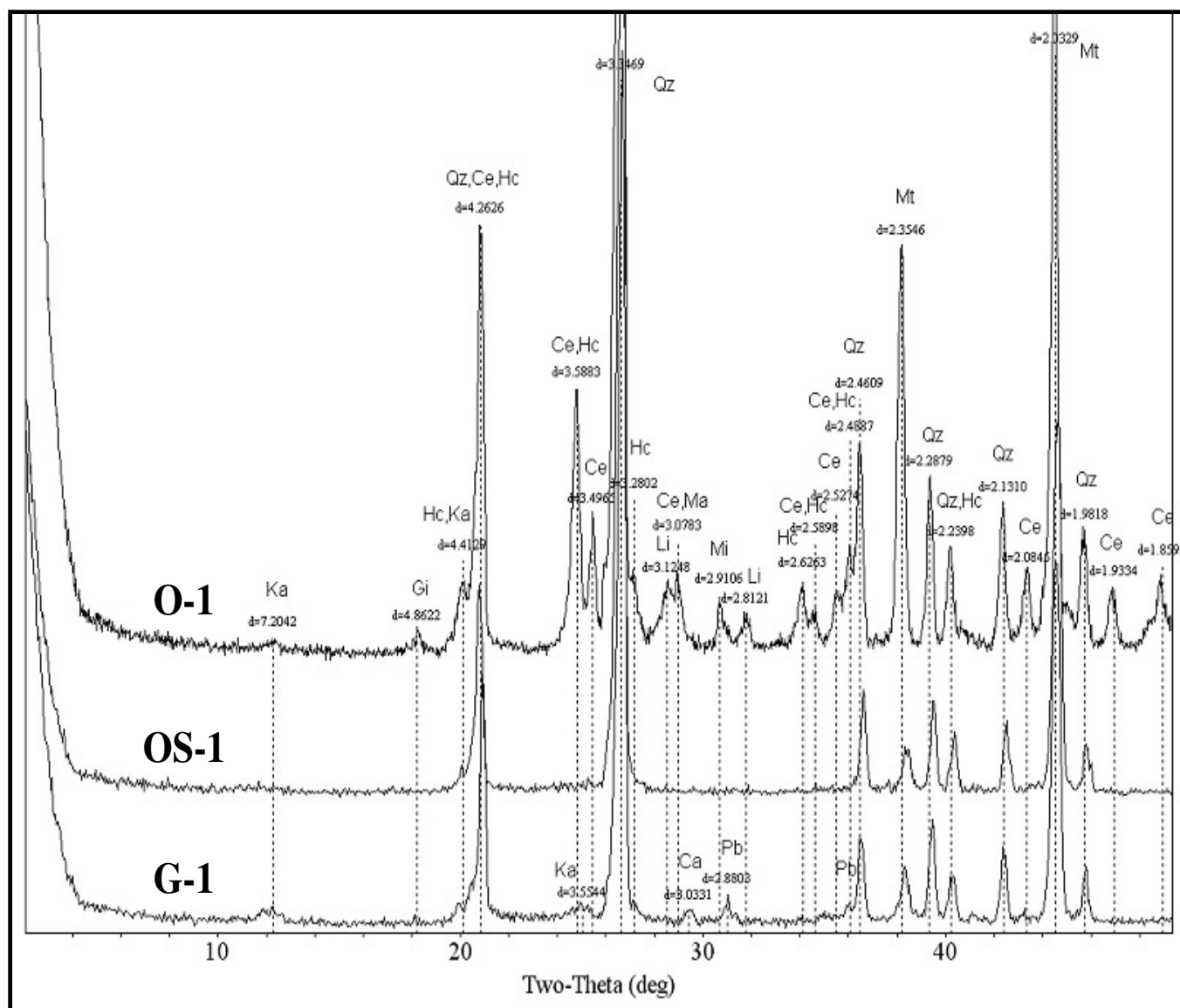
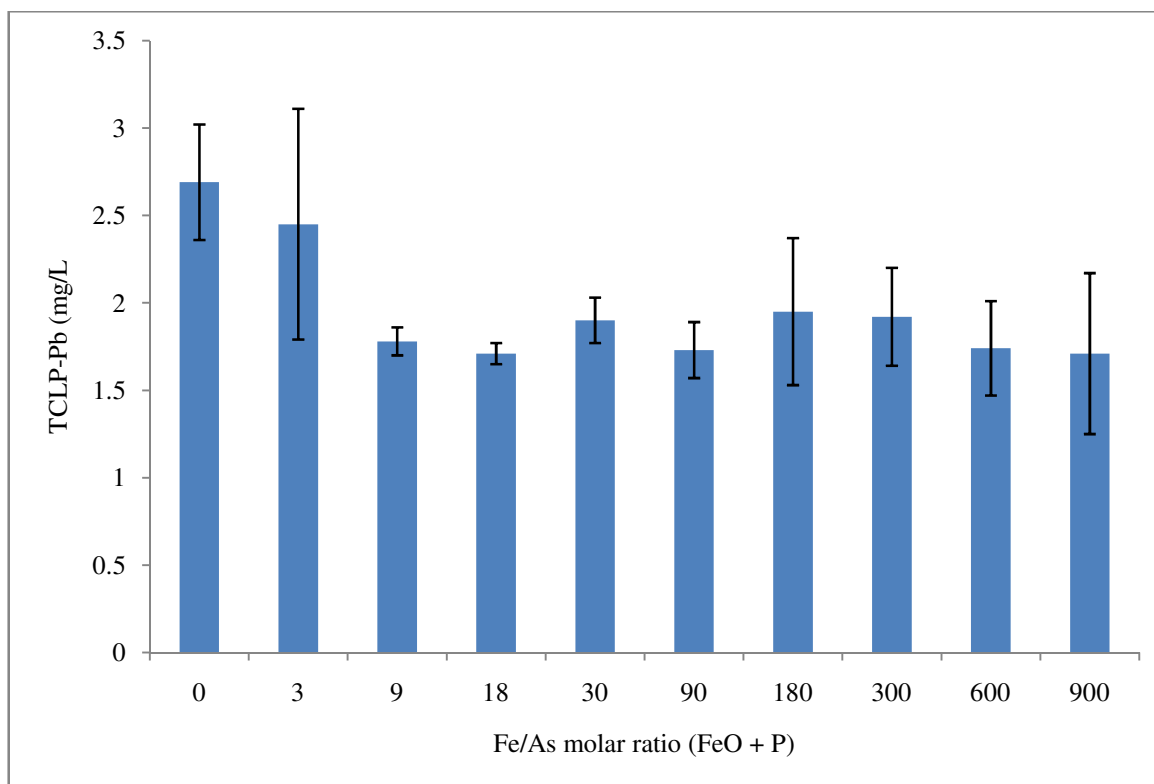
