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Phase partitioning and bioaccessibility of Pb in suspended dust from unsurfaced roads in Missouri—A potential tool for determining mitigation response

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HIGHLIGHTS

- Sequential extraction proves valuable in characterizing road dusts.
- Mining area road dusts are associated with labile geochemical phases.
- Pb concentrations substantially higher in <1 μm than >1 μm dust particles.
- *In vitro* simulated body fluid extraction shows Pb to be bioaccessible in road dust.
- E + C phase extraction correlates well with artificial lung fluid extraction.

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ABSTRACT

Airborne particulate material collected from seventeen rural unsurfaced roads in Missouri's agricultural and resource mining areas were characterized using the BCR sequential extraction procedure and simulated *in vitro* body fluids to determine the phase partitioning and bioaccessibility of Pb associated with roadway dusts. Results show that dusts produced from driving over unsurfaced roads in the mining area has a substantial portion of the Pb concentration associated with the more mobile exchangeable-plus-carbonate and reducible geochemical phases. By comparison, unsurfaced road dusts outside the resource mining area have lower metal contents, as expected, and a larger portion of the total Pb concentration associated with the immobile oxidizable and non-silicate bound residual phases. SEM/EDS analysis suggests the minerals associated with the more mobile Pb components include cerussite, Pb oxides and sulfates. Compared with the coarser >1 μm size fraction of dust, the <1 μm fraction contains a substantially higher concentration of Pb in association with clay minerals. Extraction tests using simulated body fluids show that gastric fluid can mobilize as much as 69% of the total Pb concentration in mining area road dust samples after five hours. Simulated alveolar lung fluid also was an efficient extractor of Pb from the <1 μm sample dust fraction, dissolving up to 100% of the available Pb after 100 h. Regression analysis suggests that aqua regia total Pb concentration is a good predictor of mobility and bioaccessibility and can be used to minimize costs associated with monitoring suspended dust contamination.

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1. Introduction

The geochemical controls on trace metal concentration are often ignored when a soil is being chemically characterized for regulatory purposes. This can lead to overestimation of contaminant problems associated with more concerning trace metals because the mobility and bioaccessibility can be affected by coprecipitation with other elements thus controlling solubility (Sposito, 1989). The soil environment is a diverse matrix of competing chemical activity that

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includes adsorption, weathering, and element substitution which are driven by the ambient conditions of a particular area, soil composition, and cultural influence. Developing a complete understanding of the geochemical factors influencing the behavior and bioaccessibility of a particular element in the environment is the most responsible way to develop a mitigation response to a perceived environmental contamination problem.

Environmental regulation of Pb contamination is often limited to the association of its total concentration relative to a nearby polluting activity. While this may be helpful in showing Pb enrichment resulting from the influence of a particular source, it does not build a complete case for mobility or human health concern(s). Total environmental Pb concentrations result from a combination of Pb-species in the sample and are operationally associated with different geochemical-mineral fractions. Metallic Pb and Pb-sulfide have been shown to be relatively immobile in soil and do not readily dissolve on or in the human body (Ruby et al., 1992). However, the dissolution kinetics of other Pb-species such as oxides, sulfates, and carbonates commonly found in soils from resource mining and smelting areas make this element more problematic in the environment (Spear et al., 1998; Sobanska et al., 1999; Hayes et al., 2012). Sequential extraction (SE) of metals from a sample can be helpful in defining the mobility of a trace element and used in combination with other analytical techniques such as microscopy can provide useful information on the geochemical phases with which Pb is associated in the environment (Spear et al., 1998; Schaider et al., 2007; Smith et al., 2011).

