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Determination of the bioaccessibility of chromium in Glasgow soil and the implications for human health risk assessment

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ABSTRACT

The Unified Bioaccessibility Method (UBM), which simulates the fluids of the human gastrointestinal tract, was used to assess the oral bioaccessibility of Cr in 27 Glasgow soils. These included several contaminated with Cr(VI), the most toxic form of Cr, from the past disposal of chromite ore processing residue (COPR). The extraction was employed in conjunction with the subsequent determination of the bioaccessible Cr by ICP-OES and Cr(VI) by the diphenylcarbazide complexation colorimetric procedure. In addition, Cr(III)-containing species were determined by (i) HPLC-ICP-MS and (ii) ICP-OES analysis of gel electrophoretically separated components of colloidal and dissolved fractions from centrifugal ultrafiltration of extracts. Similar analytical procedures were applied to the determination of Cr and its species in extracts of the <10 μm fraction of soils subjected to a simulated lung fluid test to assess the inhalation bioaccessibility of Cr.

The oral bioaccessibility of Cr was typically greater by a factor of 1.5 in the 'stomach' (pH ~1.2) compared with the 'stomach + intestine' (pH ~6.3) simulation. On average, excluding two COPR-contaminated soil samples, the oral bioaccessibility ('stomach') was 5% of total soil Cr and, overall, similar to the soil Cr(VI) concentration. Chromium(VI) was not detected in the extracts, a consequence of pH- and soil organic matter-mediated reduction in the 'stomach' to Cr(III)-containing species, identified as predominantly Cr(III)-humic complexes. Insertion of oral bioaccessible fraction data into the SNIFFER human health risk assessment model identified site-specific assessment criteria (for residential land without plant uptake) that were exceeded by the soil total Cr (3680 mg kg^{-1}) and Cr(VI) (1485 mg kg^{-1}) concentration at only the most COPR-Cr(VI)-contaminated location. However, the presence of measurable Cr(VI) in the <10 μm fraction of the two most highly Cr(VI)-contaminated soils demonstrated that inhalation of Cr(VI)-containing dust remains the most potentially harmful exposure route.

1. Introduction

The bioavailability of a chemical has been defined as 'the extent to which a chemical can be absorbed by a living organism' (Kelley et al., 2002) and the oral bioavailability as 'the fraction of an administered dose that reaches the central (blood) compartment from the gastrointestinal tract' (Ruby et al., 1999). Oral bioaccessibility, on the other hand, is defined as 'the fraction that is soluble in the gastrointestinal environment and is available for absorption' (Ruby et al., 1999) and, with respect to soil, 'the fraction of a substance that is released from the soil matrix in the human gastrointestinal tract and is available for absorption' (Schewald, 2001).

Chemical methods of assessing the oral bioaccessibility of potentially harmful elements to humans via oral ingestion of soil and dust have been developed over recent years. These methods have evolved from simple extraction with dilute hydrochloric acid to much more sophisticated simulations of the various components of the human digestive tract and have been applied most often to determine the oral bioaccessibility of Pb and As (Ruby et al., 1993, 1996, 1999; Kelley et al., 2002; Oomen et al., 2002, 2003; Palumbo-Roe et al., 2005; Drexler and Brattin, 2007; Van de Wiele et al., 2007; Morman et al., 2009).

Much less common has been application to other elements, including Cr, an element, unlike Pb and As, known to exist in both cationic ($Cr(III)^{3+}$) and anionic ($Cr(VI)O_4^{2-}$) forms in the environment, depending upon pH and the presence of reducing or oxidising conditions (Skowronski et al., 2001; Stewart et al., 2003a,b). The different forms of Cr also exhibit different toxicities, Cr(III) (in certain combined forms) generally being regarded as essential for human

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health and Cr(VI) as harmful (e.g. carcinogenic) and, unlike Cr(III) itself, capable of penetrating cell membranes (Pellerin and Booker, 2000; Plumlee and Ziegler, 2005). This was reflected, in the UK, in the old Interdepartmental Committee for the Redevelopment of Contaminated Land (ICRCL, 1987) 'trigger' concentrations of 25 mg kg^{-1} and 600 mg kg^{-1} for Cr(VI) and total Cr, respectively, for domestic gardens and allotments. However, the generic DEFRA Soil Guideline Values (SGVs) that replaced them, namely 130 mg kg^{-1} for residential land-use (with plant uptake) and allotments, and 200 mg kg^{-1} for residential land-use (without plant uptake) assumed that all Cr in the soil was Cr(VI) (DEFRA, 2002a,b), reportedly because of the difficulties in characterising the oxidation state of Cr in environmental samples. These values are currently under review (DEFRA, 2006).

Industrial activities leading to Cr contamination of land in the urban environment typically include metal (chrome) plating, tanning, wood and textile preservation, and disposal of power production fly ash and sewage sludge. One special case, however, is that of the disposal of chromite ore processing residue (COPR) to landfill, most notably close to former smelters (e.g. in Glasgow, Scotland, and New Jersey, USA) that employed high-lime methods in the roasting of chromite ore (Farmer et al., 1999). This led to localised contamination of land, for example in Glasgow, with Cr(VI) concentrations of up to 15,600 mg kg^{-1} (Bewley et al., 2001) and under elevated pH conditions that have led to secondary-mineral-mediated release of Cr(VI) to groundwater (Farmer et al., 2002, 2006; Geelhoed et al., 2002). Farmer and Jarvis (2009) have reviewed the evidence and discussed some of the implications of this Cr(VI) contamination for health in the Glasgow area and ways in which this might be investigated.