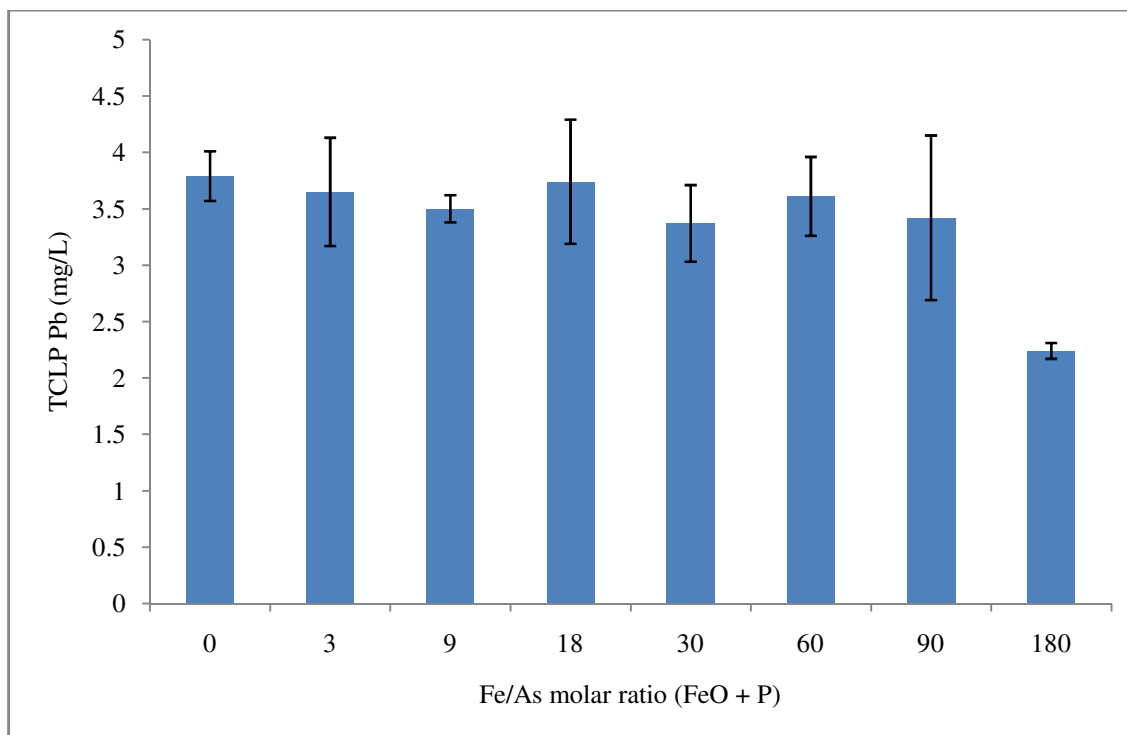


