Long-term Stability of Trace Element Concentrations in a Spontaneously Vegetated Urban Brownfield With Anthropogenic Soils

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ABSTRACT:
Trace element (TE) contamination of soil is a persistent problem in urban environments, particularly hindering the reuse of abandoned land. While phytostabilization is a cost-effective approach to managing TE-contaminated soil, little is known about the effects of these practices on soil TE concentrations decades after plant establishment. This study analyzes soil data collected from 1995, 2005, and 2015 (28, 38, and 48 years since site abandonment) in a spontaneously vegetated urban brownfield contaminated with As, Cr, Cu, Pb, and Zn. No change in concentration of any of these TE in the upper 30 cm of soil at this site was observed from 1995 to 2005. However, from 2005 to 2015, As and Cr concentrations increased in the soil C1 horizon at this site (approximately 5- to 25-cm depth), whereas Cu, Pb, and Zn remained stable. We propose that the observed increases in As and Cr resulted from downward migration from the upper 5 cm of soil and subsequent immobilization in the C1 horizon. Increasing soil pH from 2005 to 2015 could have increased As and Cr solubility, while reducing Cu, Pb, and Zn solubility. In addition, significant correlations were found between the five TE and Fe or Mn, which are known to play a role in TE sorption. This study shows the ability of a phytostabilization site to retain some TE in its upper soil horizons for several decades following plant community establishment, although continued monitoring is needed to ensure soil conditions continue to favor stability.

Key Words: Anthroposols, natural attenuation, phytostabilization, technosols, trace element contamination

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Trace element (TE) contamination of soils is a significant global health threat. Trace elements can be found in both urban and agricultural soils at concentrations greater than background levels, posing multiple risks to human health (Micó et al., 2006; Nabulo et al., 2006; Liu et al., 2013; Panagos et al., 2013; Larson, 2014). Trace elements have been identified in urban soils across the globe, with many present in concentrations exceeding soil screening criteria (Ajmone-Marsan and Biasioli, 2010). Sources of TE include, but are not limited to, leftover materials from smelting (Derome and Nieminen, 1998) and mining activities (Wong, 2003; Moreno-Jiménez et al., 2010), industrial processes such as chromium plating (Castro-Rodríguez et al., 2015), aerial deposition from industrial and mobile sources (Gandois et al., 2010), and irrigation with wastewater (Guédron et al., 2014). In addition, increasing global use of vehicles and demand for electronics will continue to increase soil TE concentrations beyond ambient levels well into the foreseeable future (Ajmone-Marsan and Biasioli, 2010; Tang et al., 2010).

In cities, the reuse of abandoned land is often hindered by soil contamination from TE, among other contaminants (Linn, 2013). These properties (often referred to as brownfields) can be converted to green space, with potential benefits such as recreation opportunities, wildlife habitat, and soil and water conservation (DeSousa, 2003; Moffat and Hutchings, 2007; Doick et al., 2009). Phytostabilization, also known as natural attenuation, is the most cost effective of several strategies for managing soil contamination (Mench et al., 2010). Effective phytostabilization requires the establishment of a plant community that will limit TE movement off site by reducing erosion and maintaining an oxic soil environment. These communities may be spontaneously vegetated or intentionally designed and planted. The immobilization of TE contamination is generally accomplished through adsorption/absorption to organic matter (OM) (Robinson et al., 2009), stabilization at or within the rhizosphere and the associated microflora (Ma et al., 2011; Sessitsch et al., 2013), or sequestration within specific plant tissue (Vesk et al., 1999; MacFarlane and Burchett, 2000). The long-term condition of brownfields and contaminated sites is subject to physical, biological, and social processes. The social aspects of management are beyond the scope of this study, although no less important. While phytostabilization approaches assume long-term stability of TE concentrations in a soil, research is lacking on TE concentrations in soils at phytostabilization sites several decades after their establishment (Kumpiene et al., 2008; Mendez and Maier, 2008; Bolan et al., 2014).

Few studies have documented changes in metal concentrations or availability in the soils of phytostabilization sites for more than a few years. Longer studies tend to involve the application of amendments such as aluminosilicates, lime, or zero-valent iron grit to improve soil conditions (Ascher et al., 2009). After 4 years of growing grass on mining spoils amended with beringite, steel shot, and OM, water-extractable As concentrations decreased (Bleeker et al., 2002). At brownfield sites in the United Kingdom, bioavailable concentrations of As, Cu, Ni, and Pb stayed constant over the course of 3 years of coppiced tree growth, although *Salix* species exhibited high concentrations of Cd and Zn (French et al., 2006). Seven years after a pyritic sludge spill, total As concentrations and $(NH_4)_2SO_4$-extractable Mn and Zn decreased because of leaching in nonamended soil (Vázquez et al., 2011). Twenty years after atmospheric deposition ceased, Cu, Pb, and Sb concentrations were stable in the soil surface of a forest because of binding with OM, whereas Cd and Zn showed evidence

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of leaching (Clemente et al., 2008). The importance of pH in maintaining stable metal concentration is a common theme in these studies (e.g., see Blake and Goulding, 2002; Clemente et al., 2006; Vázquez et al., 2011). While much research has focused on the initial conditions and short-term response of phytostabilization projects, the fate of contamination at these sites after decades of plant growth remains unclear.

Plant uptake can play an important role in influencing the fate of soil TE concentrations. Plant uptake has been shown to reduce TE concentrations (phytoextraction) under very specific conditions with active management (Dickinson et al., 2009; Mench et al., 2010). In the absence of active removal of aboveground biomass, litterfall can be an important component of TE budgets in forested catchments affected by atmospheric deposition (Itoh et al., 2007; Gandois et al., 2010), as well as in grasslands on mine tailings (Milton et al., 2004). In several cases, the litterfall contribution of TE to soil exceeded concurrent atmospheric inputs (Johnson et al., 2003; Navrátil et al., 2007; Landre et al., 2009). Trace elements can also cycle between fine roots and soil (Johnson et al., 2003). There is concern that the cycling of TE through plants could have negative impacts on terrestrial food webs (Milton et al., 2004; Tack and Vandecasteele, 2008; Niemeyer et al., 2012). However, it has been proposed that the uptake and temporary storage of TE in plants, and the subsequent return of TE to the soil upon plant litter decomposition, could enable long-term stability of soil TE (Gallagher et al., 2011).

The aim of this study was to determine the long-term stability of TE in a self-seeded, untreated brownfield by analyzing samples from the upper soil profile of a contaminated anthropogenic soil 28, 38, and 48 years after abandonment. In so doing, we ask the question: How do TE concentrations in the upper soil horizon of a contaminated site change over the course of 20 years? To address this question, our study takes advantage of soil data collected by other organizations in previous sampling campaigns 10 and 20 years prior to compare their results with current soil samples.

