# An Investigation into Remediation of Heavy Metals by Bonemeal Amendments to Contaminated Soil

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## 1. INTRODUCTION

The presence of heavy metals in soils and waters associated with industrial, mining and waste disposal activities is a common environmental problem. Many metals can be harmful to plant and animal life when present above threshold concentrations in forms that are bioavailable. The remediation of metal contaminated soil is becoming more important as the environmental and human health hazards become better defined. It is important to note that unlike many organic pollutants, metals cannot be destroyed or degraded, only immobilised or isolated in some way from sensitive environments or resources such as groundwater.

Often the simplest effective way of resolving the problem of metal-contaminated soils is to physically isolate them by capping sites or by removing the soil to a location which is less sensitive to the contamination or where containment is less problematical. However, there are numerous problems associated with these methods. Principally, the contaminant remains a potential risk so there is the sense that the problem has merely been transported elsewhere, or temporarily contained until a natural process or a land-use change sees the problem resurface. To this may be added the inherent cost of “dig and dump” methods, the fact that landfills naturally become increasingly scarce in a finite landscape and where there is decreasing tolerance for specific areas of toxic containment. It becomes clear that if not always for economic reasons, then at least for those of sustainability, we need to expand the range of options available for managing the problem of contaminated land.

Metals may be present in soils as aqueous ions in the soil solution, as ions held on exchange sites or otherwise sorbed on organic and inorganic material and as solid minerals and amorphous oxy-hydroxides. The key to remediation of contaminants such as metals is to find methods of significantly and permanently reducing their bioavailability. To accomplish this without the generation of waste soils and the subsequent need for landfill sites, the metal must be immobilised by incorporating it into a relatively inert structure, whether it be biological (bioremediation, phytoremediation), mineral (stabilisation) or by containment within a relatively impermeable matrix (solidification). Among these, the reaction of mobile contaminants with additives to form stable, relatively inert compounds represents an attractive option where such additives do not cause their own problems and the resultant stability persists over time and across the range of all potential conditions at the site in question.

## 2. BACKGROUND

### 2.1 The case for metal phosphates

For several metals, the potential exists for immobilisation through the creation in situ, of relatively insoluble metal phosphates. Phosphates of lead, zinc, copper, cadmium, nickel and aluminium can have exceptionally low solubilities (Nriagu, 1984). These minerals are also stable over almost the entire range of Eh and pH conditions encountered in the natural surface environment.

In theory, the addition of a phosphorus source would result in the conversion of any metal ions present in solution to metal phosphate. And though such removal from solution would disrupt the soil water equilibrium such that desorption of metals from exchange and surface sites would occur together with the dissolution of other more soluble metal-bearing solid phases, provided that sufficient phosphorus was present, almost all released metal would precipitate as metal phosphate. That remaining in solution would be controlled by the very limited solubility of the new mineral compound and would therefore be present at very low concentrations. Metal phosphates essentially provide a means of “locking up” the bioavailable forms of these elements, preventing them from interacting with the environment.

Such reactions are driven by the high relative stability of the end product under the existing environmental conditions. As an example of the reactions that are hypothesised to occur between aqueous metal ions and phosphate ions, a reaction leading to the formation of lead phosphate (Pb-hydroxylapatite or hydroxypyromorphite) is shown below.

$$10Pb^{2+}_{(aq)} + 6H_2PO^{-}_{4(aq)} + 2H_2O \quad \Leftrightarrow \quad Pb_{10}(PO_4)_6(OH)_{2(s)} + 14H^{+}_{(aq)}$$

The solubility of mineral phases can be described by a constant known as the solubility product ($K_{sp}$). Solubility products are commonly expressed as log $K_{sp}$ values. The more negative the value of log $K_{sp}$ the less soluble the mineral phase. Table 1 shows values of log $K_{sp}$ for lead, zinc, copper and cadmium phosphates, sulphates and carbonates in inorganic solutions. It is clear from the values of log $K_{sp}$ that the metal phosphates are significantly less soluble than other metal phases.

