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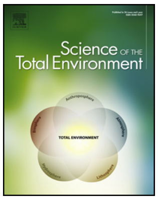

Short communication

Geogenic lead isotope signatures from meat products in Great Britain: Potential for use in food authentication and supply chain traceability

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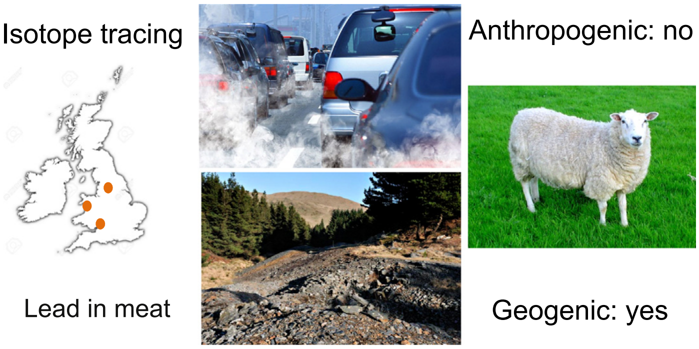
HIGHLIGHTS

- Lead (Pb) isotopes measured in modern British meat were geogenic in origin.
- The match indicates that this technique may be used to provenance biological products.
- There was no evidence for a contribution from modern anthropogenic Pb sources.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents lead (Pb) isotope data from samples of farm livestock raised in three areas of Britain that have elevated natural Pb levels: Central Wales, the Mendips and the Derbyshire Peak District. This study highlights three important observations; that the Pb found in modern British meat from these three areas is geogenic and shows no clear evidence of modern tetraethyl anthropogenic Pb contribution; that the generally excellent match between the biological samples and the ore field data, particularly for the Mendip and Welsh data, suggests that this technique might be used to provenance biological products to specific ore sites, under favourable conditions; and that modern systems reflect the same process of biosphere averaging that is analogous to cultural focusing in human archaeological studies that is the process of biological averaging leading to an homogenised isotope signature with increasing Pb concentration.

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1. Introduction

International food scares such as melamine in milk products (China), methanol in spirits (Eastern Europe), horse meat in beef products (Europe), and more recently concerns over Pb levels in noodles (India), illustrate the global nature of the food supply and importance of supply chain traceability and testing as a means of providing assurance in the integrity of our food. Although DNA analysis has a major role to play in distinguishing between species, reliable tests are required that can fingerprint the geographic origins of products entering the human food chain (authentication). In this study, we investigate the potential for the isotopes of lead (Pb), measured in animal products, to act as one such geogenic marker at a local scale.

There are four naturally occurring isotopes of Pb (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb), with the last three being end-members of the natural uranium (U)–thorium (Th) decay series (radiogenic Pb). The usefulness of Pb as a provenance tool lies in subtle, yet measurable, variations in the relative abundances of each of the radiogenic isotopes within ores of different ages. The evolution of these differences is described by the Holmes–Houtermans Model (Faure, 1986). Ores formed at different geological times therefore possess Pb isotope ratios which reflect the growth of radiogenic Pb prior to mineral formation, or 'closure'. This natural variation in Pb isotopes allows for their use as tracers within environmental systems (Gulson, 2008; Komárek et al., 2008). Pb entering the food chain is not fractionated by biological processes (Dickin, 1995; Faure, 1986; Fowler et al., 1993; Roux et al., 2008), and thus, the ingested/adsorbed Pb 'signature' of a sample directly reflects that of its source (Smith and Flegal, 1995). When Pb exposure is derived from interaction with an in situ geological source, this is referred to as geogenic exposure, and the isotope signature of a sample can be used to geographically locate the place of exposure (Montgomery et al., 2010; Reimann et al., 2014) in a manner analogous to the way in which Sr is used as a tracer in archaeological studies (Bataille and Bowen, 2012)., Although Sr is ingested through consumption of food, predominately cereals, Pb tends to be taken up though direct ingestion or inhalation of dust and soil particulates (Abrahams and Steigmajer, 2003; Farmer et al., 2011).

Mining has been carried out in Britain for millennia (Johnston, 2008; Juleff and Bray, 2007; McFarlane et al., 2014). Consequently, much of the bioavailable Pb is anthropogenic, which if present in sufficient concentrations, has the potential to swamp naturally available Pb (Kamenov and Gulson, 2014). This was illustrated by Montgomery et al. (2010) who used archaeological samples (teeth) to track the changing Pb isotope signature in humans with time; from Neolithic samples, which reflected a varied geogenic Pb source, through to the Roman and industrial 'culturally focused' Pb isotope values, which reflects an homogenised UK signature formed as Pb mined from a variety of UK sources was traded, recycled and reused.