In vitro extraction using simulated body fluids can take this analysis a step further beyond SE and provide additional information necessary to characterize the human health concern with fewer assumptions related to the SE technique. These techniques have been widely applied to various environmental contamination scenarios, but they have not been used to characterize the phase partitioning and bioaccessibility of Pb in suspended dust from rural unsurfaced roads. Unsurfaced roads are numerous in rural Missouri's diverse landscape that supports a range of land use activity from agricultural to mineral resource extraction and Pb–Zn smelting. These roads serve as important thoroughfares for local residents, recreation, and the transport of agricultural products as well as mining ores and concentrate. Suspended dusts generated by vehicular traffic on these road surfaces can be a problematic aerosol contaminant if they contain high Pb concentrations. Consequently those regularly traveling or living along such roads can receive routine exposure possibly elevating their blood-Pb levels. Murgueytio et al. (1998) showed that those exposed to elevated Pb concentrations in dust and soil from a Missouri mining area had nearly twice the blood-Pb level as those in the non-mining control group. Recent research has shown elevated Pb concentrations in suspended dust from rural unsurfaced roads in Missouri's southeastern mining region relative to non-mining areas (Witt et al., 2013a). The problem with this initial assessment is the lack of information regarding the relative mobility and bioaccessibility of the Pb-species in the total concentration. A complete characterization of the total Pb concentration can help regulatory agencies make better decisions regarding mitigation by allowing them to prioritize and/or eliminate the need for costly cleanup. Furthermore, this will provide the public with information regarding their exposure to environmental Pb in what the U.S. Clean Air Act generally characterizes as unregulated 'nuisance dust'.

The purpose of this study is to define the phase partitioning of Pb in suspended road dust by applying an established SE procedure, confirming results using scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS), and performing *in vitro* dissolution analyses using simulated body fluids. The research goals include: 1) comparison of Pb partitioning in suspended dusts between rural unsurfaced roads in mining and non-mining areas; 2) identification of Pb-bearing minerals that may contribute to the more mobile phases; 3) determination of the relationship between particle size and Pb mobility and bioaccessibility; 4) determination of the proportion of the total Pb concentration that is bioaccessible using *in vitro* dissolution analyses; and 5) evaluation of the use of total acid extractable Pb concentration as a predictor of potential human-health concern for those traveling on and living near contaminated unsurfaced roadways.

2. Methods and materials

2.1. Study area and sample collection

Suspended dust samples were collected from the Viburnum Trend (VT) mining district and in non-mining areas more than 100 km southwest in rural Missouri (Supplemental Information (SI), Fig. 1). The VT district is one of three major Pb producing areas of southeast Missouri and is characteristic of the more than 200 Mississippi Valley type ore deposits that are being exploited around the world (Leach et al., 2010). The district is underlain by dolostones of Cambrian and Ordovician age that lie within a large region of well-developed karst terrain characterized by the presence of well-developed springs, sinkholes, and gaining and losing streams. Two primary ore smelters in the region have operated intermittently in the past, one currently is operated as a secondary Pb recovery facility used to recycle automotive batteries and other Pb-containing waste.

Samples for this study were collected using a Cyclonic Fugitive Dust (CFD) sampler designed to collect and separate two dust-size fractions directly from the atmosphere as dust is suspended by a moving vehicle for a specific reach length of road surface (Witt et al., 2013b). This method of collection provides a more representative sample of fugitive dust for the determination of Pb exposure. Furthermore, this collection method provides data on air volume per road distance sampled—a feature that traditional bulk sampling methods do not offer. Two particle size fractions were evaluated during this study, the >1 μm fraction that was collected in the cyclone collection container of the CFD and the <1 μm fraction that was retained on the polypropylene (PP) filter that was mounted in the air stream of the sampler and following the cyclonic separator (Table 1).

Thirteen unsurfaced county and U.S. Forest Service maintained roads in the VT resource mining district were chosen for analysis because Pb concentrations for these roads are enriched in Pb relative to selected roads outside the mining area (Witt et al., 2013a). The sampling distances for VT roads ranged from 10.9 to 23.8 km with sample sizes ranging from 6.73 to 36.6 g. Four additional samples were collected outside the study area to use as background comparisons. Sampling distance for non-VT county roads ranged from 18.7 to 24.8 km with sample quantity ranging from 11.5 to 22.5 g.

Minimal preparation of the >1 μm cyclone collected sample was done prior to extraction. Approximately 1 g of each sample was accurately weighed and added to 50 mL polypropylene (PP) digestion tubes. The <1 μm dust fractions collected on the PP filters required extensive preparation before digestion (SI, Exhibit 1).

2.2. Sequential and in vitro bioaccessibility extractions

Aliquots of each sample were digested using the SE procedure developed and tested by the Standards, Measurements, and Testing Programme of the European Union (BCR) to operationally determine the phase relationship of Pb in road dust. The BCR SE method is well documented and has been tested for sequential analysis of sediments (Quevauviller et al., 1993; Rauret et al., 2001; Fernández et al.,