**Table 1. Values of the solubility product ($K_{sp}$) of metal phosphates, carbonates and sulphates. The lower the value of log $K_{sp}$, the less soluble the mineral phase.** Values taken from Nriagu, (1984) and Appelo and Postma, (1993). As published in Hodson and Valsami-Jones, (2000).

| Mineral name | Reaction | Log $K_{sp}$ |
|---|---|---|
| Pyromorphite | $Pb_5(PO_4)_3Cl \Leftrightarrow 5Pb^{2+} + 3PO_4^{3-} + Cl^-$ | -84.4 |
| Anglesite | $PbSO_4 \Leftrightarrow Pb^{2+} + SO_4^{2-}$ | -7.7 |
| Cerussite | $PbCO_3 \Leftrightarrow Pb^{2+} + CO_3^{2-}$ | -12.8 |
| Copper pyromorphite | $Cu_5(PO_4)_3OH \Leftrightarrow 5Cu^{2+} + 3PO_4^{3-} + OH^-$ | -65.6 |
| Chalcanthite | $CuSO_4.5H_2O \Leftrightarrow Cu^{2+} + SO_4^{2-} + 5H_2O$ | -2.64 |
| Copper carbonate | $CuCO_3 \Leftrightarrow Cu^{2+} + CO_3^{2-}$ | -9.63 |
| Hopeite | $Zn_3(PO_4)_2.4H_2O \Leftrightarrow 3Zn^{2+} + 2PO_4^{3-} + 4H_2O$ | -35.3 |
| Zinkosite | $ZnSO_4 \Leftrightarrow Zn^{2+} + SO_4^{2-}$ | 3.4 |
| Smithsonite | $ZnCO_3 \Leftrightarrow Zn^{2+} + CO_3^{2-}$ | -9.9 |
| Cadmium phosphate | $Cd_3(PO_4)_2$ | -38.1 |
| Cadmium sulphate | $CdSO_4 \Leftrightarrow Cd^{2+} + SO_4^{2-}$ | -2.46 |
| Otavite | $CdCO_3$ | -11.6 |

## 3. PREVIOUS LABORATORY EXPERIMENTS

### 3.1 The formation of metal phosphates in simple inorganic systems

A substantial body of work now exists in the scientific literature concerning the formation of metal phosphates by reaction between metal ions and a phosphorus source. Experiments usually take the form of reacting a metal source, either a dissolved metal compound (usually metal nitrate) or a metal compound such as an oxide, carbonate or sulphate with a phosphorus source, either naturally occurring calcium phosphate - apatite [$Ca_5(PO_4)_3(OH,F,Cl)$], a synthetic calcium phosphate or a highly soluble phosphate compound such as $K_2HPO_4$ or $Na_2HPO_4$. Usually the metal and phosphorus sources are reacted in a suspension of deionised water or a solution containing other ions.

The majority of experiments have been carried out using lead to investigate the formation of lead phosphate. Results from these experiments may be summarised as follows:

- In suspensions of calcium phosphate and lead ions, calcium phosphate dissolves and lead phosphate forms (e.g. Valsami - Jones *et al.,* 1998, Xu and Schwarz, 1994).
- In the presence of even very low concentrations of phosphate at pH ranging from 3 to 7 lead sulphide, lead carbonate or lead oxide will dissolve and lead phosphate will precipitate (e.g. Zhang and Ryan, 1998, 1999).
- The rate of lead phosphate formation may be limited by phosphorus or lead availability (e.g. Zhang and Ryan, 1998, 1999).
- Lead phosphate precipitation occurs rapidly on a scale of minutes to hours in laboratory experiments (e.g. Xu and Schwarz, 1994).
- The presence of other metal ions or cations may reduce the efficiency of lead removal from solution by formation of other metal phosphates or by slowing the rate of calcium phosphate dissolution and thus phosphate supply (e.g. Ma *et al.*, 1994a,b).
- The formation of coatings of lead phosphate compounds on calcium phosphate particles can inhibit further calcium phosphate dissolution and therefore reduce supply of phosphate ions and metal immobilisation (e.g. Xu and Schwarz, 1994).

A more limited number of experiments have been carried out using other metals such as zinc and cadmium (e.g. Valsami - Jones *et al.*, 1998; Chen *et al*, 1997). Both zinc and cadmium are immobilised by phosphate additions but the mechanism is often unclear. Whilst it appears that zinc is immobilised by zinc phosphate formation, the immobilisation of cadmium is thought to result from a combination of the formation of mixed calcium - cadmium phosphates, adsorption of cadmium and the formation of cadmium carbonate.

