

measure lead lability in soils

Nicola White^{1*}, Dr Scott Young¹, Dr Liz Bailey¹, Dr Neil Breward², Dr Andy Tye²

¹ - Division of Agricultural and Environmental Sciences, School of Biosciences, University of Nottingham, University Park, Nottingham, NG7 2RD

² - British Geological Survey, Kingsley Dunham Centre, Keyworth, Nottingham, NG12 5GG

*Corresponding author, Email: plxkw@nottingham.ac.uk Tel. (+44)115 846 6585



INTRODUCTION

Lead is one of the most common anthropogenic contaminants in soil, originating from smelting, coal and oil burning and petrol emissions. If lead within the soil enters the food chain, risks to human health can include damage to the brain and nervous system, digestive problems, and behaviour and learning problems in children. In order to model these risks, the total amount of lead in soil is often used. Not all lead in soil however will be available for uptake by plants, and so a more accurate measure is that of the labile lead.

This is the amount of lead in the soil available to move into solution (see Figure 1). If the lead is fixed and not labile, then risks to humans are low. Direct quantification of labile lead, without chemically altering the soil system being measured, is possible using a ²⁰⁴Pb isotope dilution method.

Figure 1: Pb dynamics in soil:

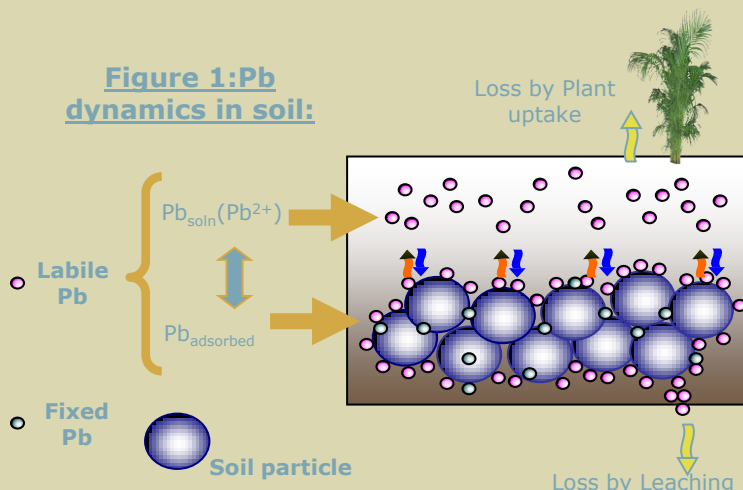
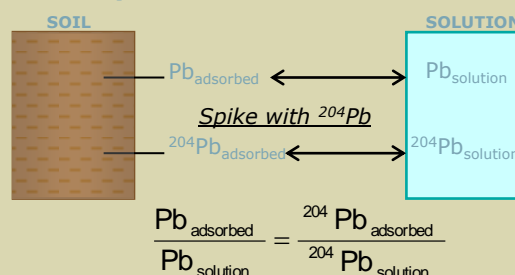


Figure 2: Theory of Isotope Dilution



The spiked ²⁰⁴Pb behaves in the same way as the natural Pb in soil, and so can be used as a measurable proxy.

$$Pb_{\text{adsorbed}} (\text{labile}) = \frac{204 Pb_{\text{adsorbed}}}{204 Pb_{\text{solution}}} \times Pb_{\text{solution}}$$

The quantity of labile Pb can be calculated, allowing a direct measurement of the labile lead in the system.