Today, a significant source of anthropogenic Pb in the UK environment remains that which was added to petrol as an anti-knock agent during the 1960s until when it was banned by the EU in 2000 (Bacon et al., 2006; Farmer et al., 2000; Farmer et al., 2010; Farmer et al., 2005; Monna et al., 1997). This 'petrol Pb' largely originates from the geologically ancient mines in Australia (Broken Hill and Mt Isa) and hence has a very distinctive ^{206}Pb/^{204}Pb composition around 16.1 (Gulson, 1986) that is clearly distinguishable from that in geologically younger, Carboniferous aged mine deposits of Britain which has a ^{206}Pb/^{204}Pb of about 18.4.

Although Pb in petrol was withdrawn in the UK in 2000, a study by Noble et al. (2008) showed that it still makes a significant contribution to the atmospheric Pb budget, with isotope values measured at London air monitoring stations showing only a very slow return to pre-petrol Pb/natural British Pb values.

Our hypothesis was that the Pb isotope signature of the livestock would reflect the animal's interaction with its environment. Samples in this study were collected from three areas of Pb mineralisation in Britain; the predominantly Carboniferous mineralisation of the Mendips and Pennines, and the Palaeozoic deposits of, central Wales (Fig. 1). Pb isotope data from these ore fields were available (Barreiro, 1996; Barreiro and Spiro, 1997a; Fletcher et al., 1993; Haggerty et al., 1996b; Moorbath, 1959; Rohl and Needham, 1998) and details of mine locations in Wales are given in Ball and Nutt (1976), providing an excellent geogenic reference for comparison with the samples.

2. Materials and methods

Samples of kidney, liver, or blood from cattle, sheep and hens (broilers and layers) were sampled from the three areas of Britain: Aberystwyth, in Wales, Pennine area of Derbyshire and the Mendip Hills of Somerset in a study commissioned by the UK's Food Standards Agency (FSA) (Knowles and Richards, 2014). These are historical Pb mining areas and so have the potential to cause elevated levels of Pb in animals. Details of the selection and origins of the samples are given in Knowles *ad bid*.

2.1. Pb isotope analysis

Pb isotope analysis of the samples was conducted using a Nu Instruments Nu Plasma, a Multi Collector-Inductive Coupled-Plasma Mass Spectrometer (MC-ICP-MS). Prior to analysis, each sample was filtered (Millipore 0.25 μm PFA) and spiked with a thallium (Tl) solution, which was added to allow for the correction of instrument induced mass bias. Samples were then introduced into the instrument via an ESI 50 μl/min PFA micro-concentric nebuliser attached to a desolvating unit (Nu Instruments DSN 100). For each sample, five ratios were simultaneously measured (^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb). Each individual acquisition consisted of 60 sets of ratios, collected at 5-second integrations, following a 60 second de-focused baseline.

The precision and accuracy of the method were assessed through repeated analysis (one standard for every 3–4 unknowns) of an international standard US National Bureau of Standards NBS 981 Pb reference solution (also spiked with Tl). The average values obtained for each of the measured NBS 981 ratios were then compared to the known values for this reference (Thirlwall, 2002). All sample data were subsequently normalised, according to the relative daily deviation of the measured reference value from the accepted reference value. Normalisation to an international standard in this way effectively cancels out the effects of slight daily variations in instrumental accuracy, and allows the direct comparison of the data obtained during different analytical sessions. Internal uncertainties (the reproducibility of the measured ratio) were propagated relative to the external uncertainty (i.e. the excess variance associated with the reproducibility of the reference material analysed during the session). Average 2SD (standard deviation) uncertainties for the ratios are as follows ^{206}Pb/^{204}Pb $\pm$ 0.012%, ^{207}Pb/^{204}Pb $\pm$ 0.012, ^{208}Pb/^{204}Pb $\pm$ 0.015, ^{207}Pb/^{206}Pb $\pm$ 0.004, and ^{208}Pb/^{206}Pb $\pm$ 0.014. Procedural blanks for chemical separation and mass spectrometry were $<$100 pg and procedural sample repeats agreed within analytical uncertainty.

Data are presented in the supplementary section and plotted in Figs. 2 and 3.

3. Results

In Fig. 2a (^{208}Pb/^{206} vs ^{207}Pb/^{206}Pb) and Fig. 2b (^{208}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb) the sample data are plotted together with published Pb isotope data from relevant local ore bodies (Barreiro, 1996; Barreiro and Spiro, 1997b; Fletcher et al., 1993; Haggerty et al., 1996a; Rohl, 1996). The plots highlight different aspects of the data: whereas (^{208}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb) plots thorogenic Pb against uranogenic Pb, hence fully separating out the geochemically different decay systems, it is dependent on using the ^{204}Pb ratios (Ellam, 2010). Older