Figure-1

X-ray diffraction of <53µm fraction of three selected shooting range soils in Florida. Ka-kaolinite, Gi-gibbsite, Qz-quartz, Ce-cerussite, Hc-hydrocerussite, Li-litharge, Ma-massicot, mi-Minimum, Ca-calcite, Pb-metallic lead, Mt-sample mount

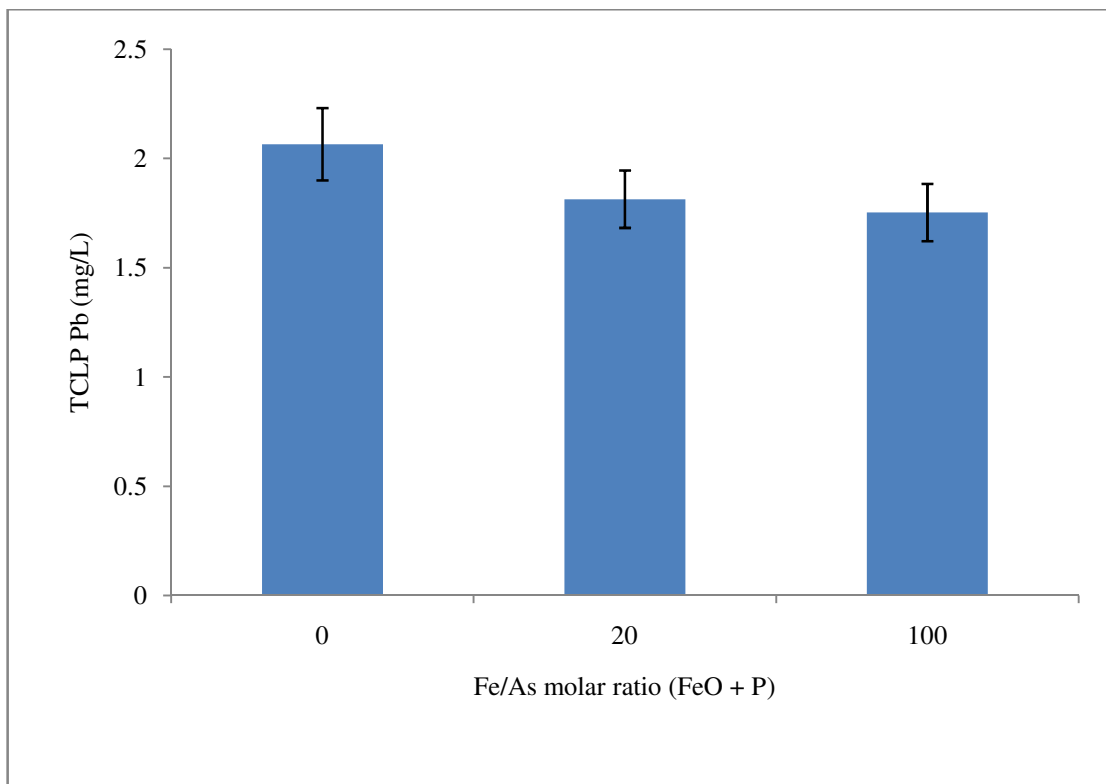


**Figure-2A**  
Range O-1: rifle-1 mid berm soil (TCLP Pb of untreated soil: 2422±333 mg/L)

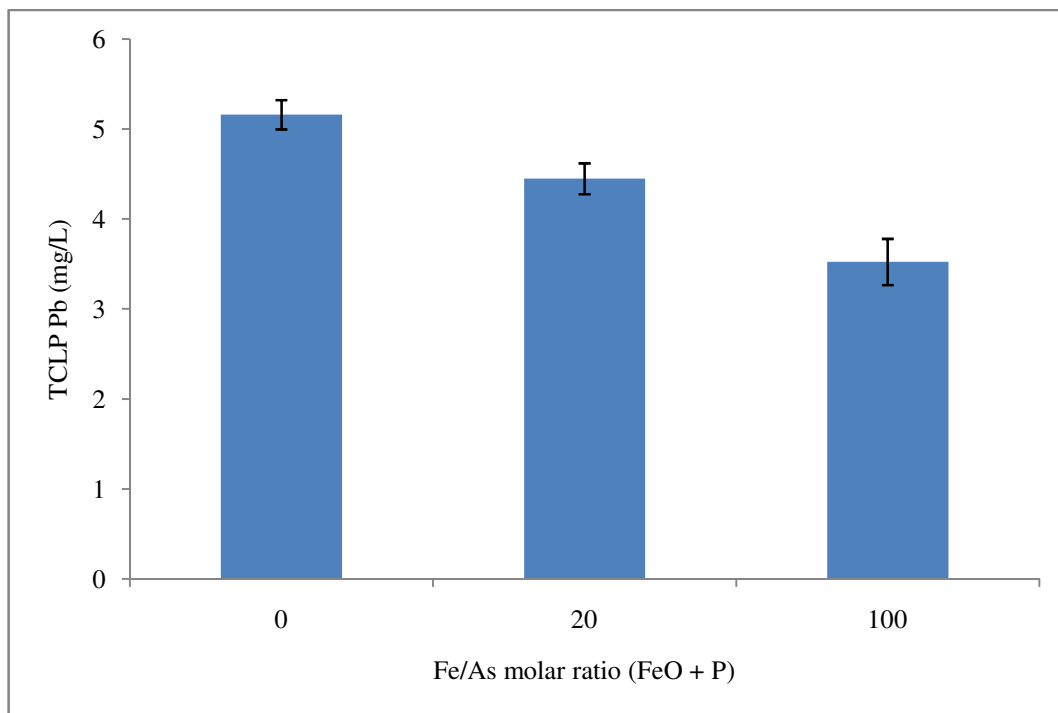


