Review

Phosphate application to firing range soils for Pb immobilization: The unclear role of phosphate

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Abstract

Phosphate treatment has emerged as a widely accepted approach to immobilize Pb in contaminated soils and waste media, relying on the formation of the highly insoluble mineral pyromorphite as solubility-controlling phase for Pb. As such, phosphate treatment has been proposed as a Best Management Practice (BMP) for firing ranges where Pb occurs in its metallic forms and several other phases (carbonates, oxides). While pyromorphite thermodynamically has the potential to control Pb solubility at low levels, its formation is kinetically controlled by pH, the solubility of the phosphate source, and the solubility of Pb species. Treatability studies have shown that excess quantities of soluble and acidic phosphate sources, such as phosphoric acid, are necessary for successful in situ treatment. Even under these conditions, Extended X-ray Absorption Fine Structure (EXAFS), the only reliable method to identify and quantify Pb speciation, showed that Pb conversion to pyromorphite in in situ treated soils was less than 45% after 32 months. Furthermore, the use of lime (CaO) to restore soil pH in acidified soil treatments inhibited further conversion. Additionally, phosphate treatment is known to reduce bioavailability through pyromorphite formation in the intestinal tract, and the phytoaccumulation of Pb; both desirable effects for Pb-impacted areas. Given the costs of phosphate treatment, the use of biogenic phosphate sources, such as bone meal, may be a more environmentally sustainable approach toward this end. In the many studies focusing on phosphate treatment, the attendant P leaching and eutrophication have been largely overlooked, along with other issues such as the enhanced leaching of oxyanionic contaminants, such as Se, As and W. The success and sustainability of applying phosphate as a BMP in firing range soils therefore remain questionable.
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Contents

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1. Introduction

Lead (Pb) contamination in soils has received much attention in recent years and several remedial alternatives have been proposed and researched, such as physical and chemical extraction and stabilization/solidification (S/S). Among these, the use of phosphate as a stabilizing agent to remove soluble Pb from the aqueous phase was suggested as early as 1974 by Nriagu [1] in a comprehensive study on the formation and properties of lead orthophosphates. Since then, extensive research on phosphate treatment of Pb-contaminated soils and solid waste has lead to the broad acceptance of phosphate as a stabilizing agent for Pb-contaminated media.

Firing ranges are the second most important source of Pb contamination according to a study by the U.S. Geological Survey [2]. In 2001, the U.S. Environmental Protection Agency (USEPA) issued a manual on Best Management Practices (BMPs) for lead in outdoor shooting ranges, acknowledging the need to minimize Pb release in the environment through range maintenance activities [3]. Among the BMPs to prevent Pb migration in soils, the USEPA included phosphate application to bind Pb particles, alone or in conjunction with lime (the latter used for pH control of acidic soils). The USEPA recommendation was based (though not explicitly stated in the manual) on the results of a series of studies on Pb immobilization in phosphate-treated soils, including their own study. Although the number of studies on phosphate-based soil treatment is quite high, there are still many unresolved questions regarding its in situ viability and environmental sustainability.

A key question when considering remedial choices or BMPs is whether the proposed approach is economically and environmentally sustainable. In other words, an investment on studying the effectiveness and the engineering details of a treatability scheme is only worth undertaking when the treatment: (a) has a potential to be financially viable in field scale applications; and, (b) does not compromise the environment in other ways. A treatability study is then directed to assess the effectiveness of treatment in reducing the contaminant concentration below an acceptable (usually regulatory) level. Furthermore, the mechanisms and kinetics of contaminant removal/immobilization need to be established to reliably predict treatment in the short- and long-term under different conditions.

The authors of this paper participated in an extensive investigation on metal contamination in firing ranges operated by the U.S. Department of Defense (U.S. DoD); the results on Pb speciation and leaching behavior for several ranges are presented in Dermatas et al. [4–8] and Dermatas and Chrysochoou [9]. The characteristics of the examined sites varied greatly with respect to such factors as the magnitude of Pb concentration, Pb fragment particle size distribution, soil pH, particle size and the mineralogy of the soils. Consequently, the remedial investigation involved the screening of a number of available technologies, including phosphate. The current literature review was conducted to identify and verify Pb immobilization mechanisms under different conditions. Thus, the review broadly includes studies on Pb-contaminated media other than shooting ranges, but the conclusions are primarily drawn with regard to phosphate application in firing ranges, both as a preventive measure, remedial option and BMP, which introduces sustainability issues.

The review attempts to examine the following questions:

1. Which are the thermodynamic constraints for formation and stability of insoluble lead phosphates?
2. Which are the parameters that affect the kinetics of lead phosphate formation and how can they be optimized under field conditions?
3. Which criteria can be used to evaluate treatment success? Which are the most pertinent in the case of firing ranges?
4. Which are the environmental impacts of phosphate-based treatment and how do these vary under different conditions?
5. When is phosphate treatment necessary/appropriate?

2. Theoretical background

The principal mechanism of Pb stabilization by phosphate, as put forth by Nriagu [1], is the formation of the mineral pyromorphite ($Pb_5(PO_4)_3X$ where $X = Cl^-$, OH^-, F^-). Depending on the monovalent ion in the structure, pyromorphite may be encountered as chloropyromorphite (CP), hydroxypyromorphite (HP) or fluoropyromophite (FP), the chlorinated species being the most stable form, followed by the hydroxylated and fluorinated species [1,10]. The term pyromorphite in the text will generally refer to all three species unless otherwise noted. Nriagu [1] constructed the stability field diagrams for Pb considering the mutual presence of phosphate, sulfate, carbonate and chloride and found that CP was the most stable Pb species in the pH range 3–11. Cerussite ($PbCO_3$) was predicted as the dominant species at pH 11–13 and massicot (PbO) at pH > 13 with Eh values > −400 mV. The redox potential was predicted to be the controlling factor for the relative stability of galena (PbS) and pyromorphite at pH 3–11, with −270 mV being the lower threshold for CP stability at neutral pH. Nriagu [1] consequently suggested that the formation of the insoluble pyromorphite could be an effective mechanism to stabilize Pb in natural waters and sediments, and to remove both Pb and phosphate from wastewater. However, Nriagu [1] pointed out that this natural mechanism had previously escaped the attention of geochemists in diagenetic sediments, probably owing to the slow dissolution of phosphate, its low solubility with respect to natural apatites, and the potential co-precipitation of Pb with Ca in apatites. Pyromorphite also escaped identification in subsequent studies, as reported by Cotter-Howells et al. [11], due to the extensive Ca substitution that shifted pyromorphites' lattice constants and its peak positions in X-ray diffractograms. Cotter-Howells et al. [11] identified CP as the predominant Pb-bearing phase in mine-waste soils by means of analytical transmission electron microscopy (ATEM) and X-ray absorption spectroscopy (XAS). Analyses of the high-density soil fractions showed that Pb was almost exclusively associated with CP, with a phosphorus-to-lead ratio of approximately 0.6, based on the total concentrations provided by Cotter-Howells et al. [11]. Given the fact that Cotter-Howells et al. [11] studied lead mine wastes originating back to 1750, equilibrium of Pb with the available soil phosphorus was probably established and therefore was not a limiting fac-

tor to CP formation and detection. Similarly, Ruby et al. [12] reported that CP was the predominant Pb-bearing phase in port facility soils, where mine and smelter waste was deposited for a period of approximately 20 years. The phosphorus source was a nearby phosphoric acid production plant; again, CP formed at the expense of thermodynamically unstable galena, and moderately stable anglesite. In both reported cases, the lead and phosphorus concentrations were significantly higher than those found in natural sedimentary environments, and enough time had elapsed to ensure equilibrium.