We hypothesized that TE concentrations in the upper soil horizon of a contaminated brownfield site would stabilize at steady-state values within 20 to 40 years after establishment of a novel forest community, through the translocation of soil TE through plant biomass, the production and accumulation of TE-binding plant OM, and through intrinsic sorption properties of the soil. However, plant communities are dynamic and may undergo changes in composition and structure over time, both influencing and being influenced by the soil contamination. In addition, if translocation pathways differ among TE and plant species, the stability of soil TE concentrations cannot be generalized and may change over time. To test our hypothesis, we (1) compared concentrations of five soil TE in a reforested brownfield in 1995, 2005, and 2015; (2) assessed the spatial variability of TE concentrations among study plots at this site in 2005 and 2015; (3) assessed the current vertical distribution of the five TE in the top of the soil profile; and (4) examined the relationships between pH, total Fe, Mn, S, C, and N and the five TE in the soil. Sampling primarily focused on the top 30 cm of this profile (excluding the thin organic horizon), which has a high density of roots.

METHODS

Site Background

This study was conducted in the 102-ha interior natural area of Liberty State Park (LSP), in Jersey City, New Jersey (centered at 40°42′14″N; 74°03′14″W). In the early 1800s, the area was a Hudson River coastal marsh. The marsh was filled in with rubble, construction debris, dredge material, slag, cinder, and other wastes and was bound with three sea walls to create a peninsula of dry land, improving access to deeper waters (US Army Corps of Engineers, 2005). These sea walls create a unique hydrological regime where there is little groundwater movement in or out of the site (US Army Corps of Engineers, 2004). The use of the site as a rail yard, marina, and industrial area, along with the historic fill, resulted in a heterogeneous soil with high total TE concentrations exceeding both residential (New Jersey Department of Environmental Protection, 1999) and ecological (US Environmental Protection Agency, 2003) soil screening criteria. After abandonment in 1967, vegetation spontaneously colonized the site and by the mid-1970s had created a patchwork of meadows, marshes, and hardwood forest (Gallagher et al., 2011). Today, much of the site has been converted to managed parkland.

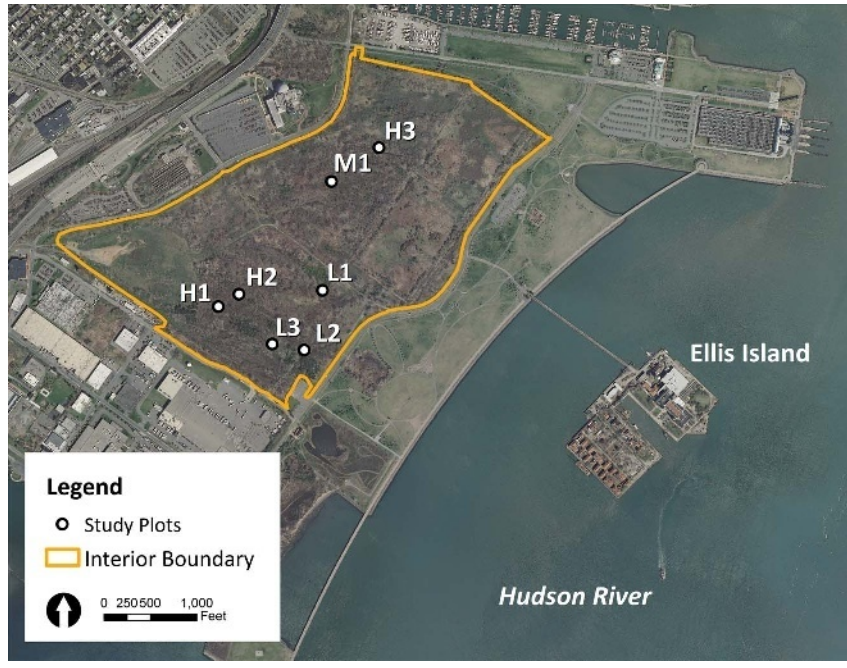

FIGURE 1. Aerial photograph of LSP, Jersey City, New Jersey, with interior boundary of unmitigated natural area and seven study plots highlighted. A color version of this figure is available in the online version of this article. full color online

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TABLE 1. Soil Electrical Conductivity, Total Organic Carbon (Measured by LOI), and Soil Texture From Composite of A and C1 Horizons in Plots L1, L2, L3, H1, H2, and H3 as part of a Separate Study in Fall 2015 (Salisbury, Unpublished)

	Min	Median	Max	Mean	SD
Organic carbon (LOI, %)[a]	2.4	7.8	21.3	9.3	4.5
Electrical conductivity (mS cm^{-1})[b]	0.07	0.08	0.14	0.09	0.02
Sand (%)[c]	72	80	93	81	5
Silt (%)[c]	4	15	24	15	5
Clay (%)[c]	0.1	4	6	4	2

[a]LOI temperature of 400°C.

[b]1:1 By volume water to soil.

[c]Soil texture was determined using a hydrometer method with 50 g of soil (sieved to <2 mm) dispersed with 50 mL of 10% Na-hexametaphosphate.

During park construction, 101.5 ha of the abandoned freight yard was left undisturbed and now serves as a long-term study site for the unassisted revegetation of TE-contaminated soil. Figure 1 shows the areal extent of the site, as well as the location of research plots that will be referenced throughout the article.

This study focuses on the top 30 cm of soil at the site, which contains three distinct mineral horizons created by the deposition of debris: the A, C1, and C2 horizons, which are approximately 5, 20, and 10 cm thick, respectively, although thickness varies by location. Liberty State Park is classed by the US Natural Resource Conservation Service as a sandy-skeletal over loamy, mixed, mesic Typic Udorthent, with 0% to 3% slope as part of the LadyLiberty soil series (Soil Survey Staff, 2010). The historical fill at the site resulted in a soil profile consisting of several unique debris horizons. The soil's organic horizon is 1 to 2 cm thick. All three layers of interest are a loamy sand and are differentiated by their colors—black (10YR 2/1) and very dark brown (10YR 2/2)—and by the amount of coal and boiler slag fragments along abrupt and clear boundaries. The horizons are typically strongly acidic (pH 5.0–5.2). The A horizon has a coarse granular structure, whereas C1 and C2 have massive structure. According to its soil series and a study by the US Army Corps of Engineers (2004), depth to groundwater in most of the site is 1.2 to 1.5 m; in addition, no redoxymorphic features were observed during soil sampling. Soil samples collected for a separate project at the site had fairly low electrical conductivities (ranging from 0.07 to 0.14 mS cm^{-1}) and loss-on-ignition (LOI) values that were much higher than would be expected for mineral soils, with a mean of 9.3% and a maximum of 21.3% (Table 1).

Much of the prior research at LSP has focused on the effects of the elevated soil TE concentrations on the site's flora and fauna. Plant community guild—grass/forbe, shrub, and forest—correlates fairly strongly with TE distribution. Early successional hardwood forests at the site are found in both areas of high and low TE concentrations. Interestingly, analysis of historic aerial photography shows that high TE areas were colonized by early successional hardwoods more quickly than low TE areas, showing the competitive advantage of this guild in highly degraded soils (Gallagher et al., 2011). The site also contains pockets of wetlands that formed on perched water tables, although these areas were excluded from the present study. Increasing metal loads decreased hardwood forest productivity (based on analysis of hyperspectral imagery) and plant diversity (Gallagher et al., 2008b) and altered community guild trajectories (Gallagher et al., 2011). The TE gradient was found to decrease the basal area growth rates of *Betula populifolia* (Dahle et al., 2014) and *Populus deltoides* (Renninger et al., 2012), but not their allometry or photosynthetic capacities. Bioconcentration factors for eight herbaceous and woody species at LSP varied by metal and by plant species, although in general metal concentrations were higher in the root system compared with aerial compartments (Qian et al., 2012). *Troglodytes aedon* (house wren) nestlings at LSP had higher concentrations of Pb, As, Cr, Cu, and Fe in their feathers in comparison to a reference site, although these concentrations had little effect on their size or fledge rates (Hofer et al., 2010). Trace element concentrations affected ectomycorrhizal fungi community composition (Evans et al., 2015) and had a direct relationship to microbial enzymatic activity (Hagmann et al., 2015). Despite these effects, the LSP community appears to be robust, as forest cover continues to increase and new tree species are beginning to colonize the site. Characterizing the temporal changes in the site's soil conditions is an important part of understanding the complex nature of plant-soil-microbe feedbacks in metal-contaminated soils at sites such as LSP (Krumins et al., 2015).