**Figure-2B**  
Range O-2: shot-gun-1 mid berm soil (TCLP Pb of untreated soil: 202±17 mg/L)

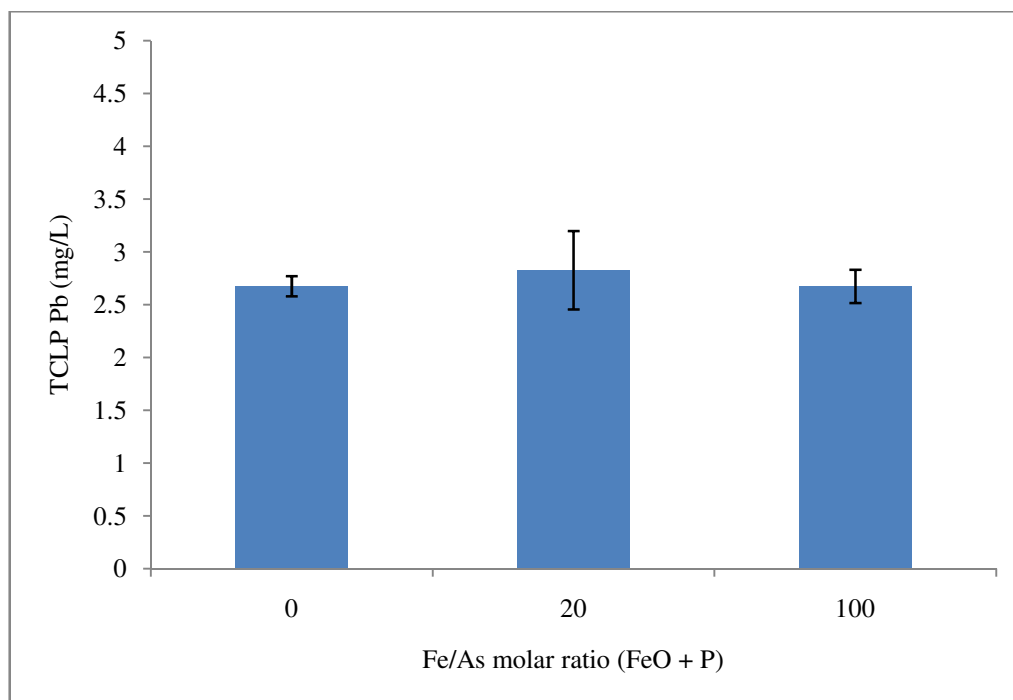




**Figure-2C**  
Range OS-1: rifle-2 mid berm soil (TCLP Pb of untreated soil: 226±10 mg/L)

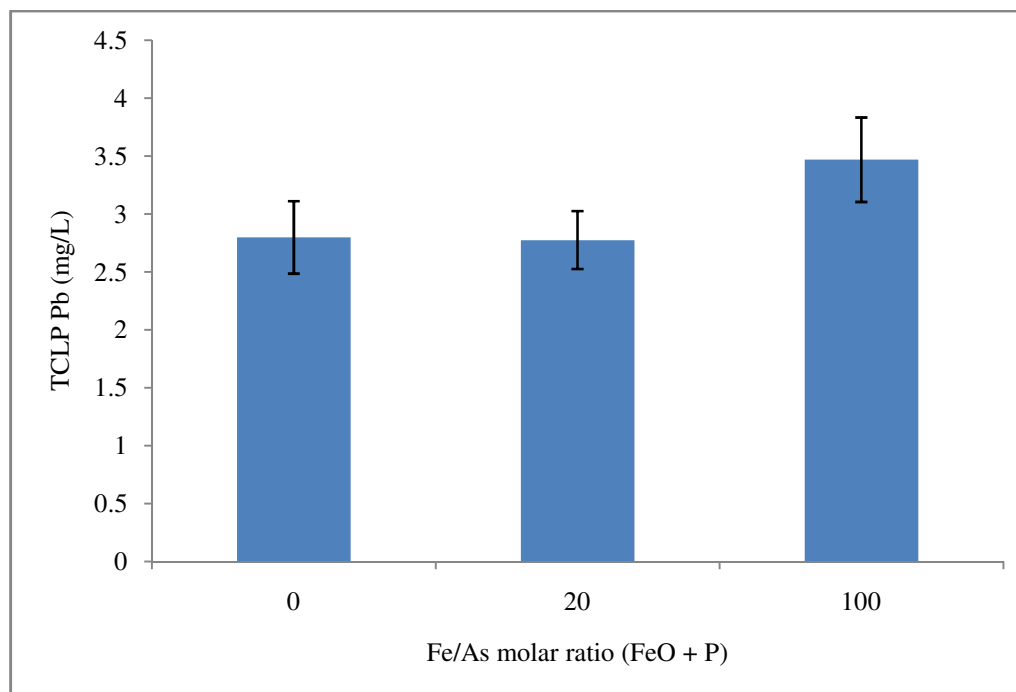


**Figure-2D**  
Range OS-3: rifle-3 mid berm soil (TCLP Pb of untreated soil: 86±5 mg/L)



**Figure-2E**

Range G-1: rifle-4 mid berm soil (TCLP Pb of untreated soil: 358±19 mg/L)

