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Bioaccessibility of Ba, Cu, Pb, and Zn in urban garden and orchard soils

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ABSTRACT

Exposure of young children to toxic metals in urban environments is largely due to soil and dust ingestion. Soil particle size distribution and concentrations of toxic metals in different particle sizes are important risk factors in addition to bioaccessibility of these metals in the particles. Analysis of particle size distribution and metals concentrations for 13 soils, 12 sampled from urban gardens and 1 from orchard found that fine particles (<105 μm) comprised from 22 to 66% by weight of the tested soils, with Ba, Cu, Pb and Zn generally at higher concentrations in the finer particles. However, metal bioaccessibility was generally lower in finer particles, a trend most pronounced for Ba and Pb. Gastric was higher than gastrointestinal bioaccessibility for all metals except Cu. The lower bioaccessibility of Pb in urban garden soils compared to orchard soil is attributable to the higher organic matter content of the garden soils.

1. Introduction

Urban soils are commonly contaminated with a number of toxic metals, with Pb perhaps being the metal presenting the most pervasive and persistent risk to human health in the urban environment (Laidlaw and Filippelli, 2008; Mitchell et al., 2014; Zahran et al., 2013). The most at-risk population in urban centers for Pb exposure and poisoning is very young children (Laidlaw et al., 2005; Mielke et al., 1999). Soil ingestion is a major route of exposure of children to Pb in urban centers (Mielke et al., 1999; Zahran et al., 2013), with seasonal fluctuation in children's blood lead levels implicating soil dust as an important contributor to children's exposure.

The most common measure of Pb exposure risk from soil is total Pb concentration in the soil. However, for several reasons, this parameter is inadequate for estimating Pb poisoning risk in children. Firstly, soils vary in texture, so that some soils have a higher percentage of finer particles. Soil particle size distribution is important because finer particles adhere most efficiently to children's hands (Ikegami et al., 2014). It is common to use the <250 μm particle size for exposure assessment, but this may underestimate Pb exposure due to preferential adhesion of smaller particles (<100 μm) that may have substantially higher Pb concentrations (Ikegami et al., 2014; Juhasz et al., 2011; Madrid et al., 2008). Secondly, the forms and chemical lability of Pb in different soils and particle sizes of soils can vary, which affects the rate and extent of Pb dissolution into absorbable forms in the gastrointestinal tract. Thus, the fraction of soil Pb that is bioaccessible can vary due to differences in soil properties (pH, organic matter, reactive Fe, particle size, etc.) (Madrid et al., 2008; Sialelli et al., 2011) and form and severity of Pb contamination (Lamb et al., 2009). Consequently, total soil Pb in itself does not predict % bioaccessibility reliably (Walraven et al., 2015). Within a given soil, an increase in % Pb bioaccessibility is commonly observed with decreasing particle size (Juhasz et al., 2011; Madrid et al., 2008). Nevertheless, the only independent soil parameter that is correlated to the magnitude of bioaccessible Pb in soils with a high level of statistical significance overall is total soil Pb (Appleton et al., 2012).

A number of in vitro assays such as the physiologically based extraction test (PBET) described by Ruby et al. (1996) have been used to measure gastric phase and intestinal phase bioaccessibility of Pb and other toxic metals in contaminated soils (Juhasz et al., 2011; Oomen et al., 2002). The Pb bioaccessibility is calculated as:

$$\text{In vitro bioaccessibility (\%)} = (\text{in vitro Pb}/\text{ total Pb}) \times 100$$

By the PBET assay, gastric bioaccessibility of Pb (typically 40–100%) is much greater than intestinal bioaccessibility (usually

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<10%), owing to the much more acidic nature of the gastric extractant (Juhasz et al., 2011). However, different in vitro assays can give quite different bioaccessibility of soil metals largely due to different gastric pH values used in these tests (Oomen et al., 2002).

In addition to Pb, urban soils and brownfields commonly contain concentrations of Ba, Cu and Zn as well as a number of other metals, which are higher than concentrations in rural soils of the same geographical region. The New York State Department of Environmental Conservation has set soil cleanup objectives (SCOs) for concentrations of potentially toxic metals based on an assessment of human exposure (NYDEC, 2006). These SCOs are 400, 270, 400 and 2200 mg kg^{-1} for Ba, Cu, Pb and Zn, respectively, for protection of human health under a restricted use designation.

Contamination in urban areas is attributable to various sources such as galvanized steel, engine emissions, and wear or abrasion of vehicle components such as tires, brake pads and metal body parts, with generally higher concentrations of these metals near high-traffic density roads (Apeagyei et al., 2011; Harrison et al., 1981; Hjortenkrans et al., 2007; Nabulo et al., 2006; Ozaki et al., 2004). The use of high levels of Cu and Zn in brake components in recent decades has led to concerns about Cu and Zn dust emitted along high-traffic density roads (Hjortenkrans et al., 2007), suggesting that the accumulation of these two metals is likely to continue in areas with heavy vehicle traffic. Brake wear debris can contain extremely high concentrations of Cu, with one study measuring an average Cu content of 10.8% in the debris (Hur et al., 2003). A study in the Puget Sound basin of Washington State, USA, estimated Zn (from tire wear) and Cu (from brake pad wear) loading to road surfaces of 914 g/km-yr Zn and 425 g/km-yr (Whiley, 2011). The concern for urban watershed contamination by Cu (and other metals) resulted in legislation in California and Washington State in 2010 to prohibit the sale of brake pads containing high concentrations of Cu and a number of other potentially toxic metals such as Cd and Pb; in 2015, the USEPA reached an agreement with the automotive industry to reduce Cu levels in brake pads to 0.5% by 2025.