Even though pyromorphite formation was shown to be a thermodynamically viable reaction [1,11,12], the primary mechanism of Pb removal by apatites continues to be debated. Apatites have been used as sorbents and ion-exchangers for heavy metal removal from wastewater, including Pb removal from aqueous systems [13]. In one of the first studies treating Pb-contaminated media with phosphate, Ma et al. [14] suggested that dissolution of hydroxyapatite (HA) and precipitation of HP was the primary removal mechanism for Pb, rather than sorption or anion exchange. Lower et al. [15,16] studied the Pb-HA interaction by microscopic methods, including atomic force microscopy (AFM), and observed HP precipitation; homogeneous nucleation was observed at Pb supersaturation conditions (100 mg/L), while heterogeneous nucleation of HP on the HA surface was observed at low Pb concentrations (1 mg/L). In all cases, phosphate diffusion from the HA surface into the solution was reported as the rate limiting step for HP formation; as a consequence, HP crystals were always closely associated with the HA surface, despite homogeneous nucleation [15]. While Lower et al. [15] performed all analyses at constant pH (∼6), Zhang and Ryan [17] found that dissolution of HA and precipitation of HP (or CP) were strongly pH-dependent phenomena. While complete HA dissolution was achieved at pH between 2 and 5 and all Pb was transformed to CP, sorption was found to affect the process at pH 6 to 7. As the apatite surface became negatively charged with increasing pH, Pb^{2+} was sorbed onto the surface, precipitated as CP, restricting further HA dissolution [17], as first observed by Xu and Schwartz [18]. Mavropoulos et al. [19] also studied the mechanisms of HA–Pb interaction and found that HP formation occured in a stepwise fashion, in which Ca–Pb solid solutions formed, dissolved and reprecipitated, with decreasing Ca content until pure HP was formed.

This was consistent with the observations of Cotter-Howells et al. [11], which indicated that the thermodynamics of the Ca–Pb substitution process may vary in natural environments, favoring Ca-rich pyromorphites. Mavropoulos et al. [19] also found that sorption mechanisms contributed to Pb immobilization by HA, estimated to be approximately 30% of the total Pb content.

In summary, the theoretical studies on Pb immobilization by apatites showed that both pyromorphite precipitation and Pb sorption on apatite could be contributing mechanisms. The influence of each mechanism was strongly dependent on pH and pore solution chemistry, making it difficult to predict the predominant mechanisms under field conditions. Lower et al. [15] indicated that typical stirred batch experiments may not be representative of soil environments where diffusion processes are rate limiting, as phosphate diffusion appeared to be the rate-limiting step in the dissolution/precipitation reaction. This observation has important implications for the evaluation of results obtained from various experimental studies (discussed below).

3. Experimental studies

In general, the factors that determine reaction thermodynamics in Pb-contaminated solid media treated with phosphate are:

- phosphate speciation (i.e., solubility of P source);
- Pb speciation (i.e., solubility of Pb source);
- pH, Eh;
- availability of water;
- solution chemistry;
- particle size of P and Pb materials.

The influence of these factors in laboratory and field experiments will be examined in turn.

3.1. Phosphate source

Table 1 provides an overview of common phosphate sources and their chemical properties, illustrating the differences in solubility. The phosphate sources may be divided into three major categories: readily soluble phosphates, such as phosphoric acid (PA); moderately soluble phosphates; such as mono-, di- and tricalcium phosphate (MCP, DCP, TCP); and, less soluble phos-

Table 1
Chemical properties of common phosphate sources for Pb treatment

Phosphate source	Abbreviation	Chemical formula/composition	Log K_{sp}[a]
Phosphoric acid	PA	H_3PO_4	–
Monocalcium phosphate	MCP	$Ca(H_2PO_4)_2 \cdot 2H_2O$	−1.14
Dicalcium Phosphate	DCP	$CaHPO_4$	−6.66
Tricalcium Phosphate	TCP	$Ca_3(PO_4)_2$	−24.0
Triple Super Phosphate	TSP	Mostly $Ca(H_2PO_4)_2 \cdot 2H_2O$	n.a.
Diammonium Phosphate	DAP	$NH_4(H_2PO_4)$	n.a.
Hydroxyapatite	HA	$Ca_5(PO_4)_3(OH)$	−55.9
Phosphate Rock	PR	$Ca_5(PO_4)_3(OH, F)$ also with CO_3^{2-} substitution	n.a.
Apatite II	Ap-II	$Ca_{5-x}Na_x(PO4)_{3-x}(CO_3)_x(OH)_2$	−20

n.a. not available.

[a] All K_{sp} values from Snoeyink and Jenkins [20], except Ap-II [21]. Congruent dissolution reactions written with respect to the containing phosphate species (e.g., $CaHPO_4 \rightarrow Ca^{2+} + HPO_4^{2-}$).

phates, such as synthetic hydroxyapatite (HA) and phosphate rock (PR). Commercial fertilizers used in some studies are mixtures and/or variations of the above compounds. Triple Super Phosphate (TSP), the fertilizer used by USEPA in the study mentioned in the BMP manual [3], is primarily MCP with some impurities resulting from processing PR with PA. PR is the primary source used to manufacture all of the above compounds and consists primarily of fluorinated apatites with high carbonate contents. The reactive properties of PR are the lowest compared to all refined products, while its availability and cost are the most favorable. Biogenic phosphate sources (bone char, bone meal) are more soluble than HA and PR mainly due to the poor crystallinity of apatites in their structure (see Apatite II in Table 1). In order to examine the P-sources used and evaluate the results reported by the various studies encountered in the literature, the readily available studies were classified into three broad categories:

1. Laboratory studies conducted on artificial systems (solids or aqueous solutions), focused on examining the underlying mechanisms of phosphate treatment: 16 studies are covered by this category, including references [14–19] and [22–31].
2. Laboratory (treatability) studies conducted on Pb-contaminated soils and waste, focused on optimizing treatment efficiency: 36 studies are presented in this review paper, including references [32–67]. Several of those studies were published by the same research group, reporting different results from the same or similar experiments; however, for simplicity purposes, they are treated as individual studies in the statistics presented in the following discussion.
3. Field studies on Pb-contaminated soils: eight studies were found [21,68–74]. Three of those [68–70] presented results from the same field study, as did [71] and [72]. Overall, five field applications were encountered in the literature.

The phosphorus sources were then classified into five categories: soluble-P (including PA and salts), fertilizer-P (including MCP, DCP, TCP, DAP and TSP), HA, PR and biogenic-P along with waste-P (phosphatic clay). The distribution of these sources used in each category of studies is shown in Fig. 1. Several studies involved multiple P sources, and some clear trends emerge from the comparison between different types of studies.

