

## USING LEAD ISOTOPES TO CHARACTERISE THEIR SOURCE, LABILITY AND SOLUBILITY IN ALLUVIAL SOILS OF THE TRENT CATCHMENT, UK.

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### Introduction

Fluvial environments are a major pathway for the dispersal of trace metal pollutants. A regional geochemical survey of the UK (G-BASE) revealed that alluvial soils of the Trent Catchment were enriched with Zn, Cd and Pb (Johnson et al . 2007). Sources of Pb contamination are likely to include petrol Pb, the Pb mines in the Peak district, industry and energy production. We investigated the source, lability and solubility of Pb using a range of isotope techniques in topsoils (0-15cm depth, n=27) and subsoils (35-50cm depth, n=19) taken within 10 m of the river bed (Izquierdo et al. 2012) throughout the course of the catchment of the River Trent. We measured Pb isotope ratios (<sup>206</sup>Pb/<sup>207</sup>Pb vs <sup>208</sup>Pb/<sup>207</sup>Pb) in the whole soil, the labile Pb pool and in soil pore waters to enable us to examine the variation and proportion of Pb from different sources in each of these pools.

### Material and methods

Full details of materials and methods can be found in Izquierdo *et al.* (2012). The concentrations of major and trace elements in pore waters and soil digests and Pb ratios were determined using an Agilent 7500 quadrupole ICP-MS along with Pb. Lead isotope dilution, using <sup>204</sup>Pb as the spike, was used to assess Pb lability (E-values) using equation 1 after Atkinson et al. (2011).

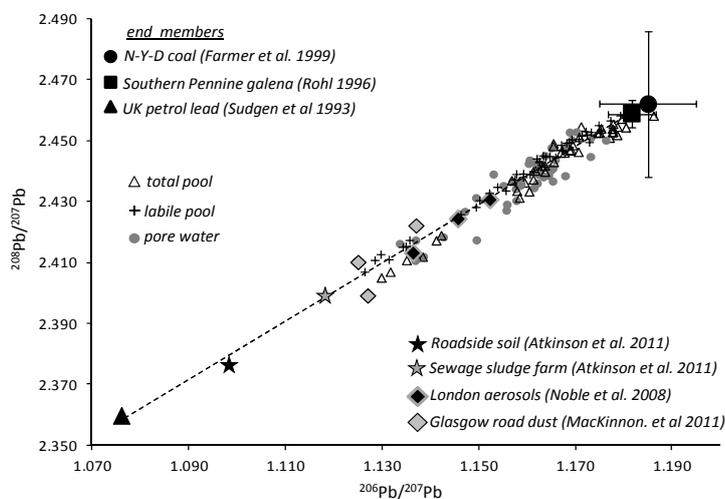
$$E - value = \left( \frac{M_{Pb}}{W} \right) \left( \frac{C_{spike} V_{spike}}{M_{Pb spike}} \right) \left( \frac{{}^{204}IA_{spike} - {}^{208}IA_{spike} R_{SS}}{{}^{208}IA_{soil} R_{SS} - {}^{204}IA_{soil}} \right) \text{ (eqn 1.)}$$

where  $M_{Pb}$  is the average atomic mass of Pb,  $C$  is the gravimetric Pb concentration (mg/L),  $V$  is the volume of added spike (L),  $W$  is the weight of soil (kg),  $IA$  denotes isotopic abundance of a particular isotope in the spike or soil and  $R_{SS}$  is the <sup>204</sup>Pb/<sup>208</sup>Pb ratio for the spiked soil supernatant. We also examined the sources of Pb in the pore water and the labile pool using the following equation (eqn 2) after Atkinson et al. (2011).

$$^{206}\text{Pb}/^{207}\text{Pb}_{\text{Non-labile}} = \frac{^{206}\text{Pb}/^{207}\text{Pb}_{\text{totalpool}} - \left( ^{206}\text{Pb}/^{207}\text{Pb}_{\text{labile}} \times \frac{\text{labilepool}}{\text{totalpool}} \right)}{1 - \frac{\text{labilepool}}{\text{totalpool}}} \quad (\text{eqn 2.})$$