The bioaccessibility of Cu and Zn have been reported for contaminated soils, although these have frequently used the simplified gastric (SBET) extraction (Lamb et al., 2009; Madrid et al., 2008). Sialelli et al. (2010, 2011) used the PBET assay for urban soils of Glasgow, UK and Torino, Italy, and determined in both studies that % Cu accessibility increased from the gastric to the intestinal phase, in contrast to the tendency of Pb and Zn to become substantially less soluble in the intestinal phase. Cu intestinal bioaccessibility in roadside soils averaged 46% compared to 39% and 48% (gastric) for Zn and Pb, respectively. Roussel et al. (2010) measured in vitro PBET bioaccessibility of Zn as well as Cd and Pb in smelter-contaminated soils, with Zn averaging lower gastric bioaccessibility (47%) than Pb (62%). In the gastro-intestinal phase, Pb and Zn bioaccessibility reduced on average to 23% and 32%, respectively.

Ba concentrations in urban soils tend to be greater than rural background levels (Mitchell et al., 2014), with research indicating that Ba is a reliable tracer for vehicular emissions, specifically brake pad wear (Apeagyei et al., 2011; Gietl et al., 2010; Monaci and Bargagli, 1997). However, because Ba is relatively abundant in many uncontaminated soils, and has a low presumed bioavailability, it has not usually been considered a heavy metal of concern. Consequently, there is little research published on “in vitro” Ba bioaccessibility in soils; one study indicates that Ba bioavailability in soils contaminated by mining activity is limited by the low solubility of $BaSO_4$ (Lamb et al., 2013). This suggests that gastric bioaccessibility of soil Ba should be relatively low. Shock et al. (2007) reported, using an “in vitro” assay (0.4 M glycine at pH 1.5 to simulate gastric extraction), that extractable Ba in a mine-dust contaminated soil ranged from 11 to 47%. However, the measured extractability was strongly affected by both particle size and soil/extractant ratio.

In summary, in addition to the particular “in vitro” assay chosen to assess either gastric or intestinal bioaccessibility of toxic metals in soils, other variables that affect bioaccessibility are soil properties, chemical nature of the metal contaminant, particle size and soil/extractant ratio. The present study was undertaken to measure Ba, Cu, Pb, and Zn bioaccessibility in urban garden and orchard soils with one widely-used assay, the PBET (Ruby et al., 1996). The goals of this study were to establish relationships between soil particle size and both total metal concentration and metal bioaccessibility in the gastric and intestinal phase for soils known to be anthropogenically contaminated with Pb and other potentially toxic metals. Because forms of historical contamination likely to be present in the soils collected from the urban gardens are diverse and include Pb from paint and vehicle emissions (Mitchell et al., 2014), whereas lead arsenate pesticide is the only significant source of Pb contamination in the orchard (McBride et al., 2015), a second objective of this study was to assess the effect of Pb source on bioaccessibility. However, we decided that the much greater measured variability in soil properties (organic matter content, pH, metal and nutrient concentrations) of the urban gardens compared to the orchard required that a number of garden soils be included in the study to give some representation of the expected variability among soils in metal distribution and extractability.

2. Materials and methods

2.1. Soil samples

Soil samples (0–15 cm depth) were collected in 2012 from specific vegetable planting locations within community gardens and urban farms in NYC and Buffalo, NY as described in McBride et al. (2014). The samples were processed by air-drying in a laboratory hood for several days, passed through a 2 mm plastic sieve, and subsequently stored in closed cardboard containers. Soil pH values were measured by weighing 10 g of dry soil into 20 ml deionized water, equilibrating 30 min, and measuring pH with a combination glass electrode pre-calibrated with buffers at pH 4 and 7.

2.2. Separation of soils into particle size fractions

Twelve soil samples from the urban garden soils and one from an old apple orchard in Ithaca, NY contaminated by Pb arsenate, were chosen for particle size fractionation and analysis of size fractions for Pb, Ba and other metals of concern. The soils were selected to represent a range of Pb and Ba concentrations, based on pseudo-total determination of metals by acid digestion of the soils, and analysis by ICP-AES, and are listed in Table 1, with “G” and “O” signifying garden and orchard soils, respectively. They were sieved to 4 different particle size fractions (<53 μm, <105 μm, <212 μm and >212 μm) by dispersing in polyethylene bottles with deionized water (soil:water = 1:2), shaking at high speed on a horizontal shaker for 1 h, and then passing through sieves in sequence from larger to smaller sieve size. All particle size fractions obtained were dried at 65 °C and weighed prior to analysis of total heavy metals by ICP-AES. The percentage of soil composed of these 4 size fractions was then determined for all 13 soils listed in Table 1. These weight percentages of the size fractions are presented in Table 2.