Early successional hardwood (SNH) assemblage is one of several habitat types in LSP and is dominated by gray birch (*B. populifolia* Marsh.), eastern cottonwood (*P. deltoides* Bart.), and quaking aspen (*Populus tremuloides* Michx.), with smaller populations of red oak (*Quercus rubra* L.), red maple (*Acer rubrum* L.), tree of heaven (*Ailanthus altissima* Mill.), and three sumac species (*Rhus copallinum* L., *Rhus glabra* L., *Rhus typhina* L.). For the past 50 years, the area covered by this assemblage has been increasing at LSP, and it is possible this assemblage could represent an alternate steady state, which could persist for many years (Gallagher et al., 2011). In addition, the dominant plant species in this assemblage have been shown to accumulate the TE of interest to this study (Qian et al., 2012). Consequently, the SNH assemblage is relevant to understanding the long-term dynamics of TE at LSP.

Soil Sampling—2015

Although there are many long-term study plots set up in the LSP interior, this study focuses on seven, which contain SNH assemblages (Table 2). Plot identifiers L, M, and H indicate relatively low, medium, and high TE concentrations, respectively. The plots were selected for this project because their SNH community has been established for at least 10 years (Gallagher et al., 2011). These plots also represent a range of high and low TE concentrations.

In late 2014 and mid-2015, the seven SNH plots were each sampled in five locations using a hand trowel or soil corer from three different horizons: the A (approximately 5 cm thick), the C1 (approximately 20 cm thick), and the C2 (approximately 15 cm thick). The three horizons were sampled in order to better understand the vertical distribution of TE in the plots. Each sample is a composite of soil from five pits within 1 m^2 at each location. Samples were brought back to the laboratory where they were air dried

TABLE 2. 2015 Study Plot Names Used in Current Article Along With Names Used in Previous Studies and Total Metal Load (Rank Composite Index Based on Concentrations of As, Cr, Cu, Pb, and Zn Measured in 2005, see Gallagher et al., 2008)

Plot	Previous label	Total Metal Load
L1	TP-41	0.85
L2	TP-48	1.56
L3	TP-43	1.64
M1	TP-18	2.85
H1	TP-14	3.08
H2	TP-14/16	3.56
H3	TP-25	4.31

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for a minimum of 48 h. Large plant material and gravel greater than 2 mm were removed from the samples, which were then ground with a mortar and pestle to break up aggregates and sieved through a 2-mm screen. Samples (<2 mm) were analyzed for pH using a 1:1 ratio by volume of soil to water with an S975 Seven Excellence Multiparameter pH meter (Mettler Toledo, Columbus, OH).

In order to generate measurements of soil TE concentrations comparable to the 2005 data set, the C1 horizon soil samples were extracted following a procedure similar to the one used in 2005 (Gallagher et al., 2008a). For this analysis, 0.5 g from the less than 125-μm fraction was mixed with 10 mL of trace metal–grade HNO_3 and heated to greater than 175°C for 30 min in Teflon bombs with an Anton-Paar Multiwave 3000 microwave digester (Anton Paar, Graz, Austria). Method blanks and a standard reference material (National Institute of Standards and Technology Standard Reference Material 1944, "New York-New Jersey Waterway Sediment") were also run with the samples. Extracts were then analyzed for As, Cr, Cu, Pb, and Zn using a Thermo Scientific iCAP 7600 inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo Scientific, Waltham, MA). Although different analytical methods were used in 2005 and 2015, several authors have found that maintaining the same sample digestion and preparation methods has greater influence on accuracy and comparability (Pyle et al., 1996; Chen and Ma, 1998; Munroe et al., 2012).

The vertical distributions of TE, Fe, Mn, and S concentrations were analyzed in the top three mineral soil horizons (A, C1, C2) in this study using an Innov-X delta x-ray fluorescence (pXRF) handheld analyzer (DS-4000; Olympus NDT, Waltham, MA). Each sample was measured four times to obtain a representative measurement of the sample. The pXRF was calibrated with a no. 316 stainless steel chip every 50 measurements. Numerous studies comparing the performance of atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, and pXRF on the same set of soil samples or reference materials have generally found good correlation between these techniques, although several found the pXRF may not be as accurate as other analytical methods (e.g., see Anderson et al., 1998; McComb et al., 2014; Radu and Diamond, 2009; Wu et al., 2012). Because a subset of 2015 samples was measured with two techniques, correlations between ICP-OES and pXRF results are presented below.

Total carbon (TC) and total nitrogen (TN) were determined in 350 (±50) mg subsamples of soil for the 2015 A, C1, and C2 samples using a dry combustion method at 900°C with a vario MAX cube C/N analyzer (Elementar Americas Inc., Mt. Laurel, NJ) and helium as a carrier gas. The upper horizons of LSP soils have high coal dust and fragment content (Soil Survey Staff, 2010), which would have inflated traditional LOI measurements made at a lower temperature by combusting some, but not all, of the coal carbon (Rawlins et al., 2008). Instead, the TC analysis completely measures both recent soil organic carbon and coal carbon (Ussiri et al., 2014). To help discern the effects of recent soil organic carbon, measurements of TN were included, presuming TN could be a reasonable representation of recent soil OM.

Soil Sampling—1995, 2005

To assess temporal changes in soil TE concentrations, this study utilized subsets of data collected in 1995 (third-decade postabandonment) by the US Army Corps of Engineers and in 2005 (fourth-decade postabandonment) by the New Jersey Department of Environmental Protection. While a large number of samples were collected in 1995 and 2005, only data from the seven SNH plots described in the previous section were analyzed for the 2015 comparison. In the earlier studies, only one horizon was sampled, because their focus was on characterization of the horizontal distribution of TE.

The 1995 soil data were part of a site characterization study and so sampled broadly following transects across the site collecting a total of 98 samples (New Jersey Department of Environmental Protection, 1995). Aerial photographs from this time period reveal that the entire site was vegetated by several types of plant guilds, making it reasonable to assume all sample plots were vegetated as well. These sample locations were later used as the plot locations for other studies. In 1995, one composite sample was collected from each plot by split spoon as a composite of the A and C1 horizons and was analyzed for TE content using graphite furnace atomic absorption spectrometry.