The laboratory studies that investigated the theoretical mechanisms of Pb-P interaction used almost exclusively synthetic HA as the P-source (11 out of 16 or ∼70%). This follows from the need to have a pure and controlled chemical environment for studying fundamental mechanisms. Treatability studies employed mostly PR (19), followed by soluble-P (5 PA and 9 P-salts) and various types of fertilizers (11; 7 using TSP). Only seven studies used HA, four studies used biogenic P-sources and one study used phosphatic clay, a waste from PR processing. However, only one study tested pure PR in the field [71,72], while another used it in conjunction with PA [68,70]. Pure PA was used in three studies [68–71,72,74]. TSP was tested in one study [71,72], while the remaining two field studies used biogenic P (Apatite II) [21,73]. The use of the various P sources suggests the following trends:
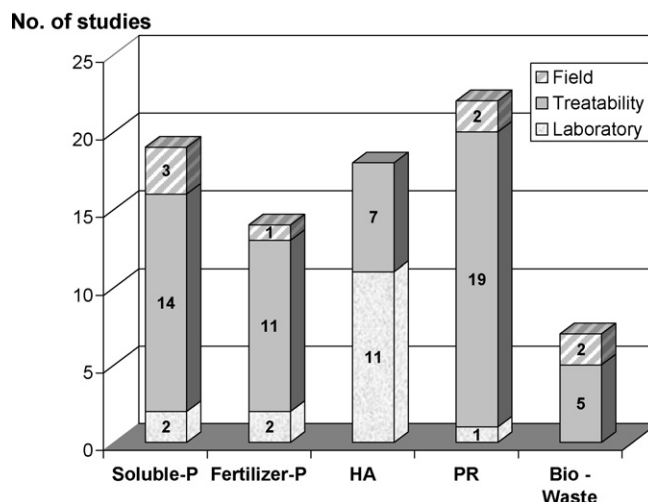

Fig. 1. Distribution of P sources used in laboratory, treatability and field studies.

- Not all results are directly transferable from one application to another due to the use of different P sources. For example, the kinetics of dissolution of Pb-bearing minerals upon addition of PR in the field may be substantially different compared to the laboratory studies by Zhang and Ryan [17,26,27]. Furthermore, the observations of homogeneous nucleation of HP formed from the reaction of pure HA and aqueous Pb may also not necessarily apply to mixed apatites, with varying compositions and degrees of crystallinity. For example, Ma et al. [33] studied aqueous Pb removal by fourteen different types of PR and reported large differences in their removal efficiencies, initial Pb(aq) concentration, and incubation time for the same PR dose.
- The reliance on PA in most field studies points to a fundamental need to provide soluble P and low pH for successful treatment (further discussed below).

It is difficult to compare the effectiveness of the phosphate source used without touching upon two other important parameters, namely the pH, and, most importantly, the analytical techniques used to evaluate treatment effectiveness, which themselves may affect P and Pb speciation.

3.2. Pb speciation

The major minerals that are encountered in Pb-contaminated media are cerussite ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$)), anglesite ($PbSO_4$), litharge (PbO) and massicot (PbO), as well as galena (PbS) in highly reductive environments, such as mines and smelters. The most common Pb species in firing range soils are metallic Pb fragments, carbonates, anglesite, and litharge, depending on the pH and the presence of sulfate [4–9,75–78]. Pb may also be encountered sorbed on iron and aluminum oxyhydroxides and on soil organic matter. In all cases, Pb species form as a result of weathering of the original metallic Pb, i.e., the bullets. The rate of metallic Pb weathering varies greatly, and values differing up to four orders of magnitude have been reported in the literature [75]. The particle size of the bullet

fragment plays a major role in the rate of Pb weathering and is a function of the firing conditions and management practices at the range [9]. For example, the use of high-velocity weapons (rifles) leads to a higher degree of bullet fragmentation (generation of Pb fines) compared to low-velocity weapons (pistols) [9]. Furthermore, the pH, Eh and soil organic matter also affect the weathering rate. Acidic, oxic, organic-rich environments accelerate metallic Pb weathering. Metallic Pb fragments have been reported to completely disappear within 40 years in acidic, organic-rich soils [79], while whole bullets were recovered from anaerobic lake sediments after more than 100 years of deposition [80]. The formation of insoluble carbonate and oxide coatings on bullet surfaces reduces the metallic Pb weathering rate with time, while accompanying increases in soil pH further reduce Pb solubility [77,78]. Vantelon et al. [81] examined the surface encrustations on Pb bullets using X-ray absorption spectroscopy (XAS) and found that the formed weathering layer was comprised of litharge-hydrocerussite-cerussite (inner to outer), resulting in a sharp decrease in the Pb concentration in the surrounding solution. The same authors indicated that the Pb solubility control by cerussite should maintain very low Pb concentrations at neutral soil pH, due to the high CO_2 partial pressure associated with respiration processes [81]. Jorgensen and Willems [76] estimated that 100–300 years may be required for the full transformation (carbonation) of Pb pellets found in Danish firing range soils.

Several authors have demonstrated that the limiting step for the transformation reactions in phosphate-based treatment is the dissolution of the ionic species (P and Pb), not pyromorphite precipitation [10,11,44]. As discussed below, the rate of dissolution of both phosphate and lead minerals depends on four factors: (1) liquid-to-solid (L:S) ratio; (2) pH; (3) solution composition; and (4) particle size/effective surface area of P and Pb sources.

3.3. Effect of liquid-to-solid ratio

The liquid-to-solid ratio affects reaction kinetics, depending on the speciation of P and Pb in the solid. In the case of sorption, the concentration of the contaminant in solution decreases with increased availability of water. In simple terms, the number of surface sites available for sorption is constant for a given amount of solid, so that the balance of the mass is distributed in solution. Consequently, when a batch treatability study is conducted with Pb^{2+} being primarily sorbed on a fixed mass of solid, the addition of water results in a lower dissolved Pb^{2+} concentration, as shown by Stanforth and Qiu [49]. The L:S ratio should thus not theoretically affect reaction rates in a Pb sorption scenario; rather it changes the necessary soluble phosphate concentration to reach saturation with respect to pyromorphite.

Conversely, when soluble Pb^{2+} is controlled by precipitation, its concentration in the bulk solution (in mol/L or mg/L) remains constant regardless of the amount of water available, all other parameters being equal. In other words, the more water available, the higher the total mass of Pb and P that can be dissolved from a given amount of solid. Upon saturation, solubility-controlling phases will stop dissolving, unless the soluble species are removed by precipitation of a different phase (in this case, pyromorphite). The pre-existing Pb- and

P-containing solids (e.g., HA, cerussite) will then theoretically keep dissolving, until they are completely transformed to a more stable product (e.g., pyromorphite). Also, the higher the L:S ratio, the faster the conversion rate to pyromorphite. It should also be noted that, once pyromorphite saturation is reached, it then controls solubility of Pb, resulting in a sharp decrease in dissolved concentrations. While this may be desirable in terms of Pb bioavailability and mobility, it slows conversion rates.

The L:S ratios encountered in the literature vary significantly, including near-field moisture values to values up to 1000. An attempt to classify soil treatability studies according to the L:S ratio proved difficult, as the variability in parameters such as speciation and amount of Pb and P-source, pH, evaluation methods, did not facilitate direct comparisons. In general, most L:S ratios encountered were much greater than anticipated field moisture conditions, and those at or near field moisture lacked information with regard to conversion rates.

3.4. Influence of pH

There is a general consensus in the literature that acidic pH values favor the dissolution of both Pb-bearing minerals and solid P-sources, while pH values exceeding 6 are unfavorable both for P and Pb solubility. As such, there are practically no batch treatability studies on phosphate stabilization at pH values greater than 7.5, with the exception of Chen et al. [24], one alkaline soil tested by Ma et al. [42], and a general pC-pH study by Stanforth and Qiu [49]. The primary reason is that most treatability studies employed solid P sources (PR, fertilizers, HA) that feature sharp decreases in solubility with increasing pH. The solubility of HA decreases two orders of magnitude with each pH unit increase going from pH 5 to 8 (Table 2), so that the availability of soluble phosphate also decreases. Snoeyink and Jenkins [20] calculated the soluble P concentration with respect to HA at pH 8 and a Ca concentration of 150 mg/L as $CaCO_3$ at 3.7×10^{-5} μg/L, an extremely low concentration which may be insufficient to attain saturation with respect to any form of pyromorphite. Controlled laboratory studies shed sufficient light into the role of pH under different conditions. Zhang and Ryan [17,26,27] studied the conversion of anglesite, cerussite and galena to CP using HA under constant- and dynamic-pH conditions in the range 2–7. HA dissolution was limited at pH 6 and 7 in all three studies, but other effects dominated reaction kinetics (discussed below), so that the results were ultimately significantly different.