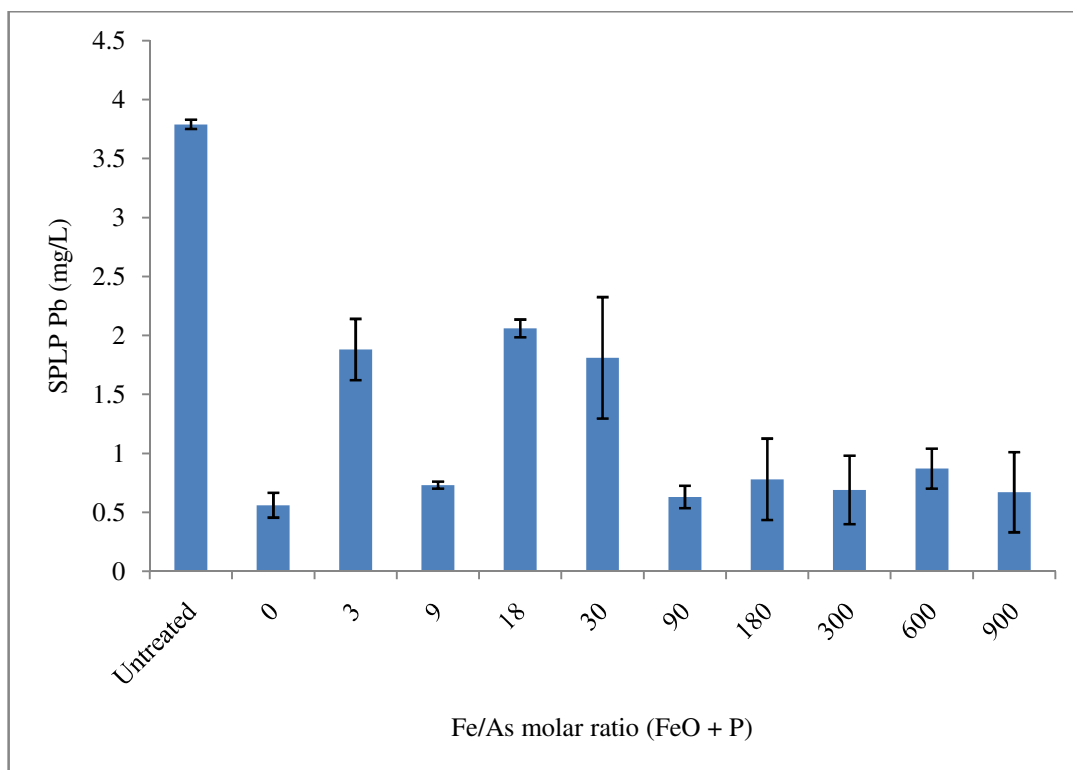


**Figure-2F**

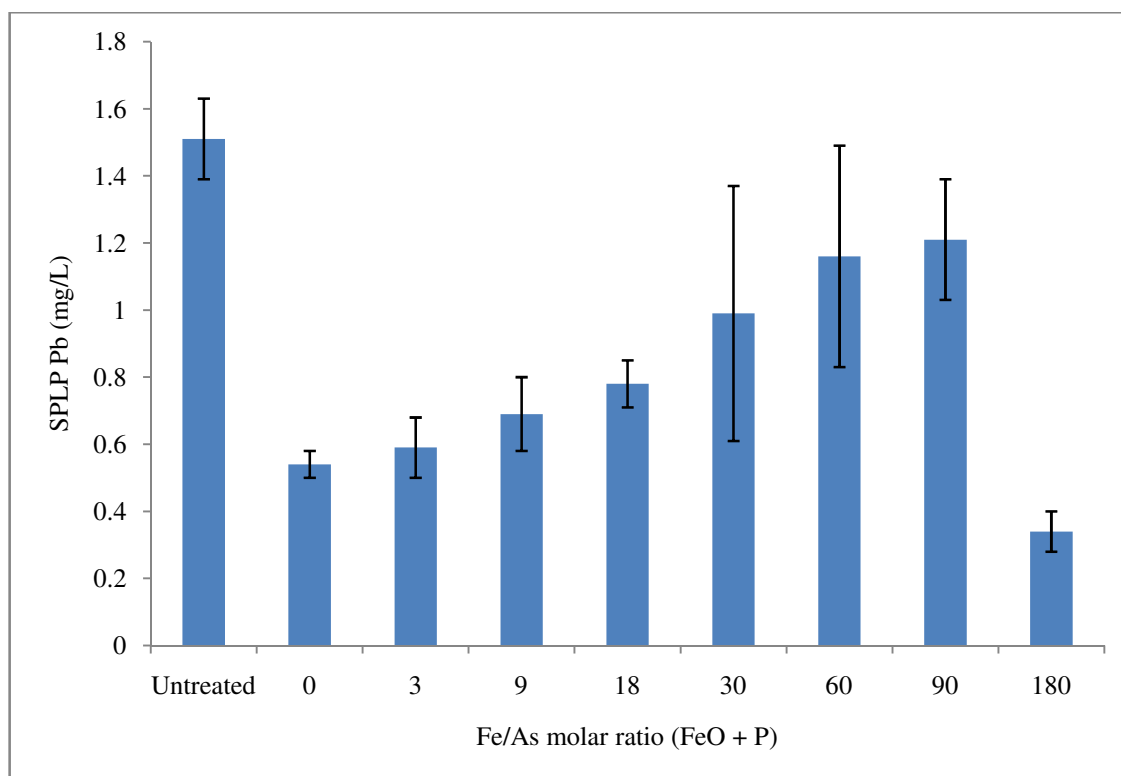
Range G-2: pistol-1 mid berm (TCLP Pb of untreated soil: 19±0.4 mg/L)

**Figure-2**

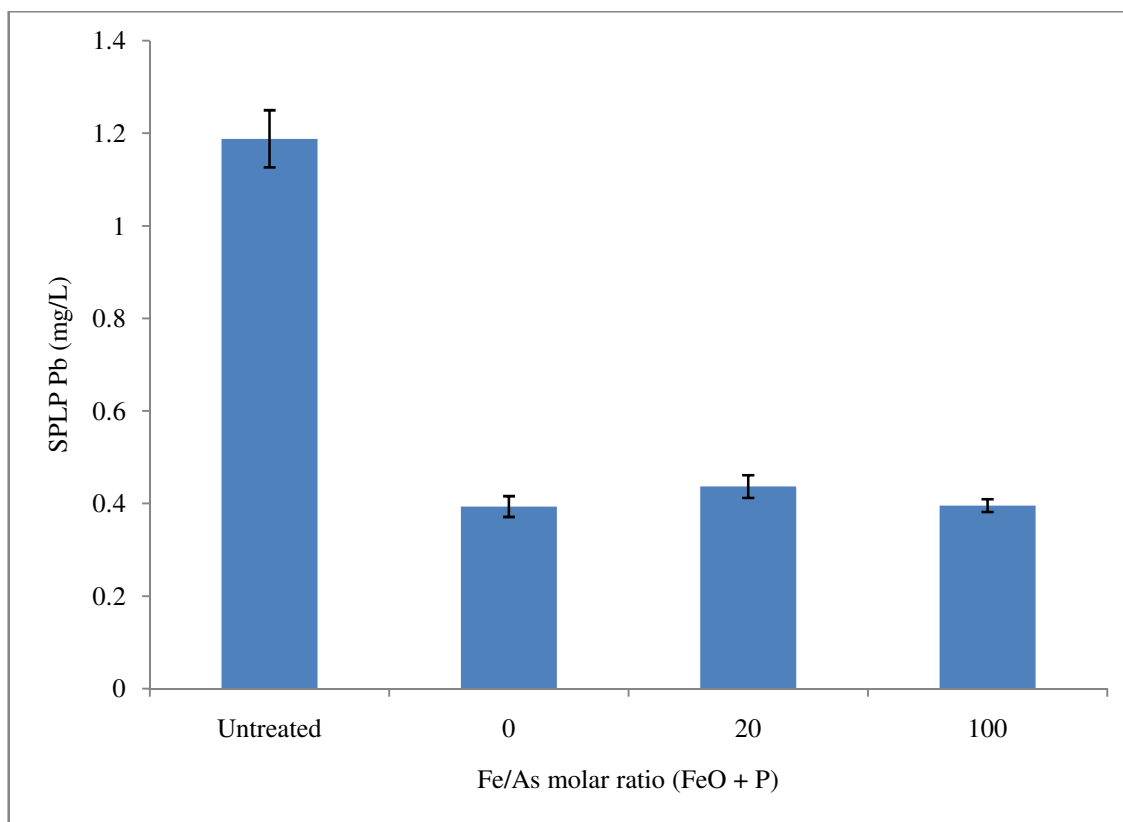
TCLP Pb concentration for the six soils before and after treatment with phosphate at P/Pb MR=4.0 (66.66% from rock phosphate + 33.33% from phosphoric acid) and iron oxide at different Fe/As MRs. (MR=molar ratio)



