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Estimation of daily intake of potentially toxic elements from urban street dust and the role of oral bioaccessibility testing

Alexander Okorie [a], Jane Entwistle [b], John R. Dean [a,*]

[a] Department of Chemical and Forensic Sciences, Northumbria University, Newcastle upon Tyne NE1 8ST, UK
[b] School of the Built and Natural Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, UK

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ABSTRACT

The pseudo-total and oral bioaccessible concentration of six potentially toxic elements (PTEs) in urban street dust was investigated. Typical pseudo-total concentrations across the sampling sites ranged from 4.4 to 8.6 mg kg^{-1} for As, 0.2–3.6 mg kg^{-1} for Cd, 25–217 mg kg^{-1} for Cu, 14–46 mg kg^{-1} for Ni, 70–4261 mg kg^{-1} for Pb, and, 111–652 mg kg^{-1} for Zn. This data compared favourably with other urban street dust samples collected and analysed in a variety of cities globally; the exception was the high level of Pb determined in a specific sample in this study. The oral bioaccessibility of PTEs in street dust is also assessed using *in vitro* gastrointestinal extraction (Unified Bioaccessibility Method, UBM). Based on a worst case scenario the oral bioaccessibility data estimated that Cd and Zn had the highest % bioaccessible fractions (median >45%) while the other PTEs i.e. As, Cu, Ni and Pb had lower % bioaccessible fractions (median <35%). The pseudo-total and bioaccessible concentrations of PTEs in the samples has been compared to estimated tolerable daily intake values based on unintentional soil/dust consumption. Cadmium, Cu and Ni are well within the oral tolerable daily intake rates. With respect to As and Pb, only the latter exceeds the TDI_{oral} if we model ingestion rate based on atmospheric 'dustiness' rather than the US EPA (2008) unintentional soil/dust consumption rate of 100 mg d^{-1}. We consider it unlikely that even a child with pica tendencies would ingest as much as 100 mg soil/dust during a daily visit to the city centre, and in particular to the sites with elevated Pb concentrations observed in this study.

1. Introduction

Urban street dust is a mixture of mineral constituents, organic matter and elemental carbon (Amato et al., 2009); the anthropogenic materials include vehicle exhaust particles, lubricating oil residues and tyre, brake and engine wear components, while the natural minerogenic and biogenic materials include weathered rock fragments, recognisable plant fragments and other plant matter pulverized by traffic and general weathering (Li et al., 2001; Howari et al., 2004; Ferreira and De Miguel, 2005; Shi et al., 2008). Some of the most common elements associated with automobile industries include As, Cd, Cu, Ni, Pb and Zn amongst others, either within the fabrication of a vehicle, component parts (e.g. brake pads, tyres), as additives (e.g. in lubricants) for engine operation or resulting from automobile corrosion (Haus et al., 2007; Mang and Dresel, 2007). Copper compounds, for example, are used in lubricants as anti-wear agents, by providing a protective layer on engine surfaces to reduce friction and prevent damages due to continuous rubbing between engine parts. Historically, lead compounds (lead tetraethyl $(C_2H_5)_4Pb$) were added as antiknock agents in petrol prior to their cessation in the UK in 1999 (Barlow, 1999). The now wide spread use of unleaded fuels however, has reduced but not eliminated the use of lead compounds in motoring activities; for example, Pb compounds are used as anti-wear agents in lubricant oils for engines (Mang and Dresel, 2007). Zinc is a major pollutant in urban dust occurring as a result of vehicle tyre wear (Smolders and Degryse, 2002; Adachi and Tainosho, 2004; Turner and Rice, 2010). The presence of Zn in tyre tread is as a direct result of its use (as zinc oxide) as an activator during the rubber vulcanising process (Smolders and Degryse, 2002). In addition, Zn compounds are among the alternatives added into lubricant oils (Mang and Dresel, 2007). For example, zinc dialkyldithiophosphate (ZDDP) is added as an agent to provide additional protection under extreme-pressure or in a heavy-duty performance situation to protect the lubricant itself from oxidative breakdown and to prevent the formation of deposits in engines (Hu, 2002; Mang and Dresel, 2007; Yong, 2008). In addition, metals such as Ni are used for plating the outer part of a vehicle, such as the tyre rims or as an alloy for plating the surface of the cylinder and pistons of an engine (Hidayah and Amran, 2008). The source of Ni in road dust is believed to result from corrosion of these components over the lifetime of the vehicle (Ferguson and Kim, 1991; Akhtar and Madany, 1993; Achilleas and Nikolaos, 2009).