In 2005, 32 of the original 98 plots sampled were selected to be representative of each plant guild in order to better assess the relationship between TE concentrations and the dominant plant communities established on the site. During this sampling, three cores were collected at each plot with a soil borer to a depth of 10 to 25 cm (C1 horizon), the depth of greatest root density (Gallagher et al., 2008a). In 2005, the plant communities of this study's seven plots were all SNH. The air-dried and sieved samples were treated with trace metal–grade HNO_3 using a microwave extraction procedure and analyzed for Cr, Cu, Pb, V, and Zn by flame atomic absorption spectroscopy in a Perkin-Elmer 603 atomic absorption spectrophotometer (Perkin-Elmer, Waltham, MA). Arsenic was analyzed with a $Mg(NO_3)_2/Pb(NO_3)_2$ matrix modifier in a Perkin-Elmer Z5100 graphite furnace atomic absorption spectrometry (Perkin-Elmer). Method blanks and National Institute of Standards and Technology Standard Reference Material 1944 (urban sediment) were used for quality control. Soil pH was measured using a LaMotte colorimetric field pH meter (LaMotte Company, Chestertown, MD).

Soil data from 2005 were previously used to generate a total metal load (TML) index for each study plot in the site as described in Gallagher et al. (2008b). Total metal load is a rank-sum index based on the 2005 concentrations of As, Cr, Cu, Pb, and Zn for 32 study plots in LSP. High TML reflects higher concentrations of the five metals.

Estimation of soil-water partition coefficients

The soil-water partition coefficient (K_d) of TE is a useful indicator of the degree of element sorption in a given soil (Tipping et al., 2003), although it does not necessarily reflect bioavailability or biological uptake (Watmough, 2008). While K_d is influenced by a number of factors, several studies have shown that pH can serve as a reasonable predictor (Buchter et al., 1989; Sauve et al., 2000; Tyler and Olsson, 2001; Watmough, 2008). Mean, minimum, and maximum K_d of Cu, Pb, and Zn in LSP soil C1 horizons were estimated based on pH measurement made in 2005 and 2015 using equations derived by Sauve et al. (2000) from a review of more than 70 studies of metal-contaminated or metal-spiked soils:

$$\text{Log}(K_d\text{-Cu}) = 0.27\ (\pm 0.02)\ \text{pH} + 1.49\ (\pm 0.13) \quad (1)$$

$$\text{Log}(K_d\text{-Pb}) = 0.49\ (\pm 0.04)\ \text{pH} + 1.37\ (\pm 0.25) \quad (2)$$

$$\text{Log}(K_d\text{-Zn}) = 0.62\ (0.03)\ \text{pH} - 0.97\ (0.21). \quad (3)$$

For the purposes of their review, Sauve et al. (2000) defined K_d ($L\ kg^{-1}$) as the ratio of total soil metal concentration (mg metal kg^{-1} soil) to metal concentration in the soil solution (mg metal L^{-1} solution). In the experiments they reviewed, total metal content was determined based on acid digestion procedures. Soil solution metals were determined based on several procedures, including extractions using distilled water or dilute salt solutions. While regression equations relating K_d to pH for As and Cr exist (Watmough, 2008), they were derived from soils with As and Cr concentrations much lower than

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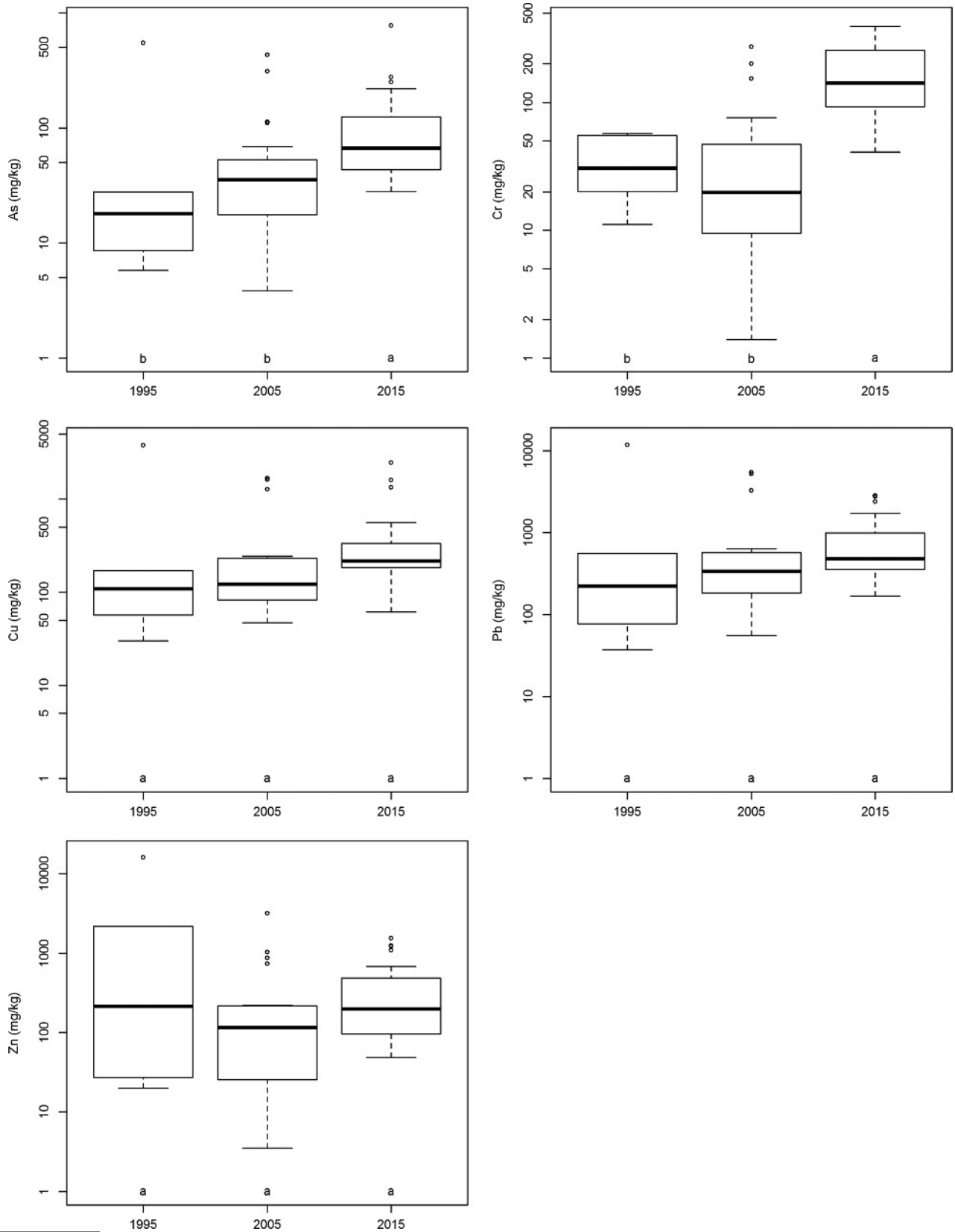

FIGURE 2. Soil TE concentrations (mg/kg) in the C1 horizon from 1995, 2005, and 2015 for seven study plots (n = 6, 21, and 35, respectively). Groups that share the same letters are not statistically different ($P < 0.05$) according to a Tukey HSD test. Note that concentrations of all TE are shown on a logarithmic scale.

