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The intake of lead and associated metals by sheep grazing mining-contaminated floodplain pastures in mid-Wales, UK: I. Soil ingestion, soil–metal partitioning and potential availability to pasture herbage and livestock

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ABSTRACT

This paper first evaluates the relative importance of the soil–plant–animal and soil–animal pathways of Zn, Cu and (especially) Pb investigated over a 15-month study period at 12 floodplain sites located within and downstream of the mineralised and historic mining area of mid-Wales, and secondly considers the implications of a sequential extraction procedure (SEP) undertaken on soils of varying particle size sampled from the study locations. Generally, very good agreement was found between the chemical partitioning of the three metals for each of the physical soil fractions subjected to the SEP. The availability of Pb to pasture vegetation, especially at the contaminated sites, is indicated with its associations with the more soluble (i.e. exchangeable and Fe/Mn oxide) soil phases, yet soil and/or plant barriers effectively restrict above-ground herbage concentrations of this metal. Consequently, with sheep ingesting soil at rates varying according to season from 0.1% to 44% or more of dry matter intake, the soil–animal pathway accounts for the majority of Pb consumption through most of the year, and at moderately and highly contaminated sites significant quantities of relatively soluble soil–Pb can be ingested at rates exceeding safety threshold limits.

1. Introduction

Historical mining, the weathering of mineral ores and subsequent fluvial redistribution across mid-Wales, has led to the deposition of contaminated sediments and enrichment of downstream floodplain soils with metals including zinc (Zn), copper (Cu) and especially lead (Pb; Alloway and Davies, 1971; Davies and Lewin, 1974; Lewin et al., 1977). Although all mining activity in the area had ceased by 1942, fluvial re-working and the erosion, transport and deposition of dissolved and suspended constituents from mine-workings, spoil heaps and river banks remain a contemporary source of floodplain soil–metal contamination (Davies, 1987; Lewin and Macklin, 1987). Deposited alluvium typically creates a fertile soil heavily used for agricultural purposes, although in mid-Wales problems of metal contamination can occur for a great distance downstream of the original mining/mineralisation source. Towards the end of the >2000 year mining history Griffith (1919) reported toxic effects to fish in the rivers draining these mineralised catchments, and to crops and livestock on associated floodplains. Incidents of Pb intoxication in cattle as a result of exposure to high concentrations in soils and mining spoil have been reported more recently in the same area (e.g. VLA, 2008), and an initial reconnaissance survey and metal analysis of soils, pasture herbage and sheep faeces was summarised by two of us (Abrahams and Steigmajer, 2003), who identified the importance of ingested soils in supplying metals, especially Pb, to grazing livestock. Our initial survey period of investigation has subsequently been extended over 15 months and soil ingestion rates have been recalculated using improved analytical techniques. This paper firstly reports on the relative importance of the soil–plant–animal and the soil–animal pathway of Zn, Cu and Pb to sheep grazing the floodplain pastures of mid-Wales over the 15 month study period. Secondly, we consider the results of a widely known sequential extraction procedure (SEP) employed on soil samples collected from the study fields. The SEP estimates soil–metal partitioning, and we: (a) compare the results from the procedure undertaken on varying soil particle size fractions, and (b) consider the implications for potential soil–metal availability to pasture plants and sheep grazing the floodplain herbage.

2. Materials and methods

2.1. The study area

The Central Wales mining district is recognised as a complex orefield in which multiple phases of mineralisation involving Pb, Zn, Cu and other elements such as cobalt and nickel have occurred (Mason, no date). Mining and the processing and smelting of ores

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have taken place in the region since Bronze Age times when Cu production was undertaken (Mighall et al., 2002). During the period of the Roman Empire there was a focus on Pb mining that is also evident later in Medieval times and from the 16th century until the early 20th century. Zinc output became important from the mid-19th century onwards. Whilst minerals such as galena (PbS, the most important primary metalliferous mineral found within the study area) can be recognised as being associated with supplying low concentrations of available Pb to plants/animals, the chemical weathering of such constituents in soils has a significant influence on metal availability to organisms. Thus, Mason (2004) notes the widespread occurrence of secondary cerussite ($PbCO_3$) and pyromorphite [$Pb_5(PO_4)_3Cl$] formed as a result of the chemical weathering of PbS: the latter is a stable soil–Pb mineral of extremely low solubility (and hence availability), whilst in comparison the former is associated with more readily available Pb to organisms (Plumlee, personal communication).

Fieldwork was undertaken in mid-Wales on the floodplains of four rivers (Afon Clarach, Rheidol, Teifi and Ystwyth) historically affected by metalliferous mining activity. The Afon Aeron was additionally identified as a control catchment. In all, twelve sample sites were selected from within the five catchments, representing the total soil Pb concentrations found across the area (see Abrahams and Steigmajer (2003) for details), and grouped into three categories: 'uncontaminated' or control soils with <150 μg Pb g^{-1} (sites U1-4), 'moderately contaminated' soils containing 150–1000 μg Pb g^{-1} (sites M1-5) and 'highly contaminated' soils with >1000 μg Pb g^{-1} (sites H1-3). All soils are associated with alluvium or gravel terraces and belong to the Conway (poorly drained gley soils on silty alluvium), Rheidol (moderately well drained brown earths on terrace gravels) or Clwyd (an imperfectly drained intergrade lying between the former soils) series (Rudeforth, 1970) that typically have topsoils which are slightly to moderately acidic in reaction (topsoil pH at the 12 study sites measured in a 1:2.5 w/v $CaCl_2$ suspension varied from 4.5–6.3, median = 5.2) and contain low/medium amounts of soil organic matter (4.5–8.9%, median = 6.0%; Steigmajer (1999)). Each site was under pasture and known to be regularly grazed by sheep. The sampling areas were restricted to that available for grazing and were thus determined by field and farm boundaries. Sites were selected specifically where the majority of that boundary lay on the floodplain, directly adjacent to the river and so affected by recurrent flood events and depositions of river material including historical mining-related contamination.