* Corresponding author. Tel.: +44 191 227 3047.
E-mail address: John.Dean@northumbria.ac.uk (J.R. Dean).

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Urban dust can be a particular risk to humans due to small particle size and inherent mobility in windy weather conditions leading to the possibility of direct and indirect exposure; direct exposure from dust can occur by inhalation and ingestion while indirect exposure results from contact with exposed skin and outer clothing which in turn can be accidentally ingested (Abrahams, 2002). Young children (up to 5 years of age) are more likely to ingest significant quantities of dust compared to adults because of the behaviour of mouthing non-food objects and repetitive hand/finger sucking during outdoor activities (Mielke et al., 1999). While many studies of total/pseudo-total potentially toxic element (PTE) content in urban street dust have been carried out (Ndiokwere, 1984; Schwar et al., 1988; Chen et al., 1997; De Miguel et al., 1997; Wang et al., 1998; Al-Shayep and Seaward, 2001; Charlesworth et al., 2003; Sezgin et al., 2003; Al-Khashman, 2007; Faruque et al., 2007; Achilleas and Nikolaos, 2009; Lu et al., 2009) little has been published on the environmental health risk to humans from the unintentional ingestion of this material and specifically its oral bioacessibility. The oral bioaccessibility of PTEs in urban dust has received relatively little attention compared with other environmental solids i.e. soils. The bioaccessible fraction is the total amount of the PTE in dust which could be released during digestion. This released fraction represents the maximum amount of contaminant available for gastric or intestinal absorption (Oomen et al., 2002). It can be assessed using *in vitro* gastrointestinal extraction.

2. Experimental

2.1. Sampling and sample preparation

The urban site chosen for the study is the city of Newcastle upon Tyne, north east England. Sampling took place within the city centre from sites around the main shopping areas and close to the city centre road network (Fig. 1). Urban dusts/sediments (>10 g) were collected from nine different sites using hand brushing with a plastic brush and plastic collection pan (Lesniewska et al., 2004; Robertson and Taylor, 2007). Each brush and pan was used only once or cleaned using acetone. A description of the sample sites and their location are given in Table S1. The samples were dried in the oven at 40 °C for several days. The samples were then passed through a plastic sieve to obtain the <250 μm size fraction for subsequent analyses.

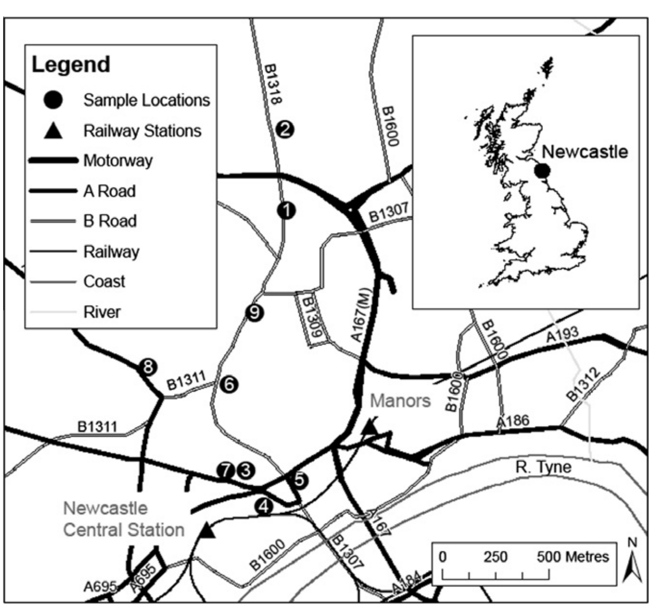

Fig. 1. Street dust sample locations across Newcastle upon Tyne.

