Science of the Total Environment 544 (2016) 730–743

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Influences upon the lead isotopic composition of organic and mineral horizons in soil profiles from the National Soil Inventory of Scotland (2007–09)

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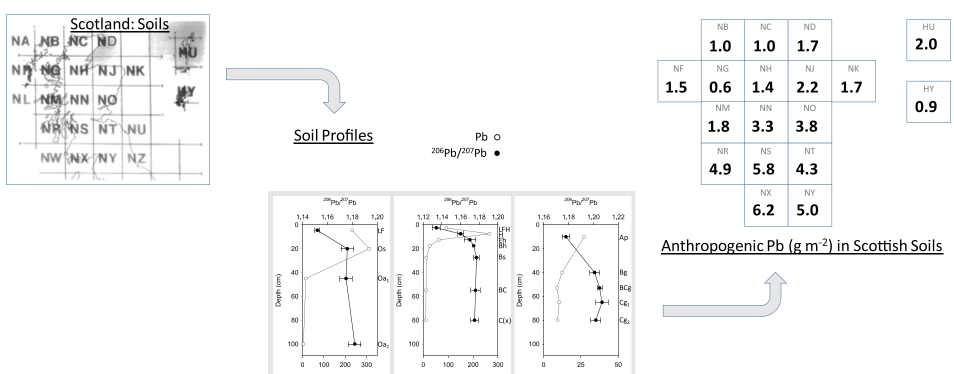
HIGHLIGHTS

- Pb isotope ratios were determined for 644 soil horizons from 169 sites across Scotland
- Pb in organic soil horizons was essentially atmospherically deposited anthropogenic Pb
- Pb in mineral top soil horizons was a mixture of anthropogenic and indigenous soil Pb
- ~50% Pb in cultivated agricultural soils (Ap) to a depth of ~30 cm was anthropogenic
- The anthropogenic Pb soil inventory was ~3 times greater in the south than the north

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 October 2015
Received in revised form 18 November 2015
Accepted 24 November 2015
Available online 10 December 2015

Editor: F.M. Tack

Keywords:
Pb
Isotope ratios
Organic soil
Mineral soil
Scotland

ABSTRACT

Some 644 individual soil horizons from 169 sites in Scotland were analyzed for Pb concentration and isotopic composition. There were three scenarios: (i) 36 sites where both top and bottom (i.e. lowest sampled) soil horizons were classified as organic in nature, (ii) 67 with an organic top but mineral bottom soil horizon, and (iii) 66 where both top and bottom soil horizons were mineral. Lead concentrations were greater in the top horizon relative to the bottom horizon in all but a few cases. The top horizon $^{206}Pb/^{207}Pb$ ratio was lesser (outside analytical error) than the corresponding bottom horizon $^{206}Pb/^{207}Pb$ ratio at (i) 64%, (ii) 94% and (iii) 73% of sites, and greater at only (i) 8%, (ii) 3% and (iii) 8% of sites. A plot of $^{208}Pb/^{207}Pb$ vs. $^{208}Pb/^{206}Pb$ ratios showed that the Pb in organic top (i, ii) and bottom (i) horizons was consistent with atmospherically deposited Pb of anthropogenic origin. The $^{206}Pb/^{207}Pb$ ratio of the organic top horizon in (ii) was unrelated to the $^{206}Pb/^{207}Pb$ ratio of the mineral bottom horizon as demonstrated by the geographical variation in the negative shift in the ratio, a result of differences in the mineral horizon values arising from the greater influence of radiogenic Pb in the north. In (iii), the lesser values of the $^{206}Pb/^{207}Pb$ ratio for the mineral top horizon relative to the mineral bottom horizon were consistent with the presence of anthropogenic Pb, in addition to indigenous Pb, in the former. Mean anthropogenic Pb inventories of 1.5 and 4.5 g m^{-2} were obtained for the northern and southern halves of Scotland, respectively, consistent with long-range atmospheric transport of anthropogenic Pb (mean $^{206}Pb/^{207}Pb$ ratio ~ 1.16). For cultivated agricultural soils (Ap), this corresponded to about half of the total Pb inventory in the top 30 cm of the soil column.

