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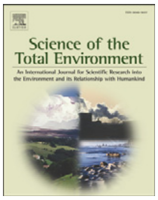

Sources, lability and solubility of Pb in alluvial soils of the River Trent catchment, U.K.

M. Izquierdo *, A.M. Tye, S.R. Chenery

British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK

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ABSTRACT

Alluvial soils are reservoirs of metal contaminants such as Pb that originate from many different sources and are integrated temporally and spatially through erosional and depositional processes. In this study the source, lability and solubility of Pb were examined in a range of alluvial soils from the middle and lower River Trent and its tributary the River Dove using Pb isotope apportionment and isotopic dilution. All samples were collected within 10 m of the river bank to represent the soil that is most likely to be remobilised during bank erosion. Paired samples were taken from the topsoil (0–15 cm) and subsoil (35–50 cm) to assess differences with depth. Lead concentrations in soil ranged from 43 to 1282 mg/kg. The lability of soil Pb varied between 9 and 56% of total metal concentration whilst Pb concentrations in pore water varied between 0.2 and 6.5 μg/L. There was little difference in the % Pb lability between paired top and sub soils, possibly because soil characteristics such as pH, iron oxides and clay content were generally similar; a result of the recycling of eroded and deposited soils within the river system. Soil pH was found to be negatively correlated with % Pb lability. Source apportionment using $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios showed that the isotopic ratios of Pb in the total, labile and solution pools fitted along a mixing line between Broken Hill Type ('BHT') Pb, used as an additive in UK petrol, and the local coal/Southern Pennine ore Pb. Various anomalies were found in the Pb isotopes of the bankside alluvial soils which were explained by point source pollution. Statistically significant differences were found between (i) the isotopic composition of Pb in the total soil pool and the labile/solution pools and (ii) the isotopic composition of Pb in the labile and solution pools, suggesting an enrichment of recent non-Pennine sources of Pb entering the soils in the labile and solution pools.

1. Introduction

Fluvial environments are a major pathway for the dispersal of trace pollutants (Bird, 2011) with alluvial soils being a major sink. For trace metals, the dominant (>90%) dispersal mechanism is via particulate-associated transport (Carter et al., 2006; Gibbs, 1973), particularly under flood conditions (Macklin et al., 1997). This can lead to the spatially extensive dispersal of contaminants from both point and diffuse sources (Bird, 2011). Overbank sediments in floodplains act as a focus for deposition and short- to long-term storage of metals (Bird, 2011; Marron, 1992), thus alluvial sediments and soils can be viewed as historical repositories of contaminants (Hudson-Edwards et al., 1998). However, these repositories cannot be viewed as permanent sinks, as, depending on spatial position metals are likely to be remobilised and released back into the drainage network through bank erosion caused by channel movement, undermining or bank collapse (Lawler, 1993; Trimble and Mendel, 1995).

The UK has an extensive Pb mining history in areas such as the Pennines, Peak District, Wales and the south west of England. Total concentrations of Pb in alluvial soils downstream from mines have been examined because of potential Pb poisoning to livestock, terrestrial and aquatic ecosystems. For example, Smith et al. (2009) reported problems of metal contamination occurring at great distance downstream of the original mining/mineralisation source in Wales. The orefields of the North Pennines, Yorkshire and Derbyshire were amongst the most productive Pb mining areas of Britain (Macklin et al., 1997) and Pb inputs to fluvial systems in Northeast England have received considerable attention (Carter et al., 2006; Dawson and Macklin, 1998; Dennis et al., 2009; Hudson-Edwards et al., 1997, 1999; Macklin et al., 1997; Shepherd et al., 2009).