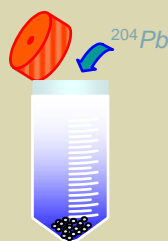
Methodology

Approximately 2g of soil was added to centrifuge tubes; soils used were contaminated with petrol emissions (Roadside), mining waste (Minespoil), and historic waste disposal (Chat Moss). Then 30ml of electrolyte was added; the electrolytes used were 0.01 M Ca(NO₃)₂ (0 EDTA), 0.0005 M EDTA, 0.005 M EDTA and 0.05 M EDTA. Samples were equilibrated for 3 days, spiked with a 0.4 ml ²⁰⁴Pb spike solution and equilibrated for a further 3 days. Equilibrated samples were then centrifuged at 2500 rpm for 15 minutes, filtered to 0.2 μm and diluted with 0.005 M EDTA. Samples were analysed using an ICP-MS (Thermo-Fisher Scientific X-series[®]). As ²⁰⁴Pb is present in the natural environment, the equation given in Figure 2 is adapted to include a measurement of the ²⁰⁴/²⁰⁸Pb ratio to account for any natural ²⁰⁴Pb, as shown in the equation below (Figure 3).

Figure 3: Determining isotopically-exchangeable Pb:

Procedure:

- 1- Suspend soil in electrolyte
- 2- Spike with ²⁰⁴Pb.
- 3- Equilibrate solid↔solution
- 4- Separate solution phase
- 5- Assay for all Pb isotopes



$$\text{Labile Pb} = \left(\frac{M_{Pb_{\text{soil}}}}{W} \right) \left(\frac{C_{\text{spike}} V_{\text{spike}}}{M_{Pb_{\text{spike}}}} \right) \left(\frac{{}^{204} IA_{\text{spike}} - {}^{208} IA_{\text{spike}} R_{\text{ss}}}{({}^{208} IA_{\text{soil}} R_{\text{ss}} - {}^{204} IA_{\text{soil}})} \right)$$

W = weight of soil used (kg).

V_{spike} = volume of spike added (L)

IA = Isotopic abundance (proportion of isotope present on mole or atom basis).

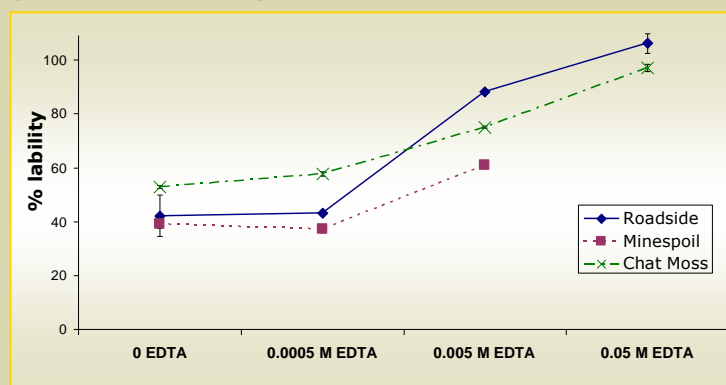
M_{Pb} is the average atomic mass of Pb either in the spike or the soil

C_{spike} is the gravimetric concentration of Pb in the spike solution.

Results

- Using a Ca(NO₃)₂ electrolyte gives the most accurate measure of the lability of Pb in a soil system.
- Increasing EDTA concentration causes the liberation of non-labile Pb, seen in all soil types tested.
 - 0.05 M EDTA appears to mobilise all Pb, giving a % lability close to 100%.
- For Minespoil soil, results are not shown for 0.05 M EDTA. The concentration of Pb was so high that when 100% Pb was mobilised, the natural ²⁰⁴Pb concentration was close to that of the spike, and so no difference could be measured.

Figure 4: % lability of lead with EDTA concentration



CONCLUSION

The use of ²⁰⁴Pb to measure the lability of Pb in soil is effective, and can be applied across a range of soil (organic to mineral) and contamination types (waste disposal, petrogenic and mine waste). Ca(NO₃)₂ provides a reliable measure of the natural lability of Pb, with the lowest EDTA concentration (0.0005 M) causing liberation of non-labile lead in all soils. Further work will develop the method, including the amount of spike used to ensure that it is not overwhelmed by the natural ²⁰⁴Pb. Equilibration time will also be investigated to ensure that the method is robust.

Acknowledgements

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