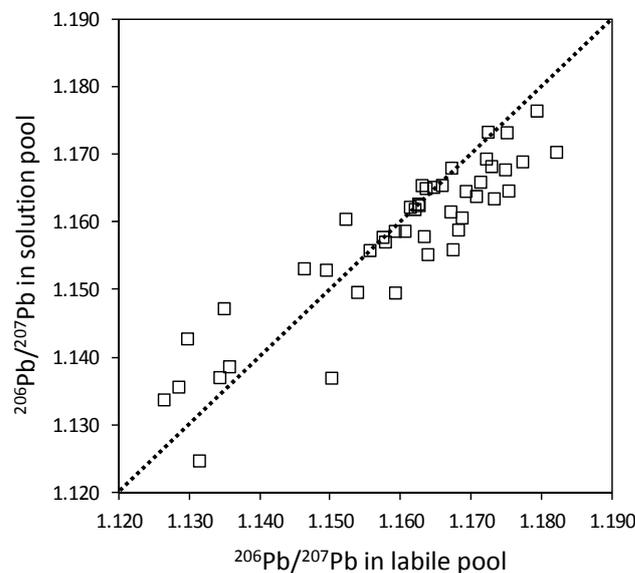
## Results and Discussion

Total Pb concentrations in the top and subsoils ranged between 43 and 1282 mg kg<sup>-1</sup>. The labile pools of Pb in the soil were found to be in the range 10-315 mg kg<sup>-1</sup> and despite the relatively narrow pH range (5.5- 8.0) they were found to decrease with increasing soil pH. Pb lability (% of total) was generally similar in both the top and sub soils reflecting the similar nature of soil properties that control Pb solubility (Fe/Mn oxides, organic matter) and the way alluvial soils build up through time. Centrifuged pore waters from the samples had concentrations of 0.17-6.47 µg L<sup>-1</sup>. Source apportionment analysis showed that Pb isotopic signatures in the total, labile and soil pore water pools fitted along the mixing line between local ore/local coal and petrol derived (tetra-ethyl) Pb sources, known as 'BHT' Pb (Figure 1).



**Fig 1:**  $^{206}\text{Pb}/^{207}\text{Pb}$  vs  $^{208}\text{Pb}/^{207}\text{Pb}$  ratio plot for the total, labile and pore water pools. Also shown for comparative purposes: potential sources, mixing line between the possible end-members, ratios for UK aerosols and contaminated soils.

As expected the local ore and/or local coal signature is dominant in the labile pools of most soils, whilst traffic-related Pb appears to substantially contribute to the elevated Pb concentrations in some samples, particularly those close to major road systems or sewage outlets. The occurrence of 'BHT' Pb in subsoils indicates considerable post-depositional vertical migration. The isotopic compositions of the labile pool and the pore water also suggests that 'BHT' Pb is enriched in the labile and pore water pools compared to their respective total soil pool, suggesting that petrol Pb is still being deposited to these soils and/or it has undergone a poor fixation since the withdrawal of leaded petrol. Theoretically, the Pb isotope ratios in the pore waters should be similar to those of the labile pool as it is the labile pool of metal, as measured using the E-value, that should buffer the soil pore water pool of Pb. Whilst a reasonable correlation was found between the labile pool and pore waters (Figure 2), further statistical analysis showed that there was still a statistical difference ( $P < 0.001$ ) between the two pools. The most likely explanation is that non-labile Pb is attached to sub-micron colloids (FeOx) in the pore waters.



**Figure 2: Relationship between  $^{206}\text{Pb} / ^{207}\text{Pb}$  ratios in the labile and pore water pools in soils from the Trent Catchment.**

## Conclusions

Alluvial soils sampled within 10m of the banks of the rivers Dove and Trent floodplain show significant spatial differences in Pb concentration and isotopic composition with strong anthropogenic influences linked to past Pb mining and smelting activity, coal mining/combustion, sewage works, canal dredging and the deposition of traffic-related atmospheric Pb. Comparison of the Pb ratios in the labile and pore water pools suggest (i) that they are enriched in petrol Pb compared to the total soil, (ii) that petrol Pb is sorbed to sub-micron colloids (in particular FeO) and this provides a potential transport pathway.

## References

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