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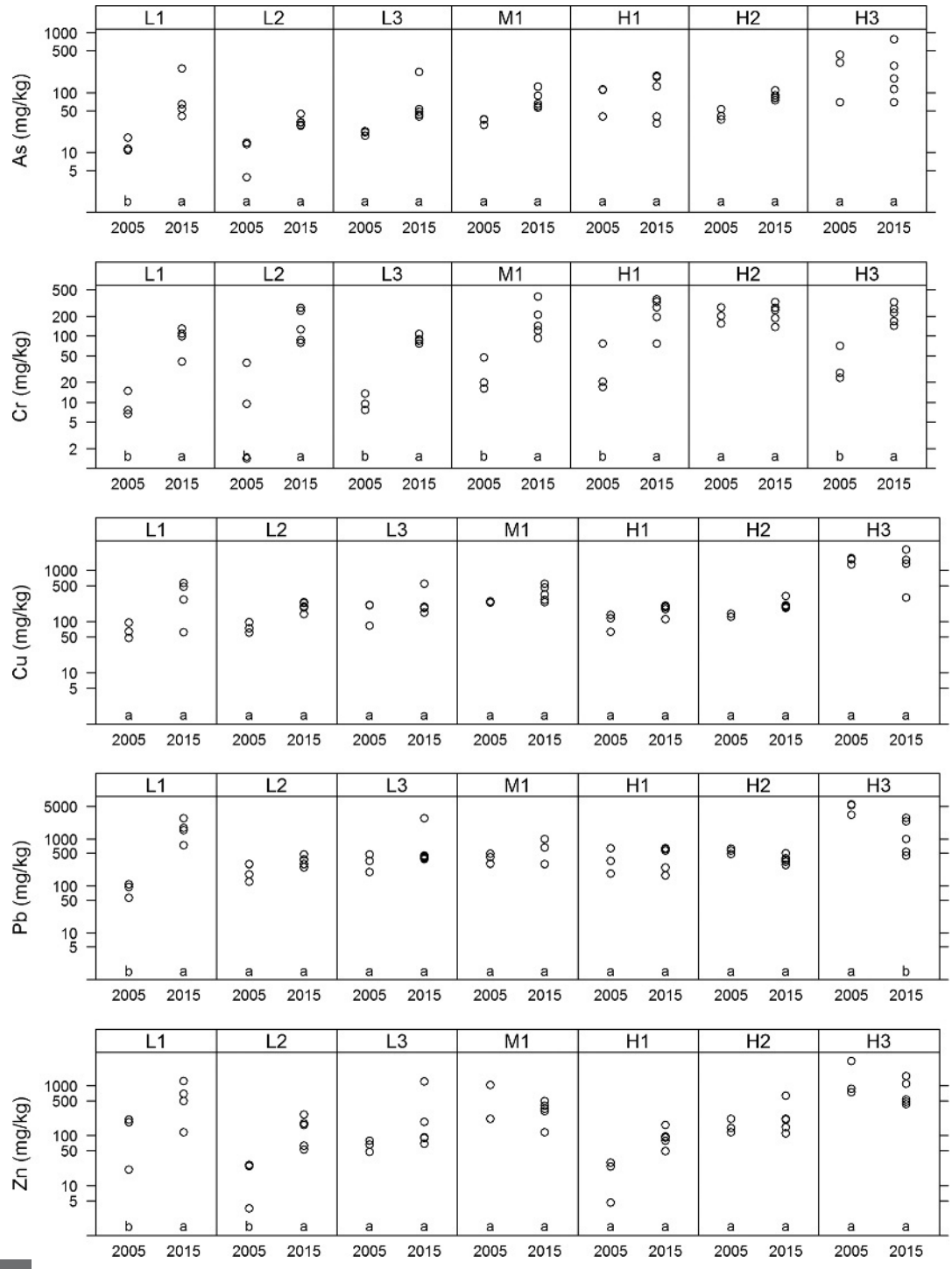

FIGURE 3. Soil TE concentrations (mg/kg) in the C1 horizon from 2005 (n = 3 per plot) and 2015 (n = 5) for seven study plots. Concentrations within plots which share the same letters are not statistically different ($P < 0.05$) according to a Tukey HSD test. Note that concentrations of all TE are shown on a logarithmic scale.

the values observed in this study and consequently may not be applicable to soils at LSP.

Statistical Analysis

For all analyses, each TE of interest (As, Cr, Cu, Pb, and Zn) was tested separately. A natural log transformation was applied to normalize the residuals of the acid extracted TE data and improve its homogeneity of variance. Differences in TE concentrations between sample years were tested using a one-way analysis of variance (ANOVA); year was used as the treatment variable. While sample number varied in 1995, 2005, and 2015 (n = 7, 21, and 35, respectively), when normality and homoscedasticity assumptions are met, one-way ANOVA is fairly robust against differences in sample size (Oehlert, 2010). Plot level variation in temporal changes in TE between the seven plots was tested using a two-way ANOVA (Type III), where year and plot were treatment variables because a Type III

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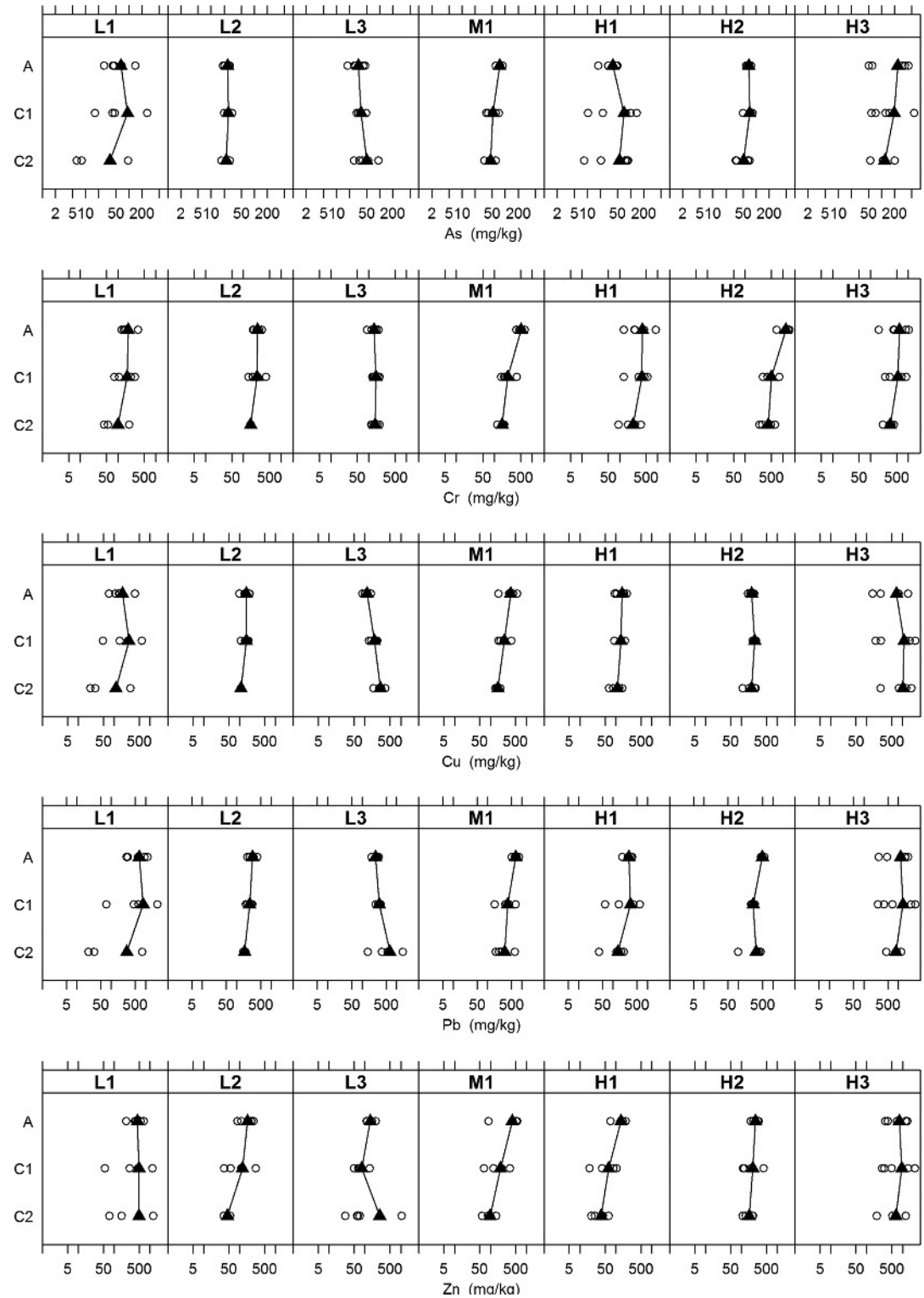