Pb species commonly encountered in firing ranges, such as a cerussite and (less frequently) anglesite can dissolve and convert

Table 2
Solubility of HA at various pH values (after [82])

pH	HA (mol/L)
5	6.3×10^{-2}
6	3.16×10^{-4}
7	1.58×10^{-6}
8	5.01×10^{-8}

to pyromorphite, as long as acidic pH prevails. The dissolution of anglesite is independent of pH, making HA dissolution the rate-limiting step in CP formation [17]. Zhang and Ryan [17] showed that HA dissolution was extremely fast at pH 2, but CP did not form at this pH value. CP formation became favored between pH 4 and 5 which also optimized the rate of HA dissolution, enabling complete conversion of anglesite to CP and the corresponding Pb concentration was suppressed to low values ($<10^{-6}$ mol/L or <207 µg/L). However, experiments at pH 6 and 7 showed that HA solubility was too low to saturate the solution with respect to CP, so that anglesite controlled Pb solubility. Consequently, Pb concentration was elevated significantly above pH 5 ($\sim$0.4 mmol/L or 83 mg/L). Similar results were obtained for cerussite; in this case, the cerussite to CP conversion rate became increasingly unfavorable with increasing pH, because the solubility of cerussite is lower than anglesite and decreases between pH 2 and 7. Similar conclusions were drawn in a subsequent study applying similar conditions on a Pb-contaminated soil with cerussite being the predominant Pb species [41]. No CP was detected at pH 6 and Pb solubility was controlled by cerussite. However, the addition of HA had a minor effect on lowering the Pb concentration. Here, sorption on apatite, precipitation of low amounts of CP and precipitation of additional cerussite upon calcite dissolution emerge as possible explanations.

Galena is rarely present in firing ranges, due to their generally oxidized conditions. However, Zhang and Ryan [27] found that the dissolution rate of galena increased with increasing pH during the initial stages of dissolution, as surface protonation controlled the rate of dissolution. Thereafter, sulfide oxidation to sulfate became the rate-limiting step for galena conversion to soluble Pb^{2+}. CP was formed only at pH >5 and high dosages of P (four times the stoichiometric ratio for pyromorphite formation). Galena was found to be the predominant solid in all experiments. The optimization of conversion rates in apatite-treated mine and smelter waste therefore emerges as a challenging task; and the use of high P dosages and highly soluble sources appears almost inevitable.

These observations [17,26,27,41] were drawn based on constant-pH experiments, and each was complemented by dynamic pH experiments to simulate digestion processes, using a sequence that progressively increased pH from 2 to 7 within 25 to 45 min. The complete dissolution of HA and Pb-bearing minerals was attained in all cases, followed by precipitation of CP. This sequence allowed for acid-induced mineral dissolution, followed by the (optimal) near neutral conditions required for CP precipitation and effective solubility control of Pb. This finding is important to consider: (a) the influence of testing methods or regime on Pb speciation; and (b) the treatment strategy for the in situ field treatment of Pb-contaminated firing ranges. Additionally, this process may occur in the stomachs of humans and/or animals, rendering Pb non-bioavailable.

The findings of Zhang and Ryan [17,26,27] were confirmed by other studies. Laperche et al. [35] also investigated the interactions of HA with litharge, massicot and cerussite and observed that HP formation was favored at pH 5. Complementary modeling showed that HP should be the thermodynamically more stable phase up to pH 8, when cerussite dominates; they

attributed the limited conversion above pH 6 to kinetic constraints.

Chen et al. [24] studied Pb, Zn and Cd sorption on natural apatite ($Ca_{9.53}Na_{0.34}Mg_{0.13}(PO_4)_{4.77}(CO_3)_{1.23}F_{2.49}$) at a wider range of pH values (1 to 12). The metals were provided in soluble form, and removal proceeded at high rates (95.5–99.9%) within 24 h at all pH values. Furthermore, different solid phases were responsible for Pb removal from solution, including FP, HP (both with and without carbonate substitution), hydrocerussite at pH >6, and lead oxide fluoride at pH >10.5, as a result of a shortage in dissolved P at high pH [24].

It should also be noted that reactions that occur in non-controlled or poorly buffered experiments alter the pH of the solution. Apatite dissolution consumes H^+, while pyromorphite formation releases H^+ [14]. If the dissolution–precipitation reaction proceeds stoichiometrically, then the net change in H^+ concentration at equilibrium is zero. However, Xu and Schwartz [18] observed an initial decrease pH from 5.8 to 4.8 upon reaction of aqueous Pb with HA, followed by a steady increase. This behavior was attributed to a greater rate of HP formation versus HA dissolution, creating a surplus of H^+ during the initial stages of reaction. After HP formation was essentially complete and aqueous Pb was removed, continuous dissolution increased the pH to 6.3. The reason that the initial equilibrium pH was not restored was that the presence of excess HA saturated the final solution with calcium and phosphate. Since the vast majority of studies employed P/Pb ratios considerably higher than the stoichiometric requirement (next section), it is likely that HA and PR application will ultimately result in the production of alkalinity, shifting away from the optimal solubility conditions for P and Pb. The actual pH increase will vary, depending on the soil properties. For example, Ma et al. [33] reported a pH increase from 7.2 to a maximum of 8.8 in the filtrate collected from a contaminated soil treated with different types of PR at 56 days (when the experiment was terminated without demonstrating equilibrium conditions). If all Pb bound in the soil by then was converted to HP or CP, the change in pH would not be significant; however, if the conversion was incomplete, this increase in pH would inhibit further reaction. Lin et al. [61] also reported a unit increase in pH (from 6.2 to 7.2) in soil treated with PR. Hodson et al. [47] reported an increase in pH up to one unit in an acidic soil treated with bone meal. In acidic soils, the pH buffering to near neutral pH is desirable in order to minimize the final aqueous Pb concentration, while the initial acidic conditions are favorable for dissolution of the P-source. Other authors [42,45,60] reported zero or negligible change in pH upon addition of PR. Ma and Rao [42] reported pH results after 2 h of soil incubation, which were most likely insufficient to reach equilibrium. Hettiarachchi et al. [45] concluded that PR dissolution was very slow even after 365 days of incubation, so that equilibrium pH was not attained. Finally, the time frame of pH monitoring is unclear in Tang et al. [60]; the authors only stated that slight increase in soil pH (0.1) was observed upon PR addition.

