Pb reactivity in soils using ^{204}Pb stable isotope dilution

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Lead reactivity in soil

The 'labile' pool of soil-borne Pb is able to respond immediately to changes in the activity of Pb^{2+} ions in the solution phase. Quantifying labile Pb in soil may therefore improve prediction of hazard arising from biological assimilation and leaching (Figure 1).

Principles of isotope dilution

A small spike of an enriched minor isotope added to soil (e.g. ^{204}Pb at 99% IA) will only mix with the labile pool of soil Pb. From the resulting isotopic abundance (IA) of ^{204}Pb in solution the 'isotopic exchangeability' of the soil Pb can be determined. This should be equivalent to the labile soil Pb pool (Figure 2).

Figure 1: Pb dynamics in soil

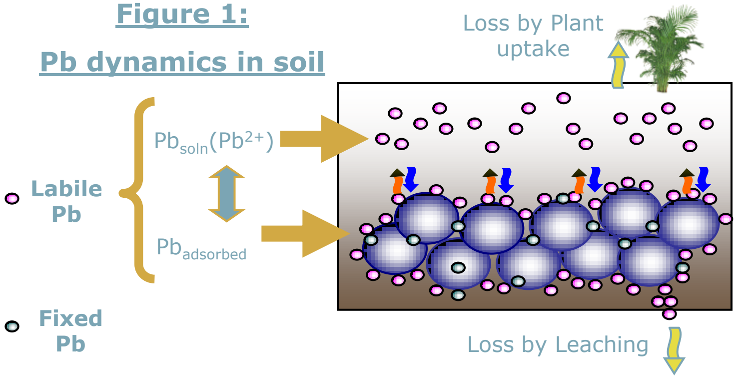
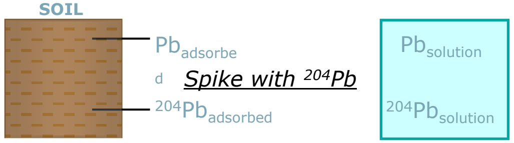


Figure 2: Theory of Isotope Dilution



$$\frac{Pb_{adsorbed}}{Pb_{solution}} = \frac{^{204}Pb_{adsorbed}}{^{204}Pb_{solution}}$$

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

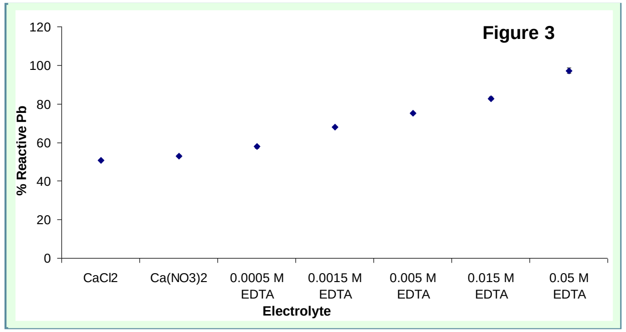
Equation (1)

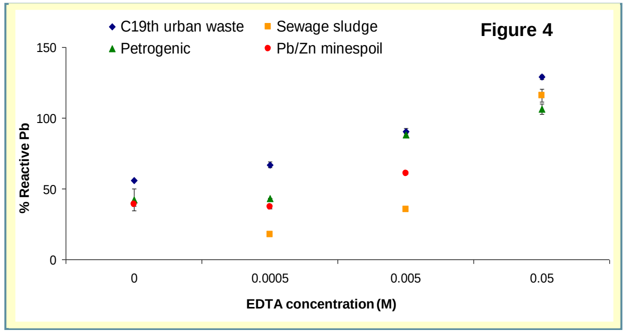
$$\text{Labile Pb} = \left(\frac{M_{Pb_{soil}}}{W}\right)\left(\frac{C_{spike}V_{spike}}{M_{Pb_{spike}}}\right)\left(\frac{^{204}IA_{spike} - {}^{208}IA_{spike}R_{ss}}{^{208}IA_{soil}R_{ss} - {}^{204}IA_{soil}}\right)$$

W = weight of soil used (kg), **Vspike** = volume of spike added (L), **IA** = Isotopic abundance (proportion of isotope present on mole or atom basis), **MPb** is the average atomic mass of Pb either in the spike or the soil, **Cspike** is the gravimetric concentration of Pb in the spike solution.