FIGURE 4. Soil TE concentrations (mg/kg) in 2015 samples from the A, C1, and C2 horizons measured by pXRF (n = 5 per horizon per plot). Solid triangles represent mean concentrations; open circles represent individual concentrations.

ANOVA can accommodate unequal sample sizes among two factors (Oehlert, 2010). Because there was no within plot replication in the 1995 data set, only the 2005 and 2015 data sets were used in the two-way ANOVA analysis. To test if TE concentrations and pH varied between horizons in 2015 within each plot, the pXRF data set was also tested with a two-way ANOVA (Type III) with horizon nested within plot. In addition, the correlation between pXRF and ICP-OES measurements was assessed with a linear regression using data from the 2015 C1 horizon samples because those samples were analyzed using both methods. All pairwise comparisons were

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TABLE 3. Range, Median, and Mean Concentrations of Total Fe, Total Mn, Total S, Total C (TC), and Total N (TN), of Samples Collected From the A, C1, and C2 in 2015 (n = 98)

	Min	Median	Max	Mean	SD
	mg/kg				
Fe	18,828	62,682	448,348	82,087	61,166
Mn	112	276	1,509	359	231
S	1,384	5,336	26,063	6,281	3,974
	%				
TC	0.3	21.5	35.7	21.2	6.8
TN	0.008	0.362	1.163	0.432	0.242

Iron, Mn, and S were measured using a pXRF; TC and TN were measured using an elemental analyzer.

conducted using a Tukey honestly significant difference (HSD) test, which constructs simultaneous confidence intervals to control the overall significance level and is appropriate for use with unbalanced data (Oehlert, 2010). The relationships between TE and Fe, Mn, S, TC, TN, and pH in 2015 were assessed using the pXRF data and Pearson correlation coefficients. All data analyses were performed using the R environment for computing (R Core Team, 2016) utilizing the car (Fox and Weisberg, 2011), lattice (Sarkar, 2008), and agricolae (de Mendiburu, 2016) packages.

RESULTS

Across the seven LSP study plots, concentrations of all five soil TE varied over several orders of magnitude (Supplementary Table 1, Supplemental Digital Content 1, http://links.lww.com/SS/A45). Comparisons of TE concentrations from 1995, 2005, and 2015 revealed two distinct temporal trends. No significant differences in the average soil concentrations of Cu, Pb, and Zn in the C1 horizon were observed between 1995, 2005, and 2015 when data from all seven plots were pooled together (Fig. 2; $P = 0.113$, 0.21, 0.08, respectively). However, As and Cr concentrations in the C1 horizon were significantly higher in 2015 compared with 1995 and 2005 ($P = 0.003$ and $P < 0.001$, respectively). From 1995 to 2015, Cu and Pb concentrations in the C1 horizon generally increased; however, the difference between years was not significant.

Because heterogeneity of TE spatial distribution is a common issue in anthropogenic and contaminated soils (Hartley et al., 2009; Nowack et al., 2010; Hartley et al., 2012), it is important to assess the interacting effects of spatial and temporal variability in long-term studies. Some variation in the temporal changes in TE concentrations was observed between plots from 2005 to 2015 (Fig. 3). The increasing trend in As from 2005 to 2015 was seen in plots L1, L2, L3, M1, and H2, but was less pronounced in H1 and H2. Plot H2 was the only plot where Cr concentration did not increase from 2005 to 2015. Within all plots, there is a generally increasing trend in the concentration of Cu from 2005 to 2015, although none of these differences were significant. Lead concentrations were fairly similar in L2, L3, M1, H1, and H2 from 2005 to 2015, although a significant increase over time was observed in L1, whereas there was a significant decrease in H3. Zinc concentrations increased significantly in plot L2, whereas there were also nonsignificant increases in L1, L3, and H1.

When comparing the 2015 soil TE concentrations measured by pXRF between the three sampled soil horizons, the only significant difference observed was in the higher concentration of Cr in the A horizon compared with the C2 horizon (Fig. 4). In plots H2 and H3, As and Cr concentrations decreased with depth, although these

TABLE 4. Pearson Correlation Coefficients for pH, Total C (TC), Total N (TN), and ln-Transformed Element Concentrations Based on pXRF Analysis of Samples From A, C1, and C2 Horizons (n = 98)

	ln(Cr)	ln(Cu)	ln(Pb)	ln(Zn)	ln(Mn)	ln(Fe)	ln(S)	TC%	TN%	pH
ln.As	0.61***	0.75***	0.83***	0.59***	0.53***	0.59***	0.35***	0.1	0.11	0
ln(Cr)		0.56***	0.52***	0.42***	0.37***	0.38***	0.05	0.4***	0.34***	–0.05
ln(Cu)			0.8***	0.66***	0.63***	0.46***	0.14	0.05	–0.05	0.14
ln(Pb)				0.68***	0.59***	0.45***	0.21*	0.12	0.17	0.05
ln(Zn)					0.71***	0.07	–0.26*	–0.18	0.1	0.49***
ln(Mn)						0.49***	0.05	–0.04	0.09	0.25*
ln(Fe)							0.77***	0.25*	0.02	–0.36***
ln(S)								0.18	–0.08	–0.51***
TC%									0.79***	–0.54***
TN%										–0.31**

*$P < 0.05$.
**$P < 0.01$.
***$P < 0.001$.

