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Short communication

Temporal and spatial variation in residential soil metal concentrations: Implications for exposure assessments

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ABSTRACT

Understanding temporal and spatial variation in soil chemicals is critical in exposure assessments. We measured eight metals in subsamples, duplicates (~0.3 m), and repeat soil samples taken 1–6 years after initial sampling (~5 m). We estimated variance components (VCs) of metal concentrations using nested analyses accounting for sampling area, land use and soil type, and calculated coefficients of variation (CVs) for repeat sample pairs. Total variance for all metals was similar, but VCs were proportioned differently by metal and sample type. Spatial variation explained the majority of variance in duplicate samples. CVs of metal concentrations were not significantly different over the long time interval, but repeat samples had larger VCs for unexplained error. Sampling area and land use were important for Ba and Mn, and Pb and Hg, respectively. Results suggest metals are stable over long times and suitable for exposure assessments, but that individual metal behavior should be considered.

1. Introduction

Human exposure assessments rely on analytically measured concentration of contaminants from specific sample locations (Paustenbach, 2000), and understanding the spatial and temporal variation of soil chemical concentrations can provide greater confidence when using these data in exposure assessments. Chronic exposure to low concentrations of neurotoxic metals and metal mixtures in soils is a current concern, and evidence suggests fetal exposures to these metals during development may impact birth outcomes (Grandjean and Landrigan, 2006). In previous studies, we measured soil metal concentrations at several residential locations in the Southeastern United States (US), and examined their potential associations with intellectual disabilities in children (Kim et al., 2009, 2010; Liu et al., 2010; McDermott et al., 2011; Zhen et al., 2008, 2009), and their associations with social and economic factors of the study population (Aelion et al., 2012, 2013). Metal concentrations were spatially interpolated at maternal residences, but no validation was carried out to examine spatial and temporal variation of soil metal concentrations.

Identification of spatial and temporal variation in soil metal concentrations is important. Small-scale spatial variation in soil characteristics may be important for chemical distribution. For example, soil organic carbon affects chemical degradation (Smalling and Aelion, 2004) and clay and sand content impacts chemical concentrations over distances of centimeters (Aelion, 1996; Einax and Kraft, 2002). Wilcke (2000) reported that the bioavailability of metals in soils can vary greatly over scales of <1 m^2. Temporal variation in soil metal concentrations is important because environmental data and health data may be collected at disparate times and assumptions are made about temporal changes in metal concentrations.

The objectives of the current study were to examine small-scale spatial variation and large-scale temporal variation in concentrations of eight soil metals. We calculated differences in metal concentrations for subsamples (multiple samples from the same grab sample) and duplicate samples (independent grab samples collected <0.3 m apart at the same time) at 11 residential sampling sites spread over a large geographic area, and repeat samples (grab samples collected within 5 m or less of the original sample 1–6 years after the initial sampling event) at three of the 11 sites, and

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estimated variance components for each metal. We further examined temporal variation by comparing coefficient of variations (CV) among repeat sample pairs for the three repeat areas individually.

We hypothesize that the spatial and temporal variation will be small for all metals due to the small spatial scale, lack of significant anthropogenic sources of metals in these areas, and limited biotransformation of metals. Despite limited variation, we hypothesize that error variance components will be lowest in subsamples compared to duplicate and repeat samples due to the lack of spatial and temporal components in subsamples. We also hypothesize that the spatial variation of metals will be greater than the temporal variation because soils are inherently geologically variable, and metals are relatively chemically stable.

2. Methods

From 2006 to 2011, grab topsoil samples (upper 5 cm; ~50 g) were collected from 11 individual residential sampling areas throughout an area in the Southeastern US approximately 320 km wide and 420 km long. Ten of the sampling areas ranged from 60 to 120 km^2, and one area was 490 km^2. Sampling areas included five urban, five rural and one mixed urban plus rural location. Samples were collected on a uniform 120-node grid at each sampling area as close to the nodes as possible. Distance between sampling nodes ranged from 0.8 to 1 km for the 10 smaller areas, and 4 km for the one large area (Area 1). Approximately 120 samples were collected at each site, with 60 samples collected at Area 1. Fig. 1 shows the entire sampling area (not to scale) with Area 22 grid nodes identified.

Two duplicate grab samples were collected at approximately 10% of sampling locations selected randomly within a sampling area, in close proximity (within $\leq$0.3 m). A total of 57 duplicate soil sample pairs (114 total samples) was analyzed from the 11 sampling areas. In addition, a subset of samples was homogenized using a tumbling method (Schumacher et al., 1991) and two ~15 g subsamples were taken from the one original grab soil sample. In total, 37 subsample pairs (74 total samples) were analyzed from the 11 sampling areas. The analytical lab was blinded to the status of both duplicate and subsample soils.

