Trace metals and metalloids in peri-urban soil and foliage across geologic materials, ecosystems, and development intensities in Southern California

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Abstract

Purpose Southern California is a mega-metropolitan area with abundant air pollution, complex geology, and diverse Mediterranean ecosystems. The objective of this study was to evaluate trace metal and metalloids (TMMs) (As, Cd, Co, Cr Cu, Ni, Pb, U, V, Zn) in soils and foliage of peri-urban areas and explore potential effects from human-development, ecosystems, and geologic material.

Materials and methods Foliage of dominant native vegetation, soil samples (0–20 cm), saprolite, and unweathered rock samples were collected across fifty-four sampling sites in foothills spanning coastal Los Angeles and Orange counties to inland San Bernardino and Riverside counties.

Results and discussion Soil As, Cd, Cu, and Pb concentrations were regionally elevated, but not as elevated as point-source polluted sites elsewhere. Soil Cd, Cr, Cu, Pb, and Zn concentrations were above EPA Ecological Soil Screening Levels. Further, enrichment factors (EF) normalized to Ti concentrations in bedrock suggest minor to moderate As, Cd, Cr, Cu, Pb, and V accumulation in soils. Our foliar TMM concentrations and bioaccumulation factors (BAF) (foliar and soil ratio) indicate no bioaccumulation and limited effects across geologic, development intensity, and ecosystems groups.

Conclusions Sedimentary-derived soils affected soil TMMs, but likely not through inheritance of TMMs but by promoting clay and organic matter availability. Proximity to higher development intensity resulted in As, Cd, Cr, Cu, and Pb accumulation in peri-urban soils. Foliar TMM concentrations and BAFs suggest geologic materials, human development, and ecosystem properties were not important factors and TMMs were likely controlled by plant uptake or ecophysiology.

Keywords Trace elements · Peri-urban soils · Soil pollution · Weathering

1 Introduction

Human activities have altered the biogeochemical cycling of trace metals and metalloids (TMMs) in peri-urban terrestrial environments through adjacent land-use changes and atmospheric emissions on local, regional, and global scales.

TMMs can accumulate in soils from the addition of dust, precipitation, and pollution from human activities (Adriano 2001; Charlesworth et al. 2011; Richardson et al. 2015). The combustion of fuels and use of brakes by automobiles have released TMMs, such as lead (Pb), chromium (Cr), and copper (Cu), to terrestrial ecosystems (Komarek et al. 2008; Cheng et al. 2014; Richardson et al. 2014; Trujillo-González et al. 2018). Smelting and other metallurgical activities can release other TMMs such as cobalt (Co), nickel (Ni), and zinc (Zn) (Adriano 2001; Reimann and Garrett 2005; Richardson et al. 2015). Lastly, agricultural, industrial activities, and commercial manufacturing can also release other TMMs such as arsenic (As) and cadmium (Cd) (Adriano 2001; Cloquet et al. 2006; Charlesworth et al. 2011; Wang et al. 2015). These contaminants can remain stored in surface soils, be transported

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to rivers, reservoirs, or coastal systems (e.g., Slotton and Reuter 1995; Chow et al. 1994; Schiff and Weisberg 1999), or eroded by wind generating potentially hazardous dust (Charlesworth et al. 2011; Mielke et al. 2010). Thus, accumulation and retention in soils can help prevent negative impacts to marine ecosystems (e.g., Katz and Kaplan 1981) and human health (e.g., Sabin et al. 2006; Hung et al. 2018), but could impact planted or native vegetation from overexposure through soil uptake (Page and Chang 1979; Adriano 2001; Clarke et al. 2015; Wang et al. 2015).