The Geochemical Baseline Survey (G-BASE) of the UK (British Geological Survey, 2006) identified the alluvial soils of the Trent valley and some of its tributaries (Dove, Derwent) as having elevated concentrations (>200 mg/kg) of Pb. Median concentration of Pb in the soils formed from the Triassic mudstone, the dominant soil parent material within our study area, is 35 mg/kg. The primary source of extraneous Pb in the alluvial soil was considered to be a legacy of the mineralization/mining area in the Derbyshire Peak District. However, other sources of Pb contamination could include (i) industrial activity from urban areas such as Derby and Nottingham, (ii) coal combustion in a number of power stations sited throughout the Trent valley and (iii) the later legacy of 'Broken Hill Type' (referred as 'BHT') Pb used as an additive to petrol but phased out by the year 2000. The Pb from leaded petrol has been found to contribute up to 35% of

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* Corresponding author. Tel.: +44 115 936 3100; fax: +44 115 936 3200.
E-mail address: mizqu@bgs.ac.uk (M. Izquierdo).

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the total Pb in integrated inventories of deposited Pb in the UK (Bacon, 2002; Farmer et al., 2005). Other anthropogenic-related point- or diffuse-pollution sources of Pb can come from direct discharges of municipal or industrial effluents to rivers (Dawson and Macklin, 1998).

This study investigated whether there were spatial changes in source, concentration and lability of Pb in alluvial soils of a tributary (River Dove) and the middle and lower floodplain of the River Trent, one of the UK's major rivers. As alluvial soils build up over substantial periods of time, it was decided to investigate the sources and lability of Pb in both top and subsoils to (i) determine whether greater fixation processes have occurred in the deeper subsoils as they have been in situ for longer periods and (ii) to assess the possibility of downward migration of Pb within the soil. This is because subsoils are likely to end up being re-mobilised by erosion of the river bank and re-cycled as topsoils. The age of the alluvial soils on the modern floodplain is <10,000 years old. The most recent terraces of the River Trent in the study area include the Hemington Terrace and the Holme Pierrepoint Terrace and these have been dated at 10,000 and 26,000 yr BP (Howard et al., 2007). To develop this understanding both Pb isotope geochemistry and isotope dilution methods to measure reactive pools of Pb were used.

Pb isotope geochemistry has proved to be a powerful tool and has been used to trace sources, reconstruct historical trends in Pb deposition and trace the impact of the introduction and subsequent withdrawal of leaded petrol for many years (e.g. Bacon et al., 1996; Farmer et al., 2000, 2001; MacKinnon et al., 2011; Sugden et al., 1993). Its use has been especially successful in the UK because the indigenous UK coal and Pennine ore Pb have a very different Pb isotope ratio to the typical ‘Broken Hill’ type Pb used in petrol (Bird, 2011; Komárek et al., 2008). In the UK, the dominant sources of Pb used and subsequently released into the environment are petrol lead (^{206}Pb/^{207}Pb = 1.06–1.09) which consist of a combination of Australian Pb (^{206}Pb/^{207}Pb = 1.04) and British Columbian Pb (^{206}Pb/^{207}Pb = 1.16) (Sugden et al., 1993), native Pennine ore Pb and UK coal-derived Pb (typical ^{206}Pb/^{207}Pb ≈ 1.16–1.19; Vinogradoff et al., 2005). The Pb used in petrol was primarily derived from the “Broken Hill Mine” in Australia (Sugden et al., 1993). However, other sources of aerosol Pb have been recorded in the UK with a range of ^{206}Pb/^{207}Pb = 1.06–1.13 (Charlesworth et al., 2006; Noble et al., 2008). Whilst peat bogs and lake sediments have been extensively studied over the last decades as they provide undisturbed long-term records of Pb deposition (Chenery et al., 2012; Eades et al., 2002; Farmer et al., 1996, 1997a, 1997b, 2005; Hansmann and Köppel, 2000), it is only relatively recently that Pb isotopes have been applied as a method for provenancing the origin of Pb in riverine environments (Bird, 2011). Shepherd et al. (2009) described a regional study of Pb isotopes in stream sediments from Northern England and concluded that the Pennine ore signature was dominant although the anthropogenic Pb contribution could be significant.