The study described here focuses on the Glasgow area, one of the 26 UK urban centres surveyed as part of the British Geological Survey (BGS) Geochemical Baseline Survey of the Environment (G-BASE) project (Johnson et al., 2005). A comparison of 14 of these urban centres (Fordyce et al., 2005) revealed that the highest concentrations of total Cr in urban soils occurred in Glasgow (range 38-4286 mg kg^{-1}), with a median of 108 mg kg^{-1} compared with a median rural soil concentration of 41 mg kg^{-1} for Scotland (Paterson et al., 2003) and 39 mg kg^{-1} for England and Wales (McGrath and Loveland, 1992). The G-BASE Glasgow survey provided some of the soil material chosen for investigation here.

The objectives of the study were three-fold: (i) to optimise extraction tests for determination of oral and inhalation bioaccessibility of Cr in contaminated soils and to apply them to selected Glasgow area soils, (ii) to investigate the speciation of Cr in both simulated oral and inhalation bioaccessibility tests and (iii) to use the bioaccessibility and speciation data to carry out assessments of human health risk.

2. Materials and methods

2.1. Sample site selection

The 27 soil samples used in this study comprised six collected in 2005 from locations in areas previously identified as at least potentially contaminated with Cr from COPR disposal (Farmer et al., 1999, 2002) and 21 chosen from the samples collected in 2001/2002 as part of the BGS G-BASE survey (Fordyce et al., 2005). The 21 samples in the latter group were selected on the basis of previous G-BASE X-ray fluorescence (XRF) -determined total Cr, Pb and As data showing any one of these elements exceeding the UK Soil Guideline Value at that time and a land use (e.g. gardens, allotments and recreational land) with a high potential for contact with the human population, especially children. The geographical distribution and a fuller description of the sampling sites are given in Fig. 1 and Table 1, respectively.

2.2. Sample collection and handling

2.2.1. G-BASE samples

At each site (1-14 and 21-27 in Fig. 1 and Table 1), <2 mm topsoil samples from 5-20 cm depth were collected and then analysed for total element concentration according to standard G-BASE procedures (Fordyce et al., 2005, 2010). Excess sample material was stored under ambient conditions in the BGS National Geoscience Data Centre. Subsamples of BGS G-BASE archive <2 mm topsoil material were selected for the present study and further sieved to <250 μm (cf. Section 2.2.2).

2.2.2. Cr-contaminated-site samples

At each site (15-20 in Fig. 1 and Table 1) a single composite sample was collected. A composite sample consisted of three individual 'flights' collected with a hand-held Dutch auger from the corners of a 2 m equilateral triangle (Palumbo-Roe et al., 2005). As with the G-BASE sampling procedure, only the surface soil (5-20 cm) was collected. The samples were oven-dried at 35 ± 2 °C. Each dried coarse sample (including the 21 <2 mm G-BASE samples) was gently disaggregated by hand with a porcelain pestle and mortar to ensure the breakage of aggregates, but not clasts, and the disaggregated sample then sieved to <250 μm.

A further ~1 kg of soil was collected in October 2006 from each of locations 20, 22 and 24, from which ~10 g was separated and milled to <250 μm for total digestion, with the remainder being sieved to separate the <10 μm fraction (1-3 g) for use in the determination of bioaccessibility via inhalation (cf. Section 2.3.4).

2.3. Sample preparation

2.3.1. Total digestion

A modified version of the United States Environmental Protection Agency (USEPA) Method 3052 (USEPA, 1996a) was used to digest the soil samples. An aliquot (0.25 g) of oven-dried soil was transferred into a Teflon microwave digestion sample vessel, to which was added 9 mL 16 M HNO_3, 1 mL concentrated HF and 1 mL 30% H_2O_2. Once any effervescence had ceased, the vessels were sealed and irradiated for 15 min in a CEM MARS5 microwave digestion system, in which the temperature was raised to 180 °C in <5.5 min and maintained for a further 9.5 min, at a pressure of 7.5 ± 0.7 atm. Each digestion run consisted of six samples in duplicate, one reagent blank and one certified reference material, a Light Sandy Soil from the Czech Metrological Institute, CMI 7002. After cooling to room temperature, each solution was evaporated on a hotplate to ~1 mL and then made up to 25 mL with 2% (v/v) HNO_3 and stored at 4 °C prior to analysis by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). All acids used were of Aristar quality (Fisher Scientific, Loughborough, UK).

2.3.2. Extraction of Cr(VI)

A modified version of the USEPA Method 3060A (James et al., 1995; USEPA, 1996b; Vitale et al., 1997) was used to extract Cr(VI) from each soil sample. The modification involved initial dry-ashing of sample aliquots to remove organic matter, the solubilisation of which had been found in a previous set of experiments to rapidly reduce extracted Cr(VI) to Cr(III) under the acidic conditions of the subsequent colorimetric determination method (cf. Section 2.4.2) (Pettine and Capri, 2005a,b).

An aliquot (2.50 g) of oven-dried soil was ashed at 450 °C for 4 h and then transferred to a 250 mL beaker to which 50 mL of extractant (pH ~12) comprising 0.28 M Na_2CO_3 and 0.5 M NaOH was added. In addition, ~400 mg $MgCl_2$ and 0.5 mL 1.0 M phosphate buffer (0.5 M K_2HPO_4 and 0.5 M KH_2PO_4) were added to suppress any method-induced oxidation of Cr(III) to Cr(VI). The mixture was then stirred unheated for 5 min before heating to 90-95 °C for 1 h, with stirring every 15 min. After cooling, the solution was filtered through a