Contrary to HA and PR, fertilizers (MCP, DCP, TSP) are acidic phosphate salts that decrease soil pH upon dissolution, thereby accelerating dissolution of both P and Pb. The degree of pH decrease depends on the fertilizer (or PA) dose, and the

buffering capacity of the soil. Hettiarachchi et al. [45] reported a decrease in pH from 7 to a minimum of 5.2 in five soils treated with 2500 mg/kg P as PA, or 5000 mg/kg P as TSP (P/Pb ratios varied between 1.3 and 28). Cao et al. [68] observed a pH decrease from 7 to ~4.5 upon the in situ application of ~7000 mg/kg P as PA (P/Pb 4) in a poorly buffered sandy soil. Two other in situ studies [71,72,74] also employed PA at a rate of 10,000 mg/kg P (P/Pb ~28 [71,72] and ~19 [74]). The final soil pH was not reported in either case, but lime (CaO) was applied to the soil 10 days after mixing to restore the soil pH to neutral conditions. Although these numbers provide an indication of the required P additions to reduce soil pH to the desired levels, it is difficult to draw generalized conclusions, since the buffering capacity of each soil impacts pH shifts, rather than the added acidity alone. It should also be noted that acidic phosphate salts release their acidity progressively, since they dissolve incongruently at slightly acidic to neutral pH values. For example, MCP dissolves incongruently to form brushite ($CaHPO_4 \cdot 2H_2O$) at pH values above 4.7 [83], an observation confirmed experimentally in our laboratory at Stevens. Brushite was identified in XRPD patterns of a firing range soil (initial pH 8.7) treated with MCP for 28 days (unpublished data). This means that a latent potential for long-term release of both acidity and phosphorus is implied by MCP (and TSP) treatment at pH values greater than 5.

Overall, the successful use of phosphate as a stabilizing agent depends heavily on the pH regime; slightly acidic conditions (pH ~5) being required to optimize the release of Pb bound in minerals, and the release of P if a relatively insoluble source (HA, PR) is used. This requirement presumably (or explicitly [68]) supported the selection of PA in all in situ field studies conducted thus far, with the exception of those studies employing biogenic P-source [21,73]. Two in situ studies [71,72,74] also resorted to lime to restore the pH back to neutral values. Specifically, Scheckel and Ryan [72] used 50 to 200 tons of 71% hydrated lime ($Ca(OH)_2$) per hectare, while Yang and Mosby [74] did not provide lime dosing information. One study [68–70] did not use lime, and the soil pH remained at ~5 even after 480 days of exposure.

Apart from pH optimization, another strategy to favor pyromorphite formation and the treatment endpoint is to increase the amount of P used. However, the P dosage has important environmental implications.

3.5. Influence of P stoichiometry

A variety of dosing rates (P/Pb ratio) have been used to treat Pb-contaminated media with P in various forms. Some studies, especially laboratory studies, used P:Pb ratios as a guide to calculate the P dosing rate. Since the aim of P treatment is to form pyromorphite in whatever form (HP, CP or FP), the amount of P added should at least satisfy the pyromorphite stoichiometry of P:Pb (3/5 or 0.6 on a molar basis). Considering the kinetic limitations discussed previously and the absence of stoichiometric behavior in most real environments, the addition of excess P is inevitable. In some studies, the excess P was calculated in increments of the theoretical ratio [17,26,27,35,37,41,48,49,54,68–70] others added the P source in a Pb-containing solution [14,18,22–24,27,50,65] or as a weight percentage of the soil regardless of the P:Pb ratio [33,34,38,39,42,44,45,51,53,55,59–61,64,71–74]. In the latter cases, the P:Pb ratio was estimated based on the respective concentration data provided by the authors. From the analysis were excluded studies that targeted several contaminants, predominantly Zn and Cd, as these are often encountered along with Pb in smelter-contaminated soils and other industrial waste, such as ash materials and dust from vitrification residues [36,40,43,52,56–58], and theoretical laboratory or sorption studies. Table 3 provides an overview of the provided or estimated ratios for the selected experimental studies, showing variability in molar ratios of P:Pb ranging from values below the pyromorphite stoichiometry (0.6) [34,54] to values exceeding the required stoichiometry by three orders of magnitude [38,39,61]. Ratios used in the reported field studies exceeded the HP/CP stoichiometric ratio by a factor of 3.4× [68–70], ~47× [71,72] and ~32× [74], despite the fact that all three studies used soluble PA as a phosphate source.

The excess P is required to ensure that enough phosphate is always in solution to scavenge the Pb desorbing and dissolving from Pb-bearing minerals; in the case of PA, it is also necessary to add enough acidity to optimize soil pH. In some cases, the excess P is solely a result of the experimental design that involves

Table 3
Overview of P/Pb molar ratios employed in select experimental studies

Laboratory	P/Pb	Treatability	P/Pb	Field	P/Pb
Ma et al. [14]	1.5–100	Rabinowitz [32]	38–52	Cao et al., Melamed et al., Chen et al. [68–70]	4
Zhang and Ryan, Zhang et al. [17,26,27,41]	0.6–2.4	Ma et al. [33]	30–172		
		Cotter-Howells and Caporn [34]	0.5–0.66	Ryan et al., Scheckel and Ryan [71,72]	28
Xu and Schwartz [18]	0.6–7.4	Laperche et al. [30,32]	0.6–1.8		
Ma et al. [22,23]	1.2–25	Ma and Rao, Ma et al. [38,39]	8–526	Yang et al. [74]	19
Chen et al. [24]	6.7	Hettiarachchi et al. [44,45,53,55]	2.8–28		
		Stanforth and Qiu [49]	0.5–6		
		Theodoratos et al. [54]	0.1–2.5		
		Zhu et al., Tang et al. [59,60]	1.7–3.3		
		Lin et al. [61]	33–1439		

the addition of the same amounts of P-source (on a weight basis) to sources of Pb with varying concentrations up to two orders of magnitude (e.g., Ma et al. [33,39], Ma and Rao [38], Lin et al. [61]). However, the ultimate fate of the excess P has not drawn much attention. In summary:

1. Pyromorphites (all forms) are the thermodynamically most stable Pb-bearing minerals having extremely low solubilities that have the potential of rendering Pb insoluble and non-bioavailable, including the extremely acidic conditions of digestion. The kinetics of pyromorphite formation is therefore the central challenge.
2. The solubility of the P and Pb sources (minerals) determines the kinetics of the dissolution reactions, and pyromorphite precipitation proceeds very rapidly once both compounds are available in solution.
3. The dissolution kinetics of Pb and P are optimized at acidic conditions (pH $\leq$5). Optimal Pb removal results are obtained when the pH decreases to strongly acidic conditions (pH $\sim$2) and is then progressively raised to 7. In general, PA and fertilizers decrease soil pH, HA and PR increase soil pH. Field demonstrations employed PA to achieve pH reduction, with some subsequently adding lime to facilitate pH rebound to neutral conditions.
4. Excess P dosing up to three orders of magnitude higher than the stoichiometric requirement appears to be necessary to promote pyromorphite formation.

These trends/observations have generally been leveraged during treatment design. The evaluation criteria for treatment success, and thus the applied methods for gauging the success of P-based treatments introduce similar challenges.

4. Criteria and methods for evaluating treatment performance

There are generally six types of criteria encountered in the literature to assess performance of P-based treatments, and these are typically linked to regulatory criteria and/or analytical protocols:

- *Aqueous Pb*: The Pb concentration is measured in a leachate. Batch, column, and/or pore water results are (at least in the US) compared against the maximum contaminant level (MCL) of 15 μg/L established by the USEPA for Pb in drinking water [84].
- *TCLP Pb*: the TCLP concentration is compared against the USEPA regulatory criterion of 5 mg/L to determine the media classification designation versus hazardous waste.
- *Bioavailability*: various tests have been employed to assess Pb bioavailability, ranging from pH dynamic tests (including the physiologically based extraction test (PBET) developed by Ruby et al. [85]), HCl extraction, and bioaccumulation in animals, among others.
- *Phytoaccumulation*: Pb accumulation in the shoots, roots and other mass of various plants has also been investigated.