### 3.2 The formation of metal phosphates in soils

Experiments using phosphorous amendments to immobilise lead and zinc in contaminated soils have met with some success. Identification of metal phosphates is harder in soils than in simple inorganic systems. This is due to the lack of ideal structure or composition of the metal phosphates that form, together with the relatively small mineral quantities involved. However, in several experiments evidence for lead phosphate formation has been obtained (e.g. Cotter-Howells *et al.* 1994). In the experiments using metal contaminated soils, bioavailability of metals has been reduced after phosphate addition (e.g. Ruby *et al*., 1993; Hettiarachchi and Pierzynski, 1999). Experiments where lead uptake by plants was measured have indicated that metal availability is significantly reduced in phosphate-treated contaminated soils (Laperche *et al.* 1997; Brown *et al.* 1999).

### 3.3 Experiments using bone meal as a phosphorus source

The use of soluble potassium hydrogen phosphate ($K_2HPO_4$) has been shown to be effective in the formation of metal phosphates (Cotter-Howells and Capron, 1996). However, the addition of such highly soluble phosphorus sources may not be practicable on a field scale due to concerns about eutrophication of streams draining the area. At the other end of the spectrum, the use of rock phosphate (natural apatite) as a phosphorous source is less effective due to its low solubility. It may not release enough phosphate for remediation to occur on an acceptable time scale.

Whilst synthetic calcium phosphates appear to have a suitable solubility for use in remediation, the cost of producing calcium phosphate in bulk might make their use too expensive (in 1999, synthetic apatite cost £800 per tonne). Valsami - Jones *et al*. (1998) noted the structural similarities between some synthetic apatites and bone meal. It was suggested that, due to these similarities, poorly crystalline apatites such as those found in crushed bone (bone meal) could provide a cost effective natural phosphate source for the remediation of soils contaminated with certain metals (in 1999, bone meal cost £174 per tonne).

To investigate the potential for bone meal additions as a remediation treatment, soil leaching column experiments were carried out (Hodson *et al*. 2001; Hodson and Valsami-Jones, 2000; Hodson *et al.* 2000; Hodson and Valsami-Jones, 1999; Hodson *et al.*, 1999). The bone meal was mixed so that it was evenly distributed throughout the soil. The columns were leached with synthetic rain solution and the solution (leachate) coming out of the bottom of the columns was collected and analysed. Contaminated soils from four UK locations were used in the experiments (Table 2).

**Table 2. Soil composition. Units = mg kg$^{-1}$.**

| Sample | pH | Zinc | Nickel | Copper | Lead | Cadmium |
|---|---|---|---|---|---|---|
| Lambton | 3.16 | 94 | 36 | 86 | 233 | < 0.02 |
| Parys Mountain (PM) | 2.71 | 4872 | 2 | 2317 | 15043 | 16 |
| Leadhills (LH) | 4.71 | 213 | 50 | 83 | 9882 | < 0.02 |
| Wanlockhead (WH) | 7.1 | 14282 | 25 | 1668 | 136260 | 63 |

Elemental analysis by inductively coupled plasma - atomic emission spectroscopy (ICP – AES). Detection levels (mg kg$^{-1}$): zinc = 0.01, nickel = 0.05, copper = 0.02, lead = 0.2, cadmium = 0.02. Lambton soils digested using both nitric and perchloric acids. Parys Mountain, Leadhills and Wanlockhead soils digested with nitric acid only. As published in Hodson and Valsami-Jones, (2000).

The Lambton soil was from a former coke works at Lambton, Sunderland. Experiments were carried out to determine the effects of various treatments of bone meal on metal immobilisation. The effects of different concentrations of bone meal (1:200, 1:100, 1:50 bone meal : soil), incineration of bone meal (incineration at 400ºC for 48 hours), bone meal grain size (90 - 500 μm and 500 - 2000 μm), and varied leaching rates on metal immobilisation were investigated.

In subsequent leaching column experiments, soils from the former mining areas of Parys Mountain, Leadhills and Wanlockhead were used. Parys Mountain is the site of a former copper mine. Leadhills and Wanlockhead were principally mined for lead, zinc, gold and copper. Experiments using the soils from these sites were carried out to investigate the effects of bone meal amendments on soils with a range of pH and metal contaminants. The bone meal amendment used was selected on the basis of results from the Lambton soil columns and was a 90 - 500 μm, unincinerated, 1:50 bone meal : soil treatment

The leaching column experiments demonstrated a clear and significant relationship between bone meal additions and metal immobilisation. Generally, bone meal amendments reduced metal release from the soils, reduced metal concentrations in the soil solution, increased soil pH, and reduced metal availability to plants and soil organisms as determined by standard extractions.