Current UK regulations on metal contamination are based on the total concentration in soil, e.g. the sewage sludge directive (MAFF, 1993) or the Soil Guideline value (Environmental Agency, 2002). However, this does not provide any indication of the chemically reactive or labile fraction of a given element in a soil system. Significant research effort over the last few years has been directed at developing isotope dilution methods to determine the reactive pool of an element in soils, this being the pool of metal in equilibrium with the soil pore water (Hamon et al., 2008; Smolders et al., 1999; Young et al., 2005). The use of stable isotopes to determine the lability of Pb in soils has been the subject of relatively few studies (Atkinson et al., 2011; Degryse et al., 2007; Gäbler et al., 1999; Tongtavee et al., 2005). In addition, Atkinson et al. (2011) undertook a source apportionment study of labile and non-labile pools of four Pb-contaminated soils and observed significantly different isotopic signatures in both pools.

This study uses Pb isotope geochemistry and isotopic dilution techniques to identify the source, concentration and reactivity of Pb in a range of alluvial soils taken from the catchment of the River Trent. In addition, the source and size of the total, labile and solution pools of Pb in paired top and sub soils were examined to develop our understanding of Pb behaviour in alluvial soils deposited over thousands of years. Information regarding the reactivity of Pb in alluvial soils is currently limited in the literature.

2. Materials and methods

2.1. Study area

The River Trent flows north through the Midlands and has a catchment area of nearly 10,500 km^2 (Large and Petts, 1996). It has a number of tributaries, including the Rivers Dove and Derwent which drain the mineralised Carboniferous Limestone Formation (Fig. 1) of the Southern Pennine Orefield. The main ore minerals are galena (PbS), sphalerite (ZnS) and pyrite (FeS$_2$), with minor amounts of cerussite (PbCO$_3$) and smithsonite (ZnCO$_3$) (Ford, 1976; Li and Thornton, 2001). Lead mining in the Southern Pennine Orefield was first documented during Roman times and peaked during the 18th–19th centuries (Ford and Rieuwerts, 2000; Li and Thornton, 2001). Mining and smelting activities have caused widespread pollution and extensive remains of the former mining and Pb smelting activities (e.g. spoil heaps, mine shafts, smelting mills) are still present. An estimated area of 250 km^2 of land in Derbyshire is affected by Pb contamination (Colbourn and Thornton, 1978). Lead-rich sediments still pulse into the Trent tributaries in their upper catchments (Bradley and Cox, 1990) and can be stored in floodplain soils downstream.

A 50 km long reach of the lower River Dove and a further 180 km reach of the middle and lower River Trent (Fig. 2), which flows over the Mercia Mudstone Group, were examined. The lower Trent has been regulated for flood control and navigation (Large and Petts, 1996). Quaternary sand and gravel river terraces have been reworked to form the alluvial deposits (locally up to 10 m thick) on which the Holocene alluvial soils rest (Howard et al., 2007). Evidence that the floodplain deposits along the River Trent have been reworked throughout their entire depth in historic times has been found (Large and Petts, 1996).

The close proximity of the Derbyshire–Nottinghamshire–Yorkshire coalfields (Fig. 1) referred to as Midlands coal in the following discussion, means that mining, smelting and industry have been additional sources of Pb contamination to the Trent catchment since the 18th century. The River Trent has provided cooling water to a number of power stations across Nottinghamshire and Lincolnshire that fired locally mined coal (Fig. 2). Local coal was also used for smelting iron ore mined close to the River Trent outlet (British Geological Survey, 2006). Agriculture in the Dove valley is dominated by pasture for grazing whilst from the confluence of the Dove and Trent, arable agriculture dominates.

2.2. Soil sampling and sample preparation

2.2.1. Soil and soil pore water collection

Soil samples were collected at 27 sites, 7 of which were from the River Dove floodplain, one was at the confluence between the Dove and Trent and the remainder along the Lower Trent floodplain (Fig. 2). The soil samples were taken at depths compatible with those in the national geochemistry baseline survey of the UK (G-BASE) i.e. 0–15 cm (topsoil) and 35–50 cm (subsoil) (Johnson et al., 2005). Soils were collected from a range of agricultural and woodland sites where the alluvial soils have been able to form naturally. Samples were not collected between Newark and Scunthorpe on the River Trent because of the construction of artificial embankments as flood defences. Five sampling sites were located in woodland, whilst the remaining sampling sites were predominantly on improved/rough pasture or arable land within 10 m of the river bank. At 19 sites, paired top and sub-soil samples were collected.