- *Extraction tests*: the sequential extraction test (SET) developed by Tessier et al. [86] has historically been the most popular extraction test used to assess Pb association with specific operational soil fractions (exchangeable, sorbed on organic matter, carbonate phase, sorbed on ferromanganese oxides and residual). The increase of Pb concentration in the theoretically most insoluble residual fraction is assumed to reflect treatment success. Single extractions using EDTA [39], acetic acid [39], citric acid [32], dilute HCl [32], HNO$_3$ [32], Ca(NO$_3$) [39] and diethylenetriamine pentaacetic acid (DTPA) solutions [67] also have been applied. The percentage of Pb leached serves as indication of its availability.
- *Pb speciation*: identification of Pb species with non-destructive techniques, including XRD, SEM, EPMA, magic angle spinning-nuclear magnetic resonance spectroscopy (MAS-NMR), X-ray photon spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). There is no regulatory criterion for these methods, but the detection of pyromorphite is used as proof of the operational mechanism and treatment success.

Fig. 2 shows the distribution of the criteria and analyses employed by the 36 treatability studies and the 8 field studies. As several studies used multiple lines of evidence to investigate treatment success, the total number of analyses is greater than 44. There are two important issues that need to be resolved with regard to the criteria and methods used to assess treatment success:

- The applicability of the chosen criterion to the actual field conditions.
- The influence of the applied analytical technique on P and Pb speciation.

There is general consensus that aqueous Pb is reduced by the use of phosphate, sometimes to concentrations lower than 15 μg/L, others not. Ma et al. [33] treated Pb solutions with various types of PR and reported Pb(aq) concentrations between 0.95 and 6107 μg/L, and treatment of contaminated soils with various types of PR yielded Pb(aq) between 0 and 196 μg/L [42].
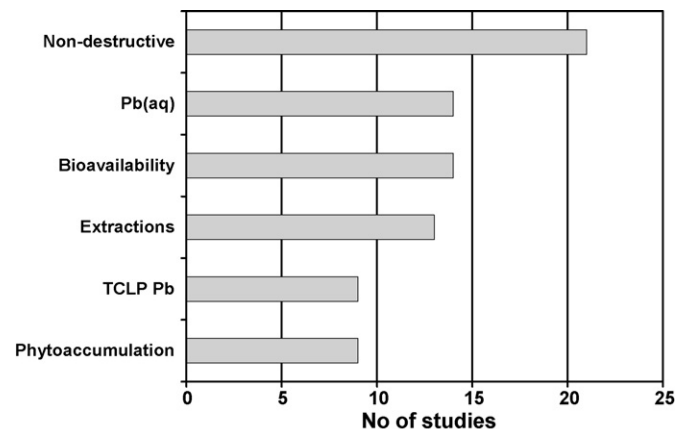

Fig. 2. Distribution of criteria and methods used to evaluate treatment performance in treatability and field studies.

Zhang et al. [41] investigated Pb solubility in aqueous HA suspensions under different static and dynamic pH conditions, and showed that aqueous Pb was below the detection limit ($2\,\mu$g/L) at equilibrium achieved in dynamic tests varying the pH between 2 and 7. The variable concentrations reported in other studies are due to several factors, the most important of which is the lack of equilibrium conditions. The kinetic constraints imposed by the solubility of the Pb and P sources also account for the higher-than-equilibrium Pb concentrations. Furthermore, the solution pH, and the activities of calcium and phosphate can also influence aqueous Pb concentrations. Consequently, it is difficult, if not impossible, to predict precise Pb(aq) concentrations under field conditions; it may only be said that the presence of phosphate has the potential to reduce Pb(aq) and thus limit downward migration.

Apart from the Pb(aq) results, there is also general agreement that phosphate drastically reduces plant uptake and bioavailability of Pb. Pb plant uptake studies concurred that Pb concentrations in the shoots decreased [37,53,54,58,59,68,69], while higher concentrations in the roots appear to be associated with the deposition of pyromorphite on their surfaces [37,69]. Only one study reported a sharp increase in Pb, Cd and Zn in the leaves of beans upon addition of P as DAP at P/Pb ratio of 2.5, while decreases were observed at all lower stoichiometric ratios [54]. The increased uptake was accompanied by a Ca-deficiency, potentially due to precipitation of the excess added P as apatite.

With regard to Pb bioavailability, there are generally two possibilities: either pyromorphite is already present upon soil ingestion, or it is formed during the digestive process. The experiments conducted by Zhang and Ryan [17,26,27] reacting anglesite, galena and cerussite with HA under digestive conditions (pH 2 to 7) demonstrated that pyromorphite precipitation was optimized and Pb solubility was minimized by the end of the digestion process (stomach and small intestine), owing to the imparted acidity in the gastric tract which optimized Pb and P dissolution, followed by pH increases and pyromorphite formation in the intestinal tract. These results were confirmed by studies employing PBET [44–46,49,53,55,60,64]. Also, Hettiarachchi et al. [55] compared PBET results with Pb accumulation in rats and confirmed that the test accurately predicted Pb bioavailability.

Hettiarachchi et al. [44,45] and Tang et al. [60] showed that reduction of Pb bioavailability may also occur in the gastric tract upon phosphate treatment. Ruby et al. [85] attributed this phenomenon to partial pyromorphite dissolution versus complete dissolution of other Pb-bearing minerals. The results of Hettiarachchi et al. [45] indicate that precipitation of a lead phosphate (pyromorphite or other) during the gastric phase was responsible for reduction of bioavailable Pb, rather than partial dissolution of pre-existing pyromorphite. However, the response of different materials (smelter slag, contaminated soils) to the three P-sources used (PA, TSP, PR) was variable during the two digestive phases with no apparent correlation between treatment conditions and bioavailability reduction [44,45]. This study illustrated that bioavailability reduction during each digestive phase cannot be safely predicted, as it depends on a multitude of factors. The only conclusion to be drawn from all bioavailability studies, both in vitro and in vivo, is that Pb bioavailability will be reduced (5–35%) as a result of phosphate treatment.

One observation that arises from the bioavailability tests is that Pb speciation changes during the test, and that has important implications for all chemical extraction and leaching tests that introduce water and/or acidity (plus other chemicals) to solid media. Extraction tests were (and, surprisingly, still are) popular tests to demonstrate changes in Pb mobility upon phosphate addition [38,39,46,48,56,65,66,68–70]. Ryan et al. [48] and Scheckel et al. [87] employed extended X-ray absorption fine structure (EXAFS) spectroscopy to prove that Pb speciation changes to more insoluble forms during the SET, rendering assessment of treatment success unreliable. Similar results were reported for PBET by Scheckel et al. [88]. The same principle applies to any extraction, including leaching tests and TCLP. Dermatas et al. [4] showed that Pb was attenuated through cerussite formation during TCLP testing of firing range soils; pyromorphite formation should also be promoted by imparting acidity and promoting dissolution of P and Pb sources.