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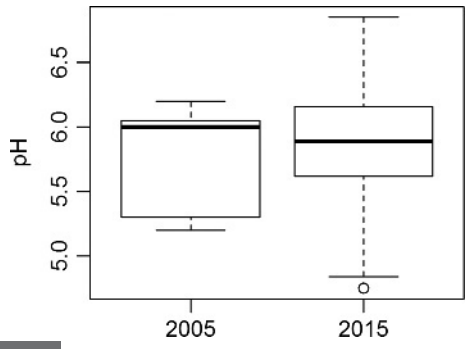

FIGURE 5. Soil pH measured in the C1 horizon in 2005 (n = 7) and 2015 (n = 35) for seven study plots.

differences were not significant. Cu and Zn decreased with depth in M1 as well, although the differences between horizons were not significant. Zinc also decreased with depth in L2 and H1, although again the differences were not significant.

Correlations were observed between pH, total Fe, Mn, S, TC, and TN and the five TE in the 2015 soil samples from all three horizons. Total Fe, Mn, S, TC, and TN ranged widely across the samples (Table 3). Zinc was the only TE that correlated significantly with pH (Table 4). Arsenic, Cr, Cu, and Pb were all positively correlated with both total Fe and total Mn, but Zn was correlated only with Mn. Correlations were also observed between S and As, Pb, and Zn. Of the five TE, only Cr had a significant correlation with TC and TN. Iron had a significant correlation with TC as well. In addition, all five TE had significant positive correlations with each other.

Soil pH remained fairly consistent between 2005 and 2015 in the C1 horizon (Fig. 5, $P = 0.57$). For 2015 samples, soil pH did not vary significantly across the three horizons (Fig. 6, $P = 0.61$). K_d values were estimated for Cu, Pb, and Zn based on soil pH. K_d values for these three TE increased from 2005 to 2015, in all of the plots except M1 (Table 5). Overall, predicted K_d values were highest for Pb, followed by Cu then Zn.

The pXRF and ICP-OES analyses for the three soil horizons sampled in 2015 produced comparable results for soil concentrations of Zn (slope confidence interval contained 1, Table 6) and fairly good results for Cu and Pb (slope confidence intervals are close to 1). The pXRF method underpredicted As and overpredicted Cr compared with the ICP-OES analysis.

DISCUSSION

Understanding temporal trends in the vertical distributions of TE is important for understanding the stability of TE within specific soil horizons, the long-term bioavailability of TE to shallow- and deep-rooted vegetation in recovering landscapes, and the potential for TE to migrate out of a system via groundwater. Aside from atmospheric deposition, there have been no new inputs of TE into the soil system at LSP during the study period. In addition, because the site grade is relatively flat, ranging from 0% to 2% (US Army Corps of Engineers, 2004), lateral flow of pore water was unlikely to have influenced the redistribution of TE among individual plots. Consequently, the observed increases in As and Cr in the C1 horizon must have resulted from the amount of As and Cr leaching into the C1 horizon (presumably from horizons above) being greater than that leaching out. On the other hand, the stability of Cu, Pb, and Zn concentrations in the A and C horizons over time suggests that either there was no vertical movement of these metals, or inputs and outputs of these TE in these horizons were approximately balanced. In the latter case, TE uptake by plants would need to have been approximately equal to subsequent TE release as a result of leaf litter decomposition.

The analysis of soils collected from the seven hardwood LSP plots in 1995, 2005, 2015 supports the initial hypothesis that TE concentrations were stable for three of the five TE examined. The concentrations of Cu, Pb, and Zn did not significantly change in the surface soils of the seven hardwood plots studied over this time period. These findings are supported by other work showing that changes in metal concentrations are more likely to occur in the first few years following the cessation of pollution input and that in subsequent years concentrations stabilize (Ramos Arroyo and Siebe, 2007; Clemente et al., 2008). However, concentrations of As and Cr increased significantly in the C1 horizon from 2005 to 2015 (Fig. 2).

Small spatial scale variability in temporal trends of TE concentrations in highly heterogeneous reforested brownfield sites is not unexpected (French et al., 2006). Indeed, while the seven LSP study plots show consistent temporal trends in TE concentrations when analyzed in aggregate, some variation between study plots was observed. In most cases, plot L1 exhibited the greatest increases in TE concentrations, whereas H3 exhibited no change or slight decreases in TE concentrations. H2 was an outlier for Cr, exhibiting no change, whereas Cr increased in every other plot. The most dramatic difference between L1 and H3 (as well as H2) is their TML index. It is possible that because L1 started with lower TE concentrations, it has been able to accumulate TE at a higher rate. On the other hand, with its significantly higher TE concentrations, soil in the H3 plot may be close to saturation with respect to the amount of TE it can sorb. These results highlight the challenges of monitoring and predicting temporal trends of TE concentrations in highly heterogeneous, contaminated soils.

Fe- and Mn-(hydr)oxides, Al-oxides, soil humics, and clays are all potential sorbents for As, Cr, Cu, Pb, and Zn (Sparks, 2003). All seven plots had low clay content, but high total Fe and Mn concentrations. The concentration of total Fe in particular was at the high end of the typical range found in soils (Bodek et al.,

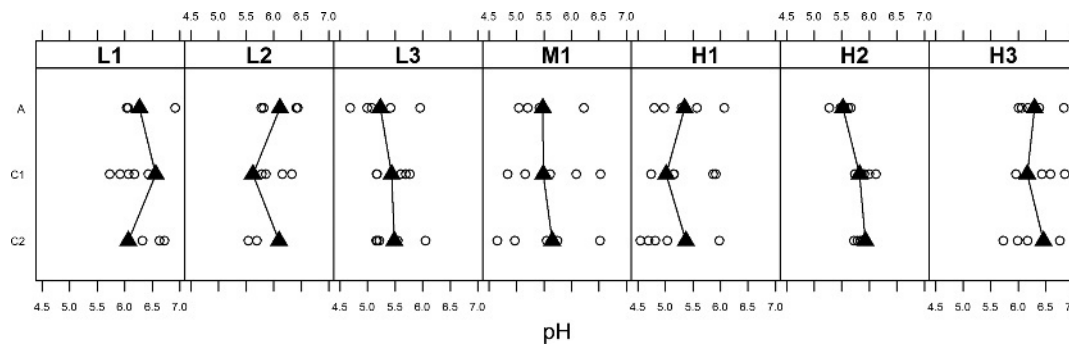

FIGURE 6. Soil pH of the A, C1, and C2 horizons in 2015 (n = 5 per horizon). Solid triangles represent mean pH; open circles represent individual pH measurements.

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TABLE 5. Mean with Minimum and Maximum Solid-Solution Partition Coefficients (K_d) Estimated for Cu, Pb, and Zn in Soil From Plots Sampled in 2005 and 2015 (Based on pH and Equations 1, 2, 3)

	Copper		Lead		Zinc	
Plot	2005	2015	2005	2015	2005	2015
L1	1,288 (724–2,291)	1,424 (794–2,552)	20,417 (6,607–63,096)	24,733 (7,866–77,795)	562 (229–1,380)	722 (290–1,798)
L2	1,371 (767–2,449)	1,380 (771–2,468)	22,856 (7,328–71,285)	23,451 (7,486–73,497)	649 (262–1,603)	677 (273–1,681)
L3	887 (513–1,535)	948 (545–1,649)	10,375 (3,548–30,339)	11,911 (4,016–35,343)	239 (101–562)	288 (121–687)
M1	1,288 (724–2,291)	1,112 (629–1,967)	20,417 (6,607–63,096)	17,291 (5,581–53,707)	562 (229–1,380)	488 (197–1,210)
H1	783 (457–1,343)	906 (522–1,574)	8,279 (2,884–23,768)	11,402 (3,834–33,958)	179 (77–417)	280 (117–671)
H2	783 (457–1,343)	1,234 (696–2,188)	8,279 (2,884–23,768)	18,980 (6,174–58,361)	179 (77–417)	514 (210–1,258)
H3	1,459 (813–2,618)	1,746 (959–3,180)	25,586 (8,128–80,538)	36,421 (11,193–118,596)	748 (301–1,862)	1,192 (466–3,048)
	Mean (Min-Max) From Literature					
	4,799 (6.8–82,850)		171,214 (60.56–2,304,762)		11,615 (1.4–320,000)	

Minimum and maximum K_d values calculated based on standard error of equation coefficients. For comparison, mean, minimum, and maximum values for various soil types reported in the literature are also provided (Sauve et al., 2000).