2.2. Instrument and reagents

All chemicals used were of analytical grade. Concentrated hydrochloric acid (HCl) and concentrated nitric acid (HNO_3) were obtained from Fisher Scientific UK Ltd. (Loughborough, UK). Sodium hydrogen phosphate (NaH_2PO_4) and potassium hydrogen phosphate (KH_2PO_4), α-amylase (bacillus species), lipase (pig) and bile salts (bovine) were obtained from Sigma–Aldrich Co. Ltd. (Gillingham, UK). Sodium chloride (NaCl), potassium thiocyanate (KSCN), anhydrous sodium sulphate (Na_2SO_4), potassium chloride (KCl), calcium chloride ($CaCl_2{\cdot}2H_2O$), ammonium chloride (NH_4Cl), sodium bicarbonate ($NaHCO_3$), magnesium chloride ($MgCl_2{\cdot}6H_2O$), sodium hydroxide (NaOH), hydrochloric acid (HCl), 30% hydrogen peroxide, urea, uric acid, anhydrous D+ glucose, D-glucosaminehydrochloride, pepsin (pig), bovine serum albumin (BSA) and pancreatin (pig) and concentrated nitric acid (69%, HNO_3) were all obtained from Merck Speciality Chemicals Ltd. (Poole, England). Mucin (pig) was obtained from Carl Roth GmbH (Karlsruhe, Germany). D-Glucuronic acid was obtained from Fluka Chemicals Ltd. (Gillingham, UK). A multi-element standard for As, Ni, Cu, Zn, Cd and Pb and internal standard solution containing Sc, In, and Tb were purchased from SPEXCertPrep (Stanmore, UK). Ultra pure water of conductivity 18.2 MΩ-cm was produced by a direct Q™ Millipore system (Molsheim, France). A range of certified reference materials (CRMs) i.e. street dust (BCR 723), bush branches and leaves (NCS DC 73349), soil (GBW 07401) and Montana soil (SRM 2711) were purchased from LGC-Promochem Ltd. (London, UK). ICP-MS measurements were carried out with an ICP mass spectrometer X series II from Thermo Electron Corporation (Winsford, UK). All digestions were carried out using a Start D multiprep 42 high throughput rotor microwave digestion system supplied by Analityx Ltd. (Milestone Microwave Laboratory Systems) (Peterlee, UK).

2.3. Procedure for pseudo-total PTE extraction

In each case the pseudo-total PTE concentration was determined using aqua regia. A 0.5 g dust sample (in triplicate) was weighed into a PFA (a perfluoroalkoxy resin) (65 mL) microwave vessel pre-cleaned with concentrated HNO_3. Then 13 mL of aqua regia (HCl: HNO_3, 3:1 v/v) was added to the dust (sample or CRM). The sealed vessels were placed inside a rotor of the microwave digestion system and submitted to microwave dissolution for 25 min using an operating temperature of 160 °C and a power of 750 W. Ventilation (cooling) time of 30 min was allowed while the vessels were still in the oven. After cooling, the digest was filtered using a Whatman filter paper (grade 41, pore size 20 μm) into a 50 mL volumetric flask and diluted to the mark with Milli-Q water. For each digestion reagent blanks were also prepared and subsequently analysed. The filtrate obtained from the digestion was stored in the fridge (4 °C) prior to analysis.

2.4. Procedure for in vitro gastrointestinal extraction

The *in vitro* gastrointestinal extraction test is based on the Unified Bioaccessibility (BARGE) procedure (Wragg et al., 2009) as outlined below.

2.4.1. 'Gastric' extraction

An accurately weighed sample (0.6 g) was placed into a 50 mL screw- cap Sarstedt tube and treated with 9 mL of simulated saliva fluid by manually shaking the sample-fluid mixture in the screw-cap vessel. Then, after 5–15 min 13.5 mL of simulated gastric fluid