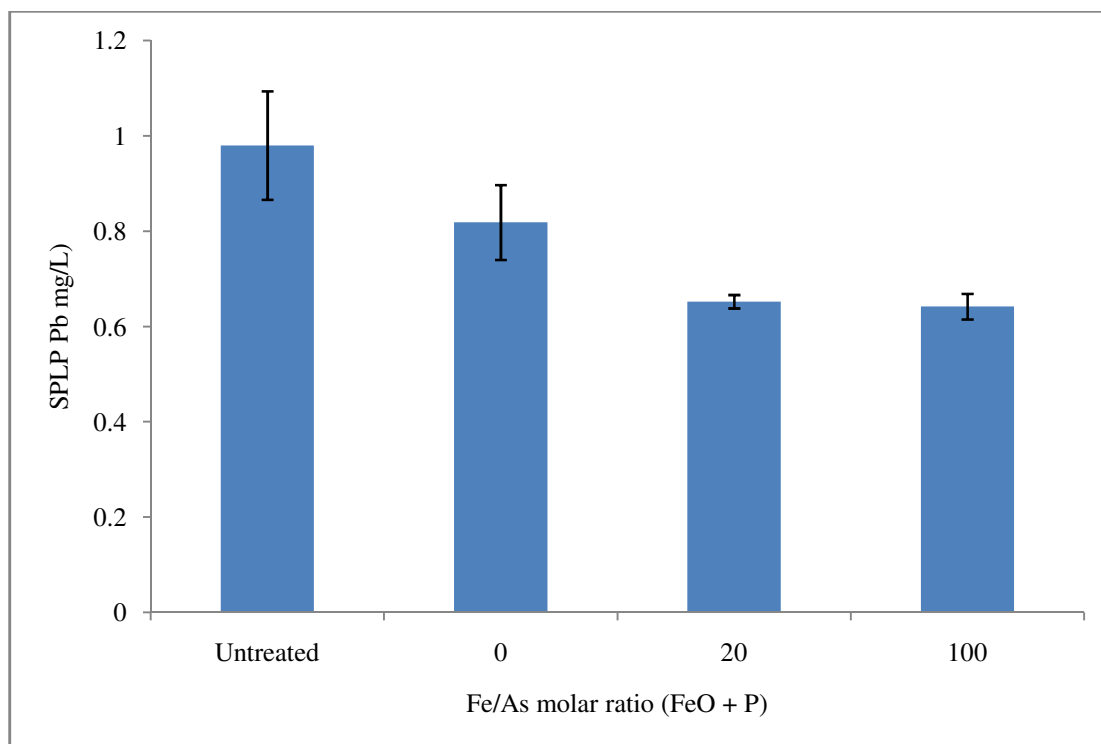
**Figure-3A**  
Range O-1: rifle-1 mid berm soil



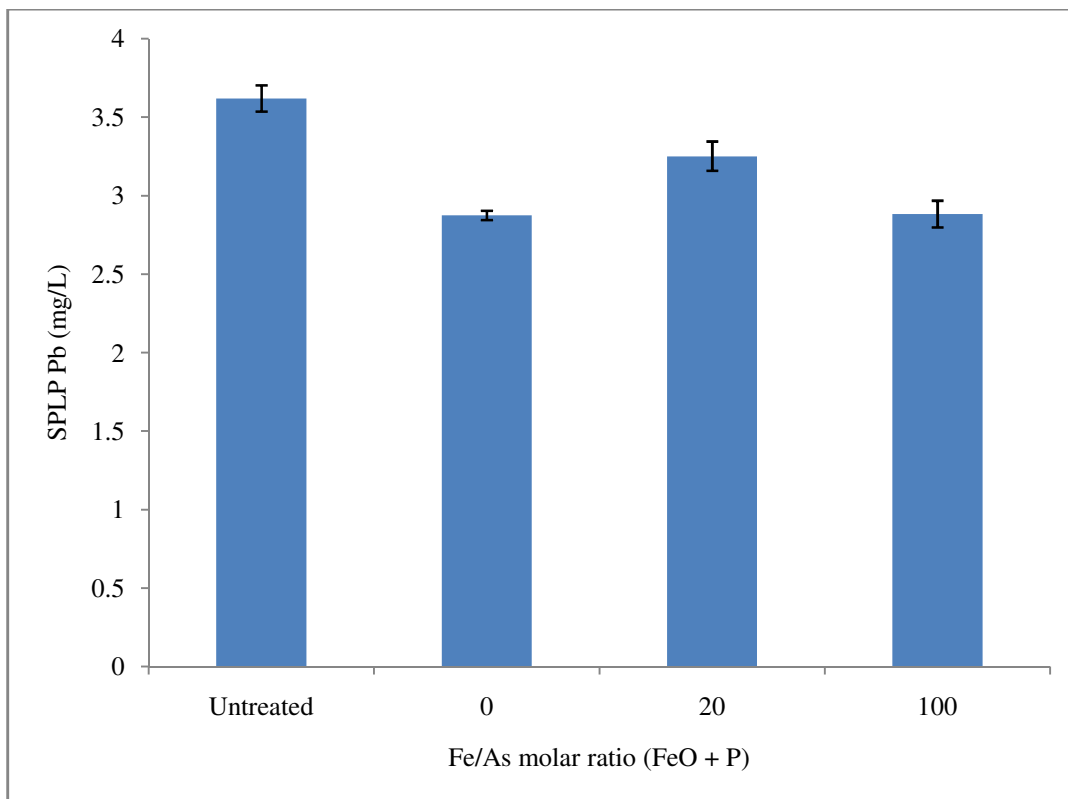
**Figure-3B**  
Range O-2: shot-gun-1 mid berm soil



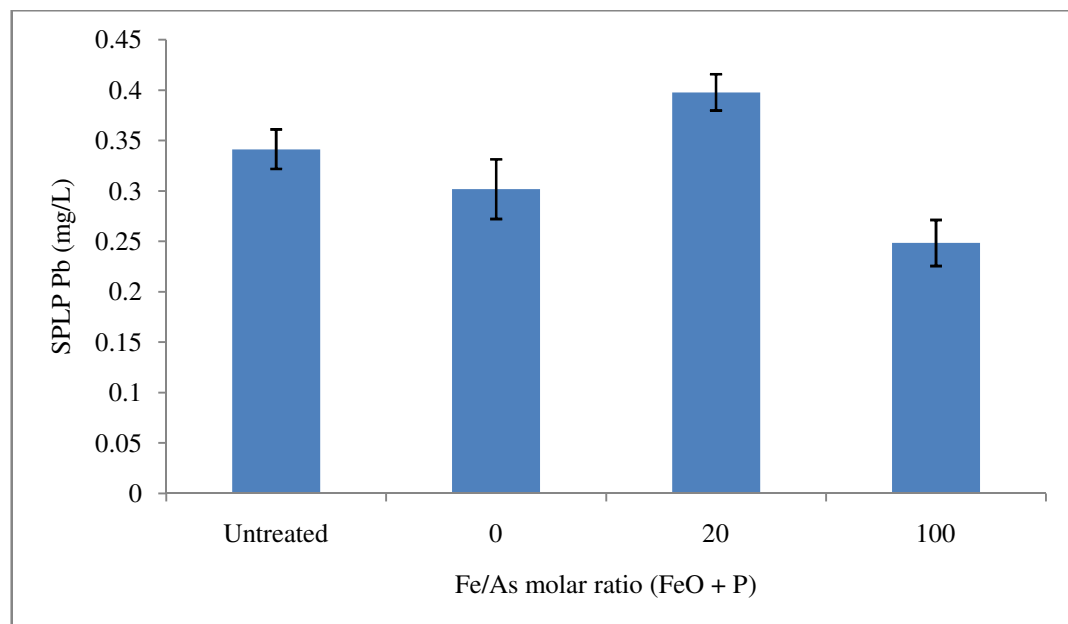
**Figure-3C**  
**Range OS-1: rifle-2 mid berm soil**