1988). Although concentrations of total Fe and Mn rather than their (hydr)oxides were quantified, soil at the LCP site is oxic, and a previous mineralogical analysis of three soil pits at LSP identified the presence of Fe oxides (3%–12% of optical grain count) (Soil Survey Staff, 2010). This and our observation of positive correlations between all five TE and Fe or Mn (Table 4) strongly suggest that Fe and Mn (hydr)oxides play an important role as TE sorbents at this site.

Organic matter plays a complex role in TE geochemistry. Depending on OM form and environmental conditions such as pH, OM can immobilize or mobilize TE in soil (e.g., see Bolan et al., 2014; Brown et al., 2000; Li et al., 1999; McBride et al., 1997; Ruttens et al., 2006). Total OM measured by LOI in LSP soil (Table 1) is much higher than expected for mineral soil (Jones, 2012), most likely because of the presence of coal dust and fragments in the soil (Soil Survey Staff, 2010). Given the difficulties of measuring recent soil organic carbon in soils with high coal content, care should be taken in the interpretation of the TC correlation data (Rawlins et al., 2008). Only Cr showed significant correlations with both TC and TN, suggesting OM could be an important sorbent for Cr. Jardine et al. (2013) similarly observed higher Cr sorption rates in the A horizon of soils, which correlated with increasing total organic carbon and decreasing pH. While it is somewhat surprising, correlations were not observed between TC and the other four TE, it is possible that weaker relationships between OM and the TE could be obscured by the high coal-carbon content in the soil.

The two elements that increased from 2005 to 2015—As and Cr—would be present as oxyanions given the oxic conditions in the plots as well as their pH (Takeno, 2005). We assume oxic conditions for all samples because they were collected from the unsaturated zone of upland soils. Thus, As(V) and Cr(VI) should have been the dominant oxidation states. The pXRF TE results show that there were pools of As and Cr in the horizon closest to the surface that may have served as a source to enrich the C1 horizon. While total Fe and Mn concentrations were fairly constant through the soil profile, the Natural Resources Conservation Service pedon data suggest Fe-oxide distribution may be more uneven, and there could be more Fe oxide in the lower horizons (Soil Survey Staff, 2010). Oxyanion sorption decreases with increasing pH as soil particles and OM lose their positive charges (Smith, 1999). The increase in As and Cr from 2005 to 2015 coincides with an increase in pH in six of the seven plots, suggesting that a change in soil pH may have contributed to the mobilization of As and Cr in this period. Similar results were observed by Clemente et al. (2008) when 20 years after cessation of adjacent smelter activities As showed evidence of moving downward into the soil profile and then becoming immobilized by Fe and Al (hydr)oxides. Arsenic immobilization has also been observed in forested catchments and mining soils (Huang and Matzner, 2007; Moreno-Jiménez et al., 2010).

The three elements that showed no overall change in concentration from 1995 to 2015—Cu, Pb, and Zn—are expected to be present as divalent cations in the oxic and slightly acidic conditions in these plots (Takeno, 2005). Estimated K_d values for Cu, Pb, and Zn in each plot are all lower than mean values reported in the literature, although they are at least two orders of magnitude greater than the reported minimum values (Table 3). This suggests a moderate degree of mobility of these TE in the soil solution. Greater

TABLE 6. Linear Regression Coefficients for Comparison of ICP-OES (as Independent Variable) and pXRF (as Dependent Variable) TE Concentrations in Horizon C1 Collected in 2015 Using a 95% Confidence Interval (n = 35)

Element	Slope	Slope LCL	Slope UCL	Intercept	Intercept LCL	Intercept UCL	r^2
As	0.7	0.62	0.78	1.15	–12.36	14.66	0.9
Cr	1.7	1.27	2.14	11.59	–84.17	107.35	0.64
Cu	0.92	0.85	0.98	–31.78	–72.33	8.78	0.96
Pb	0.72	0.54	0.9	–22.16	–209.23	164.92	0.66
Zn	0.91	0.71	1.12	–48.65	–170.88	73.57	0.7

LCL: lower confidence limit; UCL: upper confidence limit.

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mobility in soil solution means these elements could be more available for plant uptake (Bolan et al., 2014).

The cycling of Pb (Heinrichs and Mayer, 1980; Watmough and Dillon, 2007), Mn (Navrátil et al., 2007), Cd, and Zn (Landre et al., 2009) through forest biomass and return to the forest floor has been documented in forests affected by atmospheric pollution and in unpolluted environments. This is consistent with prior research on plant TE bioaccumulation at LSP showing that plant translocation is an important driver of Cu, Pb, and Zn soil concentrations over time (Gallagher et al., 2008b; Qian et al., 2012). With some variation among species, these LSP studies showed that TE concentrations in aboveground and belowground plant tissue decreased in the following order: Zn > Pb > Cu > Cr > As. The three TE present in the highest concentrations in the site's plants—Cu, Pb, and Zn—correspond to the TE with whose concentrations were constant in soil from 1995 to 2015. These patterns were observed despite the fact that the route of TE accumulation in plants varies among metals. In a forest contaminated with Cu, Ni, Pb, and Zn from smelter emissions, fine roots were important for Cu and Pb plant-soil transfer, whereas foliage was more important for Zn (Johnson et al., 2003). Similarly, Qian et al. (2012) found Zn had the highest bioconcentration factors in the leaves of *B. populifolia* and *P. deltoides*, whereas bioconcentration factors for As, Cr, and Cu were higher in the roots (Pb was not analyzed in this study).

CONCLUSIONS

While there is an expectation and need for phytostabilization or natural attenuation sites to retain TE contamination for prolonged periods, there is a paucity of follow-up studies that track TE concentrations beyond the first decade of plant community establishment. By utilizing soil data collected 28 to 48 years after site abandonment, this study documented changes in soil TE concentrations in a spontaneously vegetated urban brownfield over the course of 20 years. The results demonstrate that in this period Cu, Pb, and Zn concentrations in the upper mineral horizons remained fairly stable but that As and Cr concentrations increased deeper in the soil profile. Bioaccumulation in plant material (and later decomposition), favorable pH, and mineral and organic sorbents in the soil all play an important role in retaining TE in soil over the long term. The apparent transfer of As and Cr from the surface to deeper in the soil profile may have been driven by changes in pH at the soil surface and highlights the need at least for these elements to continue monitoring soil conditions in vegetated brownfields through longer periods.

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