### 3.4 Metal immobilisation and changes in pH

Using the acidic Lambton soils, it was found that metal immobilisation and soil pH increased with increasing bone meal concentration and decreasing grain size. Incineration of the bone meal was found to make little or no difference to the result. A 1:50 bone meal:soil, 90 – 500 μm unincinerated bone meal treatment was found to be highly effective at immobilising metals and was used in subsequent experiments using the other soils.

For the Parys Mountain, Leadhills and Wanlockhead soils, bone meal amendments reduced metal release and increased soil and leachate pH. The one exception was for Cu concentrations in the leachate from the Wanlockhead soil where concentrations were initially higher in the leachate from the bone meal treated soils. It is thought that in this case the bone meal additions raised the pH of the soil above a threshold pH, causing the formation of soluble organo-copper complexes.

In the light of the leaching column experimental results, batch experiments were carried out to investigate whether the metal immobilisation observed with bone meal amendments could be attributed solely to the change in pH rather than the formation of metal phosphates specifically (Hodson *et al.*, 2001; Hodson *et al.*, 2000). For each of the four soils described above three sets of triplicate experiments were run, each of 24 hours duration:

- Soil was shaken with artificial rain solution.
- A 1:50 mix of bone meal and soil was shaken with artificial rain.

- Soil was shaken with a sodium hydroxide solution of a suitable concentration so that afterwards, the pH of the solution was the same as that at the end of the bone meal and soil batch experiment above.

After 24 hours the samples were centrifuged and the metal concentration and pH of the solution was determined.

Both the bone meal and NaOH treatments resulted in metal immobilisation but the effect was found to be significantly greater for the bone meal, indicating that immobilisation in the case of bone meal amendment is not due solely to the rise in pH caused by its dissolution.

### 3.5 Bioavailability of metals in soils after bone meal treatments

Bioavailability is a measure of the exposure of a receptor to a source, and may be understood in this context as the ease with which organisms may extract metals from the soil. This was assessed by two standard chemical extraction techniques, 0.01 M calcium chloride solution (Houba *et al.,* 1996; Pickering, 1986) and diethylenetriaminepentaacetic acid solution **(**DTPA) extractions (Lindsay and Norvell, 1978; Soon and Abboud, 1993). The applicability of these two methods is derived from experiments in which the metal content of plants grown on metal-contaminated soils was compared to the amount extracted from the soil by a variety of chemicals. It has been suggested in the scientific literature that these extractions indicate the degree to which metals in the soil are available to plants.

The bone meal additions either reduced or had no effect on the extractability of metals. Where there was an effect, extractability of metals was not reduced to zero. Generally, it was found that metal extractability by $CaCl_2$ was reduced by bone meal additions, whereas results for DTPA extractions were more equivocal. This difference may indicate the difficulty in assessing bioavailability of metals through chemical extractions.

### 3.6 Possible mechanism of metal immobilisation

It is suggested that bone meal amendments could cause metal immobilisation by one, all or a combination of the following:

- precipitation of metal phosphates by combination of metals with phosphate released from bone meal;
- adsorption of metal ions onto the bone meal surface; or
- precipitation of some other insoluble metal phase as a result of the pH rise that occurred in the bone meal treated soils.

However, a number of observations indicate that the first alternative probably predominates. Experiments where grain size was varied showed that a higher bone meal surface area increased immobilisation. Surface dependant mechanisms include all of the above options, the first and third via dissolution rate, the second directly through adsorption. However, since $CaCl_2$ extractions displace adsorbed ions from exchange sites, the fact that bone meal additions resulted in a decrease in $CaCl_2$ extractable metals indicates that metal immobilisation was probably not due to adsorption of metal ions onto either soil particles or the bone meal itself.

Whilst some metal immobilisation may have been due to pH rises several results indicate that this was not the sole or dominant cause. Identical pH adjustments with NaOH failed to match the immobilisation associated with bone meal amendments. Also, in several observations where no pH difference was noted between leachates from treated and untreated soils, release of metals was still found to be significantly lower where bone meal was used.

Identification of metal phosphate solid phases in treated soils is problematical. Foremost is the fact that the metal concentrations in soil solution would not result in much solid precipitate and the surface area available for the nucleation of such precipitates is vast. Metals and phosphate have been observed to occur together in treated soils using electron microscopy but due to small grain sizes it was not possible to determine whether they occurred together in a single phase or as adjacent but separate phosphate and metal phases. A possible lack of ideal chemical composition and structure in metal phosphate precipitates may also prevent them matching ideal end-member compounds which are used as standards for analysis. Thus the failure to identify such phases in treated soils does not necessarily indicate their absence.

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