All soils were acid digested and analyzed for arsenic (As), barium (Ba), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), and nickel (Ni) using inductively coupled plasma atomic emission spectroscopy (ICP-AES) using EPA Method 6010 and for total mercury (Hg) with the cold vapor method using EPA Method 7471 (Aelion and Davis, 2007; Aelion et al., 2008, 2009a, 2009b; Davis et al., 2009). All results were reported in mg/kg, and reported values below the minimum detection limit (MDL) were set to ½ the MDL for that metal for all subsequent data analyses.

In 2012, soil sample locations from three of the original sampling areas were randomly chosen for collection of repeat samples (59 sample pairs, or 118 total samples). The temporal differences in repeat samples were 1.5 (Area 22), 4.7 (Area 4) and 5.6 (Area 1) years after the original sample collection and analysis. The original latitude and longitude coordinates were entered into a GPS device (Garmin eTrex, Garmin, Olathe, KS, USA) in order to sample as close as possible to the original sampling location, recognizing the GPS device accuracy was ~5 m. Most repeat sample spatial ranges were smaller than 5 m because site photographs and sampling field notes containing information on vegetation cover and physical landmarks helped to increase the certainty of sampling at a spatial scale similar to that of the duplicate samples. Samples were collected and analyzed in the same manner as previously described.

A nested procedure was implemented in SAS version 9.4 software (SAS Institute, Cary, NC). The absolute values of differences between subsample, duplicate, and repeat soil pair metal concentrations were calculated and these and metal concentrations were log transformed due to positive skewness. Each metal was modeled as a separate dependent variable nested within sampling area, Anderson land use type (Anderson et al., 1976), and soil type (USDA, 2013). This type of procedure allows for an unbalanced sampling design, and estimates the variance components for errors and other model covariates to soil metal concentration. The coefficient of variation (CV) for repeat soil pairs was calculated for each metal for each area, and compared using the non-parametric Kruskal–Wallis test.

3. Results and discussion

In general total variance of subsample, duplicate, and repeat samples was similar (Table 1A–C). This suggests that the spatial (in repeat and duplicate sample pairs) and temporal (in repeat samples only) components contributed a similar amount of variance as the analytical + mixing component. Although total variance of the different samples was similar, there were differences in allocation of the proportion of total variance for different samples and for individual metals.

The subsampling error (analytical + mixing) variance component explained a small percentage of total variance with the exception of As and Hg (Table 1A), for which subsampling error explained 68% and 61% of the total variance, respectively. In contrast, duplicate error variance components explained >50% of the variance for five of eight metals (As, Cr, Cu, Pb, and Ni; Table 1B), suggesting that the small spatial scale component explained the greatest proportion of the total variance in these metal concentrations. Rawlins et al. (2009) compared the sampling variances from duplicate samples 20 m apart and subsamples for soils in the UK. They observed that the duplicate sample error variance components were an order of magnitude greater than subsample error variance components for the three metals they investigated, Cu, Ni and zinc (Zn). Our subsample error variance component for Ni was an order of magnitude less than the duplicate error variance component; however no consistent pattern was observed for most metals. Einax and Kraft (2002) examined sampling variance of As, Cr, Cu, Pb, Mn and Ni in top soil collected at 25-cm intervals in Germany, and measured similar ranges and concentrations as our study. Similar to our findings, they found that the sampling uncertainty, due to the large range of metal concentrations, was higher than the uncertainty of sample treatment and analytical measurements.

In contrast to our hypothesis, repeat error variance components explained a smaller proportion of the total variance than either subsample or duplicate error variance components, suggesting the spatial + temporal component intrinsic in our repeat error did not sufficiently explain the variation in metal concentrations. The repeat sample models had high proportions of unexplained

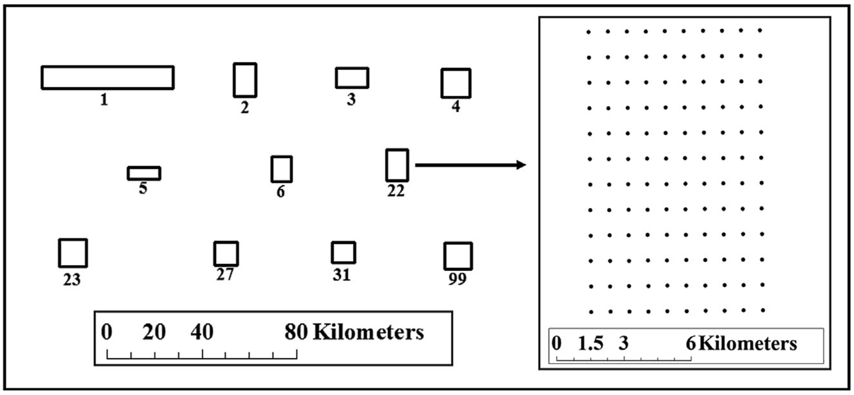

Fig. 1. Relative sizes of sampling areas (distances between areas not to scale) and close up of grid nodes for tentative sampling locations in Area 22.