Methodology

In each experimental stage, the weight of soil (2 g), electrolyte volume (30 mL), pre-spike equilibration time (3 days) and spike volume (400 µL) were kept constant. The advantage of using ^{204}Pb lies in its low natural abundance (1.4% IA). Large changes in Pb^{2+} equilibrium from spike addition were therefore avoided. Labile Pb was calculated using Equation (1).





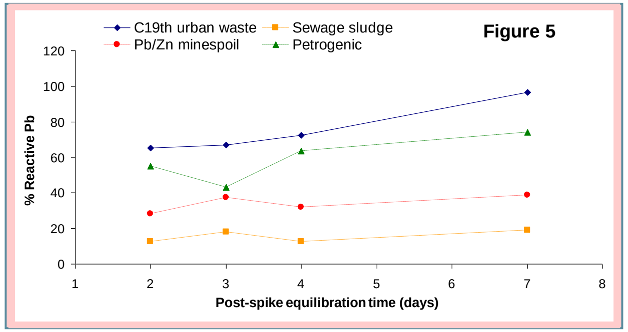


Table 1: Pb reactivity

Soil contamination history	Pb lability (% of total)
C19th Urban waste	68
Sewage sludge	14
Pb / Zn minespoil	38
Roadside	54

Stage 1 – Variable: electrolyte

A fenland arable soil contaminated with C19th urban waste was used to assess the effect of electrolyte on measured Pb lability. Calcium electrolytes and 0.0005 M EDTA gave very similar estimates of labile Pb reactivity despite producing substantially different levels of Pb solubility, suggesting a robust assay (Figure 3). Increasing EDTA concentrations appeared however to extract 'non-labile' Pb, producing a progressive increase in the 'apparent' lability of the soil Pb.

Stage 2 – Variable: electrolyte and contamination type

Electrolytes were tested on a range of soils historically contaminated from different sources (C19th urban waste, sewage sludge, Pb/Zn minespoil, petrogenic Pb (roadside)). Ca electrolytes (0 EDTA) and 0.0005 M EDTA were again found to be effective equilibrating electrolytes for all soils (Figure 4). However, higher concentrations of EDTA extracted non-labile Pb. The most commonly used extractant for trace elements, 0.05 M EDTA, extracted 100% Pb for all the study soils. Results show that the method is robust and applicable to soils with varying contamination histories provided non-aggressive electrolytes are used.

Stage 3 – Variable: post-spike equilibration time

Theoretically the ^{204}Pb spike will eventually mix with the entire soil Pb pool if equilibrated for a sufficiently long period, blurring the distinction between 'labile' and 'non-labile' forms of metal. In practice, spike equilibration periods of up to 4 days showed virtually no increase in the apparent labile pool of Pb (Figure 5). After 7 days equilibration there was a measureable increase in isotopically exchangeable Pb. Data indicates that 2-4 days post-spiking equilibration time is sufficient to provide a robust measurement of natural Pb lability in soil.

Conclusions

- Pb reactivity is effectively measured across a range of soils and contamination sources.
- Equilibrating soil in Ca salts or 0.0005 M EDTA with post-spike equilibration times of 2-4 days gives the most reliable measure of Pb reactivity.
- EDTA concentrations in excess of 0.0005 M EDTA mobilise non-labile Pb and so should not be used as extractants to measure reactive Pb.
- Proportion of labile Pb in soil varied with contamination history (Table 1).

Acknowledgements:

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