**Figure-3D**  
**Range OS-3: rifle-3 mid berm soil**



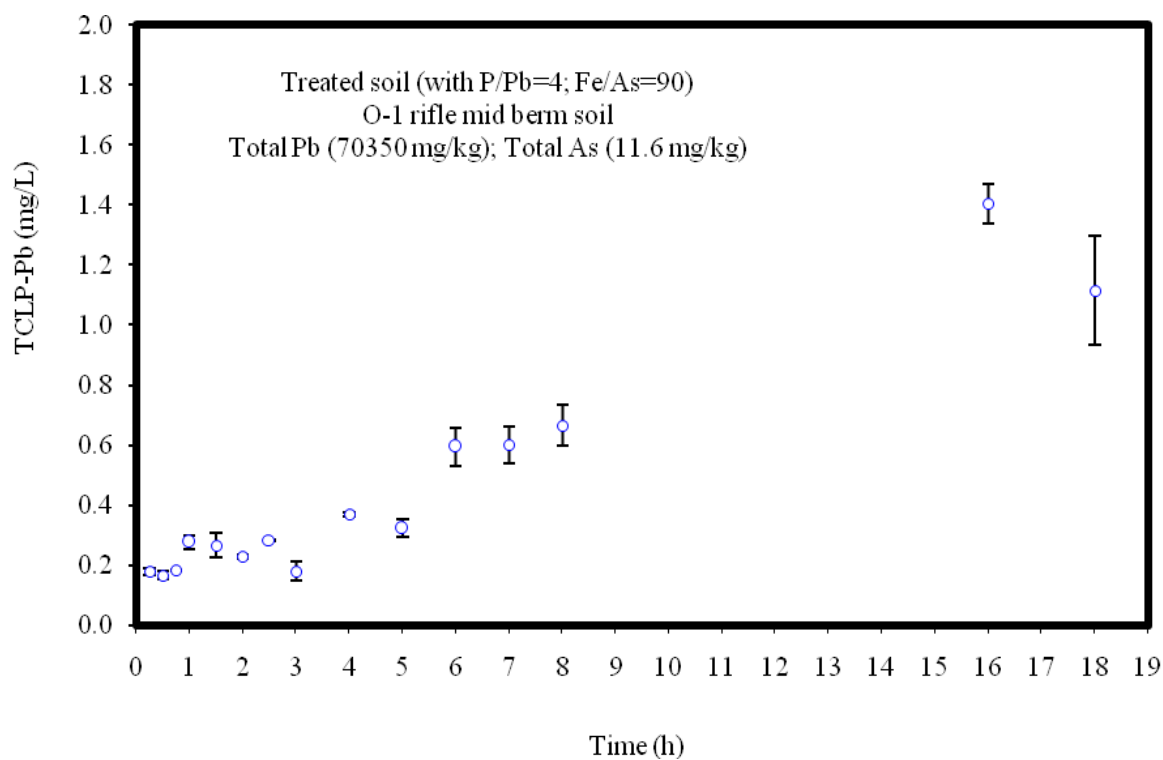
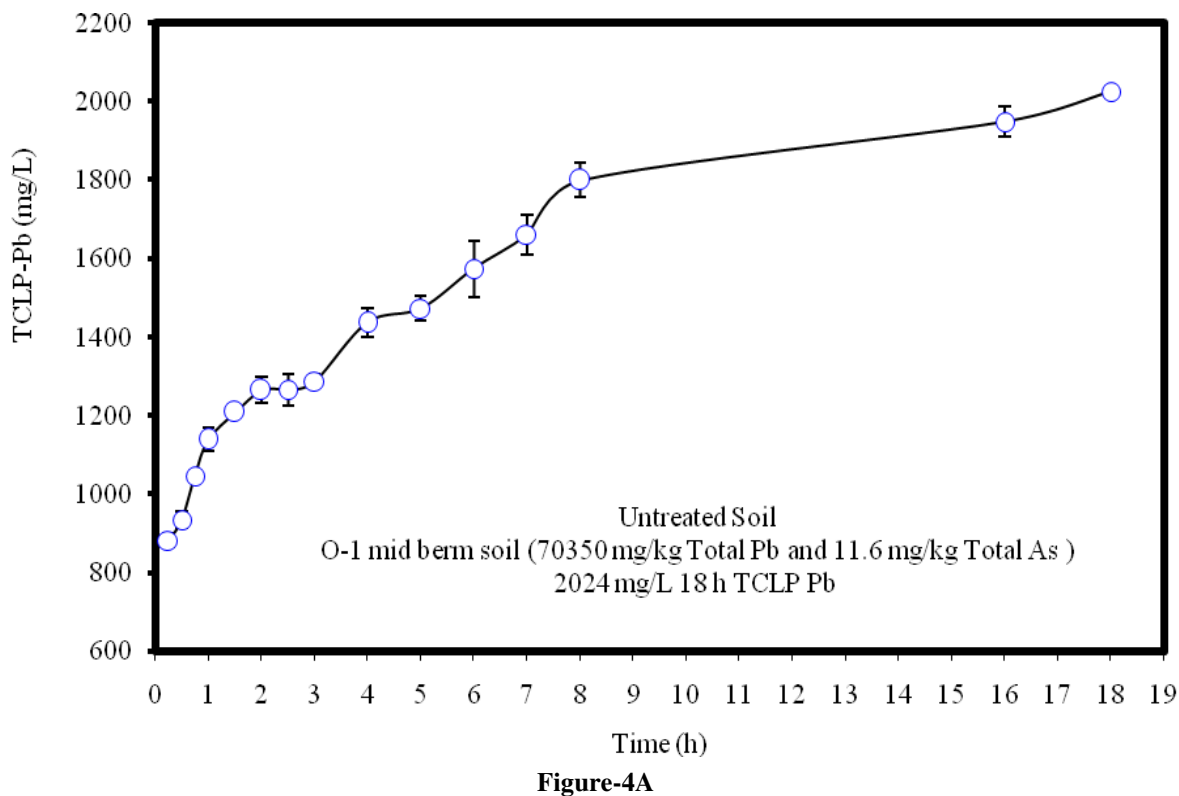
**Figure-3E**  
**Range G-1:rifle 4 mid berm soil**