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http://dx.doi.org/10.1016/j.scitotenv.2015.11.127
0048-9697/

1. Introduction

Clair Patterson's finding in the 1960s that more than 90% of the atmospheric Pb in the northern hemisphere at that time was derived from anthropogenic sources such as car-exhaust emissions (in the era of leaded petrol), coal combustion and metal ore smelting (Patterson, 1965; Murozumi et al., 1969) has subsequently been supported by many historical studies based on the Pb analysis of cores from ice sheets, peat bogs and lake sediments (e.g. Boutron et al., 1991; Shotyk et al., 1998; Renberg et al., 2001). Such studies have often included Pb isotope analyses, which have provided valuable information on the relative contributions of Pb from sources of differing Pb isotopic composition associated with various human activities over the past few thousand years (e.g. Shirahata et al., 1980; Rosman et al., 1997; Bindler, 2011). Based partly on the isotopic evidence (e.g. $^{206}Pb/^{207}Pb$ ratios), it is widely accepted that accumulations of Pb in ice, peat and sediment cores are anthropogenic in origin and that they are the result of long-term and long-range atmospheric deposition (e.g. Steinnes et al., 2005a; Zheng et al., 2007; Steinnes, 2009; Klaminder et al., 2011).

In Scotland, there have been numerous studies of the isotopic composition of sources of Pb (Sugden et al., 1993; Farmer et al., 1999, 2000) and of Pb in peat, lake sediments, moss and other terrestrial plants in the rural environment (e.g. Farmer et al., 1996, 1997, 2002, 2010, 2015; MacKenzie et al., 1997, 1998; Eades et al., 2002; Weiss et al., 2002; Patrick and Farmer, 2007; Cloy et al., 2008; Kylander et al., 2009). With the exception of a few studies on urban and suburban soils (e.g. Farmer et al., 2011; MacKinnon et al., 2011), most Pb isotopic work on Scottish soils has focused on the rural environment, in particular at the Glensaugh field station and long-term monitoring site in the rural North East (e.g. Bacon et al., 1992, 1995, 2004, 2006). Data for organic soils at Glensaugh, which is a site distant from any point sources, show typical $^{206}Pb/^{207}Pb$ ratios to be 1.15–1.17 in surface horizons but 1.18–1.20 in deeper horizons (Bacon et al., 1992, 1995, 2004, 2006; Farmer et al., 2005). Long-range atmospheric transport and deposition of Pb has been invoked in explanation, with contributory sources including car-exhaust emissions ($^{206}Pb/^{207}Pb$ ratio ~ 1.08), Pb ore smelting (~1.17) and coal combustion (~1.18) (Farmer et al., 1999, 2000, 2010). Hilltop peat cores at Glensaugh have shown anthropogenic Pb inventories in the range 6–9 g m^{-2}, with ~40% deposited prior to 1900 and a further ~20% between 1900 and 1930 from ore smelting/coal combustion during the UK industrial era, prior to the introduction of leaded petrol, which was in use in the UK until its total ban in 2000 (Farmer et al., 2005).

There is, however, an alternative view that there is little evidence for long-range atmospheric transport of Pb. While conceding the influence of human activities in and around urban centres, a few large-scale soil surveys in both Europe and North America have concluded that soil Pb contamination results principally from local point sources with only minimal influence of long-range atmospheric transport (Reimann et al., 2009, 2011, 2012). One such study provided Pb isotope data for European cultivated agricultural soils (Ap, 0–20 cm) that included ~50 soils for the whole of Scotland, collected on a 50 km grid (Reimann et al., 2012).