Since chemical/analytical methods only provide information with regard to the aqueous phase, they were mostly complemented with non-destructive analyses of the solid phase. We now turn our attention to these methods. XRD was the most frequently applied method, attempting to identify pyromorphite formation in the treated media. SEM and EDX or WDS analyses were also often provided. While XRD and SEM may provide useful evidence for pyromorphite formation, three severe limitations exist:

a) High detection limit: This concerns mostly XRD. Scheckel et al. [88] investigated the identification of 1 wt.% CP by XRD and found that is was difficult, if not impossible to distinguish the CP peaks from the background noise. The authors concluded that it is virtually impossible to identify CP by XRD in soils with Pb concentrations less than 50,000 mg/kg (5%) Pb and 30,000 mg/kg (3%) P. These values represent extreme contamination and very high P addition and are unlikely to be encountered at most contaminated sites. High degrees of contamination have been encountered in the gravel and coarse fractions of firing range berm soils, but these are due to the presence of large metallic bullet fragments [5]; however, these are removed by simple screening and are therefore not favorable candidates for phosphate treatment. One would therefore expect that pyromorphite could not be detected by XRD in most cases where moderate Pb contamination exists. Various techniques were employed to overcome this limitation, including soil centrifugation to isolate Pb-containing heavy fraction, analysis of isolated grains, and of suspension precipitates. XRD patterns are usually presented over a narrow area of *d*-spacings and intensities, zooming-in on pyromorphite peaks. While this may be useful for visualization purposes, it may introduce false peak identification, especially when the two-theta (or *d*-spacing) range is truncated. For example, brushite, a dissolution product of MCP, shares secondary peaks with the primary peaks of pyromor-

phite (*d*-spacing 2.92 Å); the isolated analysis of XRD peaks would result in loss of information.

b) They are only qualitative: While quantitative XRPD has been applied to quantify minerals and metal speciation in contaminated solid media [89,90], no attempt to quantify pyromorphite minerals was ever made on XRD patterns of treated media, partly due to the difficulty to identify them in bulk samples. This information could shed some light into the degree of Pb transformation, as peak intensities alone can often be misleading and, at best, semi-quantitative. There is no capability of conducting bulk quantitative phase analysis using SEM.

c) They provide no statistically reliable picture of overall treatment: The lack of quantitative results and the limited ability to present XRD patterns and SEM data in a publication leads to the presentation of data that, while showing mineral presence in one sample, provide no statistically reliable idea of its abundance and the degree of Pb transformation.

The only non-destructive method that overcomes the above limitations is EXAFS. EXAFS reliably identifies Pb species in bulk samples with a detection limit of 50–100 mg/kg [11] and can provide their relative abundance with a linear combination fitting or principle component analysis [88]. The main limitation of EXAFS is the limited availability of synchrotron radiation sources, which renders its wide application unlikely in the near future. EXAFS is also limited to the identification of mineral phases with known EXAFS spectra, but this does not appear to be an issue for Pb species.

Ryan et al. [71] and Scheckel et al. [72] reported EXAFS quantification results for a field experiment using various phosphate sources, alone or in conjunction with iron-rich paint processing by-product or composted biosolids, and up to 32 months curing time. The results showed that only 45% of total Pb was transformed to pyromorphite (the authors did not distinguish between HP and CP) after 32 months in a plot with 1% PA (P/Pb ~28), and that the transformation reactions were essentially complete within 3 months, with only lead carbonate increasing up to 32 months [71]. This is a curious result, given the excess of P and soil acidity. Perhaps the reason for incomplete transformation was the addition of lime (CaO) 3 months following the PA application, which, by raising soil pH to 7 and adding Ca, potentially precipitated HA and rendered the remaining P largely unavailable. 3.2% P (as TSP) and 1% P (as PR) resulted in 29% and 33% pyromorphite formation, respectively [71]. The addition of iron-rich by-product to TSP resulted in improved performance (up to 41% conversion), while the addition of biosolids decreased the conversion rate (max of 16% pyromorphite).

These results are rather surprising, given that all the optimal conditions for pyromorphite formation were provided: soil acidification, soluble phosphate sources and high P concentrations. Galena and adsorbed Pb were found to be surprisingly persistent Pb species, and lead carbonate even increased in the 0.5% P (as PA) treatment. Thus, while pyromorphite formation is thermodynamically favored, it is also kinetically inhibited under the field conditions purposely engineered to strongly favor its formation.

In other words, even though we cognitively recognize that P will immobilize Pb, we can neither definitively prove it in most circumstances, nor is its transformation complete under realistic time frames. If this is the pragmatic reality, it seems entirely legitimate to question whether support for P treatment should continue when the disadvantages of using P are considered.

5. Sustainability of phosphate treatment

To date, with the excess dosages of P evaluated in the many studies, little attention has been dedicated to the ultimate fate of the excess P. The environmental impact of phosphate-based treatment has two aspects: (a) since the dosing rates are so high and the proven effectiveness limited, are the impacts associated with production and consumption of resources to apply treatment worth it? and, (b) the potential consequences of excess P leaching and release of other contaminants into the environment.

The first issue focuses on the environmental impacts of mining and processing phosphate rock to produce the raw apatites, commercial fertilizers and phosphoric acid. Phosphate mining affects topography and vegetative cover and results in emissions in the surrounding environment. Phosphate rock contains radionuclides in concentrations that are 10 to 100 times than the corresponding radionuclide concentrations found in most natural material. The PR mining industry is an intensive solid waste generator: 67% of all material handled is waste and only 33% marketable product [91]. According to EPA data, the phosphate mining industry generated 31% of all mining waste, with 23% generated in Florida [92]. Process outputs, apart from phosphogypsum, include slag, ferrophosphorus, dust, carbon monoxide and phossy water mud [91]. Furthermore, the production of phosphoric acid requires large amounts of sulfuric acid, along with soda ash, silica and energy. Even though the use of PR to treat lead-contaminated soils would probably constitute a negligible fraction of the overall phosphate production, solving an environmental challenge using chemicals derived from a waste intensive process is a questionable approach in terms of overall sustainability. The use of P-containing wastes and biogenic P sources would appear a more sustainable approach in this respect.

High P concentrations may also lead to excess leaching of oxyanionic elements, including selenium, arsenic and tungsten (which also speaks to the second issue). Southeastern Idaho faces environmental damages related to selenium emissions resulting from phosphate processing plants [93].

The second aspect of the environmental sustainability of phosphate treatment addresses the leaching of phosphorus itself. As previously described, the amount of phosphorus applied to promote pyromorphite formation well exceeds the stoichiometric amount necessary to convert all Pb into pyromorphite. This implies that ultimately higher amounts of P will be available in solution than Pb can bind; consequently, a significant amount of phosphorus may leach into the environment. Downward migration of soluble compounds would be favored by the fact that most firing ranges use sandy soils to construct the impact berms. The

pre-existence or addition of Ca can prevent P migration by binding it in insoluble apatite; however, the practice of adding lime has been shown to slow down conversion reactions, as previously noted. Accumulation of soluble P in surface water and groundwater promotes eutrophication, a widely studied phenomenon. According to the USEPA the recommended water quality criteria for lakes, reservoirs, rivers and streams, the P concentration should be in the range 8–128 μg/L, depending on the region [94].

There is only limited data available with regard to P concentrations and migration in the treated soils, whether in batch or in pilot scale applications. The P concentrations provided in batch and column studies do not provide any insight into actual P leaching in a potential BMP-type application or an in situ treatment, as the experimental conditions (high L:S ratio, mixing, lack of equilibrium) do not allow a comparison with any regulatory standards, or even between the studies themselves. Cao et al. [68] measured the total P present in a vertical soil profile extending 80 cm below the surface and 20 cm below the treatment zone. Their data indicate that there was downward migration of P over time, especially in the plots using phosphoric acid as the P-source. The fact that approximately 80% of the total P was retained in the soil profile after 480 d of treatment does not imply that P leaching did not occur, as the fate of the remaining 20% and the P concentrations in the soil pore water were not addressed. Ma et al. [14] and Ma and Rao [42] provide water soluble P concentrations that are in the range of hundreds μg/L to mg/L, well exceeding the USEPA water quality criteria. Conca and Wright [21] reported phosphate concentrations up to 50 mg/L in the effluent of a permeable reactive barrier treating acid mine drainage with apatite II. The EPA BMP manual recognizes the threat of eutrophication and recommends that phosphate not be applied near surface water bodies [3].