**Figure-3F**  
**Range G-2: pistol-1 mid berm**

**Figure-3**

SPLP Pb concentration for the four soils before and after treatment with phosphate at P/Pb MR=4.0 (66.66% from rock phosphate + 33.33% from phosphoric acid) and iron oxide at different Fe/As MRs.(MR=molar ratio)



**Figure-4**  
**Kinetics of Pb release from untreated and P-treated (at P/Pb molar ratio of 4.0) O-1 soil during 18h TCLP extraction**

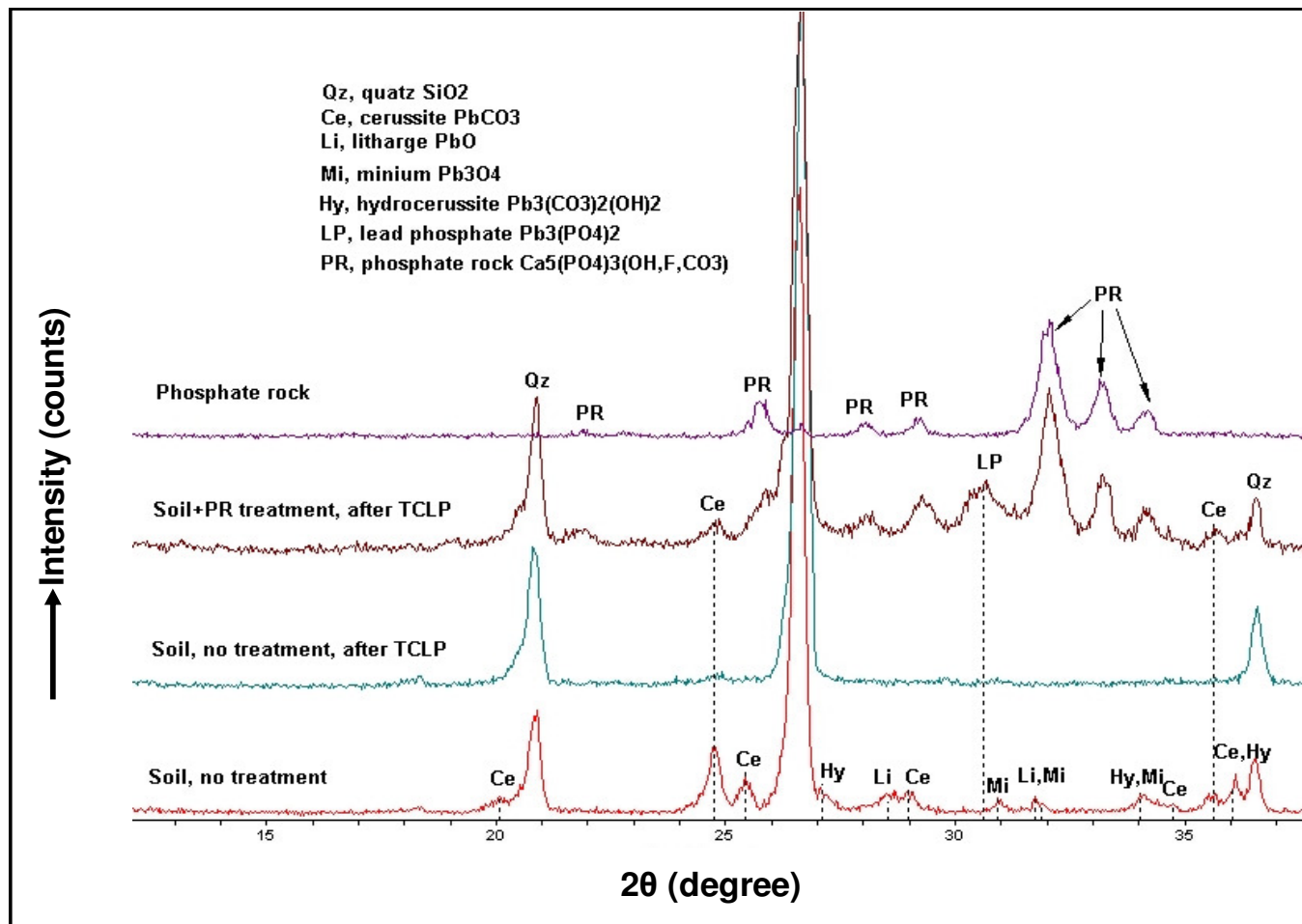


Figure-5  
X-ray diffraction patterns of phosphate rock and <53  $\mu\text{m}$  fraction of O-1 soil before and after P-

## Conclusion

Phosphate treatment reduced TCLP-Pb concentrations in the soils down to below or close to the regulatory limit of 5 mg/L. Even though the SPLP-Pb also reduced substantially in the P-treated soils, Pb concentrations could not be controlled below the drinking water regulatory limit of 15  $\mu\text{g/L}$ . Sole P treatments also reduced TCLP-As probably due to precipitation of As-phosphate phases. However, P addition increased SPLP-As while addition of Fe oxides reduced SPLP-As below that of sole P treatments. A kinetic study showed that dissolution of Pb from the soil; P from PR, and subsequent Pb immobilization can indeed occur during TCLP extraction. Visual MINTEQ predicted SPLP-Pb more accurately than TCLP-Pb probably because TCLP extraction does not produce stabilized results by standard time. P leaching concentrations both in TCLP or SPLP were extremely high because the soils are sandy soils with low P adsorption capacity; though the leaching of P was reduced by the addition of iron oxides. The combination of phosphate and iron oxide effectively immobilized Pb and As in contaminated shooting range soils, though, not without its limitations.

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