The National Soil Inventory of Scotland (NSIS) was recently resampled on a 20 km grid and samples taken from a range of soil horizons and depths. This exercise has provided an ideal opportunity to carry out a much more detailed and systematic survey of the Pb status of Scottish soils, in particular of the Pb isotope composition, to investigate the geographical spread, extent and source of Pb contamination in Scotland. A similar country-wide survey has recently been carried out in The Netherlands, where Walraven et al. (2013a, 2013b) concluded that the Pb isotope composition of the additional Pb in ~350 rural top soils (A, 0–20 cm) differed clearly from lithologically inherited Pb, as observed in the corresponding subsoils (BC, C, 100–120 cm), and argued for an anthropogenic origin.

The specific objectives of this project were to (i) determine the Pb isotopic composition of soil profiles for which Pb concentrations had been measured as part of the recent NSIS 2007–09 Survey, (ii) establish the baseline Pb isotope composition of mineral soils and the potentially anthropogenically influenced Pb isotope composition of both mineral and organic soil horizons throughout Scotland, (iii) compare the Pb isotope composition of surface soil horizons with that of bottom (i.e. lowest sampled) soil horizons and (iv) assess the causes and extent of any observed variations in Pb isotope composition, including the magnitude of the potential anthropogenic contribution.

2. Materials and methods

2.1. National Soil Inventory of Scotland (NSIS)

The National Soil Inventory of Scotland (NSIS) consists of samples taken on a regular grid pattern in 1978–88 (NSIS 1) and resampled in

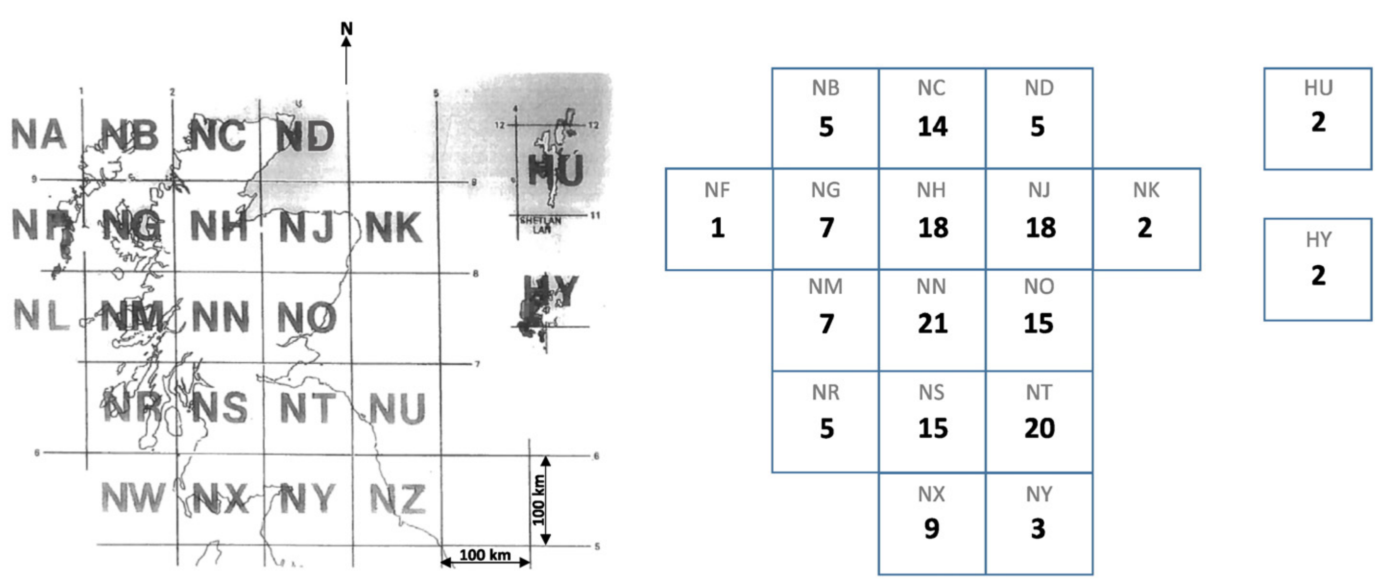

Fig. 1. Map of Scotland with the Ordnance Survey (OS) National Grid imposed and the corresponding diagrammatic version showing the distribution among individual OS zones of the 169 soil profile sites considered in this study.