2.2. Method for evaluating the soil–plant–animal and soil–animal pathways of Pb, Zn and Cu

With fields <4 ha in area, a 3.5 cm diameter screw auger was used to collect (from a 'W' shaped traverse walked at each site) a representative topsoil sample by bulking at least 25 0–15 cm depth cores. Following preparation, samples were analysed for their pseudo total metal content utilising a HNO_3–$HClO_4$ digestion. Above-ground pasture vegetation and the faeces of sheep were routinely collected from the fields every other month over a period of 15 months from January 1999 to March 2000. Vegetation was cut using Teflon-coated stainless steel scissors, taking care to avoid pulling up the root mass, and where possible, removing only that above 1 cm from the soil surface. A 'W' traverse was utilised to obtain a bulked representative sample collected from at least 25 points. Mixed pasture herbage samples were collected, but no attempt was made to evaluate species composition. Faecal matter was collected with a stainless steel trowel, avoiding any that had been in obvious contact with the soil surface. Faeces were taken from at least 20 different specimens in each field, and bulked to form a representative sample. Many details regarding preparation and analysis of these samples have been previously reported by Abrahams and Steigmajer (2003) and for the sake of brevity are not repeated here. In the laboratory vegetation samples were divided into two: the first left unwashed to reflect any contamination with soil particles in the field environment and the second, representing metal uptake from soils and translocation to the above-ground portion of the plant, thoroughly washed three times in deionised water, or until the washings were free from visible soil particles. The inefficiency of washing has been previously cited by Fortmann and Johnson (1984) as a problem in interpreting the results from such a preparation procedure. Subsequent comparison of both washed and unwashed vegetation samples in our work, using titanium (Ti) as a stable marker of the constituent proportion of soil particles, indicated an efficiency of the washing procedure between 60 and 93%. On this basis the recorded concentrations of metals in washed herbage may be an over-estimation of that actually present in the plant tissues, attributable to contamination with soil particles enriched in these elements.

Soil ingestion by grazing sheep was estimated from the Ti concentrations of soils and faecal material. The samples were digested using a HCl–$HClO_4$–HF procedure and Ti^{47} concentrations (this isotope was preferred as it displayed a greater precision and accuracy under analysis and has no known spectroscopic interferences) were determined by inductively coupled plasma-mass spectrometry (ICP-MS) using a VG Elemental PlasmaQuad II instrument with Ru^{102} as an internal calibration standard (Smith, 2004). Soil ingestion rates were estimated as a percentage of dry matter (DM) intake according to the formula of Thornton and Abrahams (1983) and assuming pasture digestibility of 72% (Green et al., 1996):

$$\%\ \text{soil ingestion} = \frac{(1 - D_h)Ti_f \times 100}{Ti_s - D_h Ti_f} \qquad (1)$$

Where D_h is the digestibility of the vegetation, Ti_s is the Ti concentration of the soil (minimum–maximum = 1544–3827 μg g^{-1} in our study, median = 3316 μg g^{-1}) and Ti_f is the Ti concentration of the faeces (19–2365 μg g^{-1}, median = 740 μg g^{-1}).

2.3. Method for the sequential extraction procedure

Following collection of the representative topsoils, the samples were air-dried, (as recommended in the Community Bureau of Reference (BCR) standardised sequential extraction procedure (Quevauviller et al., 1993a,b; Ure et al., 1993)) in the laboratory and stored at 4 °C, to reduce further microbial action on the form of soil–metals, until required. Particle size is important in laboratory analyses (Salomons and Förstner, 1984) as it is considered to be a factor governing both the total concentration of soil–metals and also their potential bioavailability (e.g., Macklin and Dowsett, 1989). Whilst the <2000 μm 'fine earth' fraction is often cited to be geochemically reactive and used in bioavailability research (Quevauviller et al., 1993a; Hudson-Edwards et al., 1996; Dawson and Macklin, 1998), others have advocated the use of finer fractions: <1000 μm (Davidson et al., 1998; Zhang et al., 1998), <170 μm (Li and Thornton, 2001; Maskall and Thornton, 1998) and <63 μm (Bird et al., 2003; Bradley and Cox, 1987; Ho and Evans, 2000; Ure et al., 1993). In our research, following an initial analysis undertaken on the <2000 μm fine earth, the sequential extraction procedure was additionally performed on the <63 μm (silt and clay) and 63–2000 μm (sand) constituent particle sizes to assess the variability in metal partitioning and the reliability of data from analysis solely of the <2000 μm 'reactive' fraction reported in previous studies. Air-dried soil samples were disaggregated using an acid-clean agate pestle and mortar prior to being passed through a stainless steel sieve stack to collect the <63 μm, 63–2000 μm and <2000 μm fractions. Samples for each particle size were thoroughly homogenised before sequential extraction.

The SEP used was adapted from that designed and developed by the BCR (Community Bureau of Reference; now the Standards,