Also, since firing ranges and other contaminated sites often contain numerous heavy metals, the influence of P on these metals, especially oxyanions (Se, As, W, etc.) should not be overlooked. Peryea and Kammereck [95] studied As leaching in phosphate treated soils which were originally contaminated with lead arsenate pesticide and reported a total loss of 44% in As from phosphate treated columns, compared to 5% from untreated ones. Enhanced As leaching upon phosphate addition was also reported by Theodoratos et al. [54] and Basta and McGowen [57]. Lead shot contains 6–8 g/kg As [96]. Chen et al. [97] studied As distribution in a shooting facility in Florida and reported concentrations between 0.50 and 107 mg/kg, whereby the Florida DEP established a threshold of 0.8 mg/kg for ingestion pathway. Chen et al. [97] also reported that higher As concentrations were mostly found in the subsurface, contrary to Pb accumulation on the surface, which pointed to a higher As mobility. Dermatas et al. [7] reported significantly higher As concentrations, up to 1057 mg/kg, in a shooting range soil with high Pb contamination. Consequently, As leaching in phosphate-treated soils needs to be addressed, especially in field studies.

Similarly, excess phosphate has been found to accelerate tungsten (W) leaching [98]. In fact, an Occupational Safety and Health Administration (OSHA) protocol uses P for solubilizing W [99]. Tungsten has known increased use in several military applications, and in shots used for bird hunting, and is therefore increasingly found in firing ranges. Its association with leukemia clusters renders W an emerging environmental hazard [98] and its rapid leaching in the presence of phosphate should be taken into account.

In view of these issues, it is worth considering if phosphate treatment of firing range soils, either as BMP or as remediation measure, is necessary and if so, under which conditions.

6. Outlook—when is phosphate treatment necessary?

The literature review of studies related to phosphate treatment of solid media showed that, while there is promise to effectively immobilize Pb from the thermodynamic point of view, there are complicating factors limiting its applicability. The limiting factor for treatment success is the solubility of Pb and P, which depends largely on their speciation and pH, and ultimately dictates the rate and extent of pyromorphite formation. Phosphate sources commonly used are divided in soluble sources (phosphoric acid, phosphoric salts and fertilizers), which are highly processed forms of insoluble phosphate sources (apatite and phosphate rock). Acidic conditions favor the solubility of P and subsequent pyromorphite formation, while neutral to alkaline conditions do not favor a sufficiently high rate and extent of pyromorphite formation. This caused the almost invariable use of phosphoric acid in field applications conducted thus far. Also, kinetic inhibition of pyromorphite formation forced the use of significantly higher than stoichiometric P/Pb ratios in both lab and field studies, and unrealistically high L:S ratios in the lab.

When a soluble phosphate source, such as phosphoric acid, MCP or TSP, is used, solubility of Pb minerals is the limiting factor for pyromorphite formation. The predominant forms of Pb encountered in firing ranges are cerussite and hydrocerussite (lead carbonates), along with litharge (lead oxide), all of which are relatively insoluble, but still more bioavailable than pyromorphite. These minerals form as a result of oxidation of metallic Pb, which is introduced by firing of bullets. The rate of metallic Pb weathering is highly variable depending on the environmental conditions, thus Pb speciation should be investigated prior to treatment. Especially since metallic Pb oxidation increases soil pH with time, the weathering process further reduces the solubility of secondary Pb minerals (carbonates and oxides), while also creating an alkaline, non-favorable environment for pyromorphite formation. Laboratory studies have shown that phosphate treatment can only be effective at pH values lower than 5 when cerussite is the predominant Pb phase. Consequently, phosphate application as a BMP can only be successful in acidic soils where metallic Pb oxidation or lime application have not previously raised the pH to near neutral pH values. However, placement of firing ranges in acidic soils and the use of the latter for berm construction should be altogether avoided in order to prevent rapid Pb migration in the subsurface.

If phosphate is applied as a remediation technique in already contaminated firing range soils, soil pre-acidification emerges as a necessary step to condition pyromorphite formation, especially in highly Pb-impacted zones where pH is most likely alkaline. Since acidic pH environments are generally favorable for migration of most toxic metals, pH adjustment using lime emerges as

a necessary complementary treatment step, but this may in turn hinder the Pb transformation process. High P dosages exceeding the stoichiometric amount to transform all Pb to pyromorphite are also employed to overcome the kinetic inhibition of pyromorphite formation. The fate of the excess P added has been largely overlooked thus far. Also, while resource consumption and cost are bound to increase with the use of excess P, little to no information is available in the literature with regard to the overall costs of phosphate treatment. Furthermore, close monitoring of soil pH levels and Pb speciation is critical to ensure that the more bioavailable Pb forms (carbonates, oxides) do not persist in the long term.

The qualitative, and most importantly, quantitative delineation of Pb speciation has proven to be a challenging task, especially towards reliably evaluating treatment performance. Chemical extraction methods have been shown to alter Pb speciation and provide unreliable results. Non-destructive techniques are necessary for reliable investigations. The most widely available ones, XRD and SEM, face limitations such as high detection limits, and lack of quantitative and statistically representative data. There is currently only one technique to reliably quantify Pb minerals in phosphate-treated soils, and that is EXAFS, a complex, non-destructive method with extremely limited availability due to the need for synchrotron radiation. It is doubtful whether the average shooting range owner and operator has access to this technique; at best, the U.S. Department of Defense may have the means to utilize this assessment technique.

An alternative view of phosphate-based treatment performance evaluation is to judge it by its potential to reduce Pb bioavailability. One may argue that even if P is added to Pb contaminated soils and pyromorphite has not formed in situ, there is a latent benefit in the application if the primary concern is Pb ingestion from these soils. In short, if pyromorphite did not form in the range soil, research suggests that it will form during the digestive process, if ingested. While this is a nice fall back position, it can also lead to irresponsible stewardship and does not solve issues associated with other metals commonly found in firing ranges. Thus, while reduction in bioavailability may passively occur, we are not likely to rely or regulate on this basis. Also, the potential reduction in Pb bioavailability by 5–35% should be weighed against the hazard posed by excess P leaching. Accordingly, topsoil screening, removal, coverage, site isolation and traditional S/S techniques emerge as alternative approaches considering cost-effectiveness of the available solutions.

Of all the potential impacts of Pb presence in firing ranges, ingestion by animals and transport by surface runoff are probably the key exposure pathways. In the absence of phosphate treatment, vertical migration of Pb is limited, and thus not a major concern, due to the low solubility of carbonates and oxides, except for acidic soils. Ingestion may only be a concern in shooting ranges, where hunting results in a random and widespread Pb contamination. In firing ranges using impact berms and confined target areas, other management practices may be employed to limit bullet ricochet and fragmentation, such as use of deflectors, along with frequent screening of berm and surrounding soil.

The benefits of phosphate treatment should be weighed against its disadvantages, including primarily phosphorus leaching and eutrophication, enhanced leaching of arsenic, selenium and tungsten; and, secondarily, that its manufacture is an energy, resource and waste intensive process. In this light, the use of biogenic phosphate sources and P-containing waste emerges as a possible solution; however, P leaching should be more thoroughly considered and documented.

In closing, the striking omission of the P-based remediation literature for treating various Pb wastes is the secondary effects of P leaching. Accordingly, this appears to constitute the "path forward".

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