TMMs are also naturally present in soils due to retention from the rocks and minerals in their parent material. TMMs can be within minor constituent minerals such as sulfides, carbonates, and oxides (Adriano 2001; Botinelly et al. 1985), accessory silicates such as tourmaline (see Marschall and Jiang 2011), substituted into common mafic silicates such as Cu, Zn substituted for Fe in amphiboles and pyroxenes (e.g., Chukanov et al. 2020; Reguir et al. 2012), or uncommonly as elemental forms. When rocks and minerals undergo chemical weathering, TMMs are released from their immobile, mineral phases to more bioavailable, mobile phases. Once mobilized, TMMs can leach to surface waters and groundwaters (e.g., uranium (U) and vanadium (V)) or are taken up and accumulated by plants (e.g., Zn). TMMs released during weathering can be misinterpreted as human-derived pollution (Rasmussen 1998). Thus, it is imperative for geologic processes that influence trace metals to be taken into account while characterizing the geochemistry of a human-perturbed system. However, "geochemical background" can be difficult to ascertain due to the heterogeneity in parent materials, biological cycling, and pedologic processes (see Reimann and Garrett 2005). Using generalized soil concentrations as geochemical background can be flawed when underlying lithologies have high TMM concentrations. Thus, leveraging geologic parent material is an important but underutilized tool for normalizing TMM concentrations and assessing natural and anthropogenic inputs to soils.

Southern California is a useful testing ground to evaluate human, geologic, and ecosystem controls on TMM retention or enrichment. Southern California has a complex geology due to tectonic activity that has dispersed different bedrock lithology throughout the region (Jahns 1954; Jennings et al. 1977). Further, there is a substantial climatic gradient from coastal Mediterranean to hot dry desert, which has several implications for vegetation-precipitation controls on trace metals. The variation in precipitation and temperature can impact TMM release during weathering (Webb and Girty 2016) and leaching (Yuan et al. 2011) as well as the formation of secondary oxides or clays (Weitkamp et al. 1996; Graham and O'Geen 2010) that can sorb and retain trace metals. Further, the composition of plants can affect foliar fog-interception rates (e.g., Azevdeo and Morgan 1974) and aboveground uptake and cycling (Gray 1983). Lastly, Southern California has a large human

population and urban footprint with ample peri-urban environments. Moreover, soil and air quality has been impaired in the region (e.g., Sabin et al. 2006; Hung et al. 2018) as natural aerosols and dust as well as human-derived particulates have facilitated the transport of TMM dispersal in the region (see Chow et al. 1994; Hughes et al. 1999; Sabin et al. 2006; Charlesworth et al. 2011).

The objective of this study was to determine if TMMs in soils and plants in peri-urban environments are controlled by retention from their original geologic materials or are controlled by accumulation of inputs from local human development or ecosystem properties (climate and plant community). First, we hypothesized that soil and plant TMM concentrations would be highest for sedimentary and volcanic rocks due to their typically higher mafic mineral content and high surface area from inherited clay minerals. Second, we expected wetter, forested ecosystems would have higher TMM concentrations than dryer shrubland and desert ecosystems due to greater wet deposition and higher production of organic matter for sorption and retention. Lastly, we hypothesized that plants and soils in more urbanized, developed areas would have higher TMMs than less developed areas due to localized atmospheric deposition. This study is another step towards further separating human and natural processes driving TMM across the Southern California region.

2 Materials and methods

2.1 Peri-urban sampling sites across the Transverse and Peninsular ranges in Southern California

To determine the effect of geologic materials, climate, and urbanization on TMMs in plants and soils, a network of fifty-four sampling sites were sampled in January and June 2019 in this study. These sites span from coastal Los Angeles and Orange counties to inland highlands and deserts of San Bernardino and Riverside counties in Southern California (Fig. 1). Sites were chosen to capture the major rock types (igneous, metamorphic, sedimentary, volcanic) found across the region with replication. Further, sites were chosen to capture the variation in ecosystems, in which vegetation is dependent on local climate (described in Section 2.3). The sampling sites covered a wide range in mean annual temperatures (16.4 °C to 22.6 °C) and precipitation ranged from 65 mm/year in the inland hot desert to 1340 mm/year at the base of the Transverse Mountain range. Based on the Köppen climate classification system, the climate gradient ranged from Csb warm summer Mediterranean climate to BWh hot desert climate. Lastly, sites were peri-urban, to capture the impacts of land-use without being directly physically altered by human development. To avoid localized impacts, sampling sites were on foothills and terraces of the Transverse and Peninsular mountain ranges, with elevations ranging from 70 m up to

Fig. 1 Panel A shows the 54 sampling sites with their rock type across 30-year mean annual precipitation based upon data from PRISM. Panel B shows sampling sites and their ecosystems across 2016 National Land Cover Data from NLCD 2016
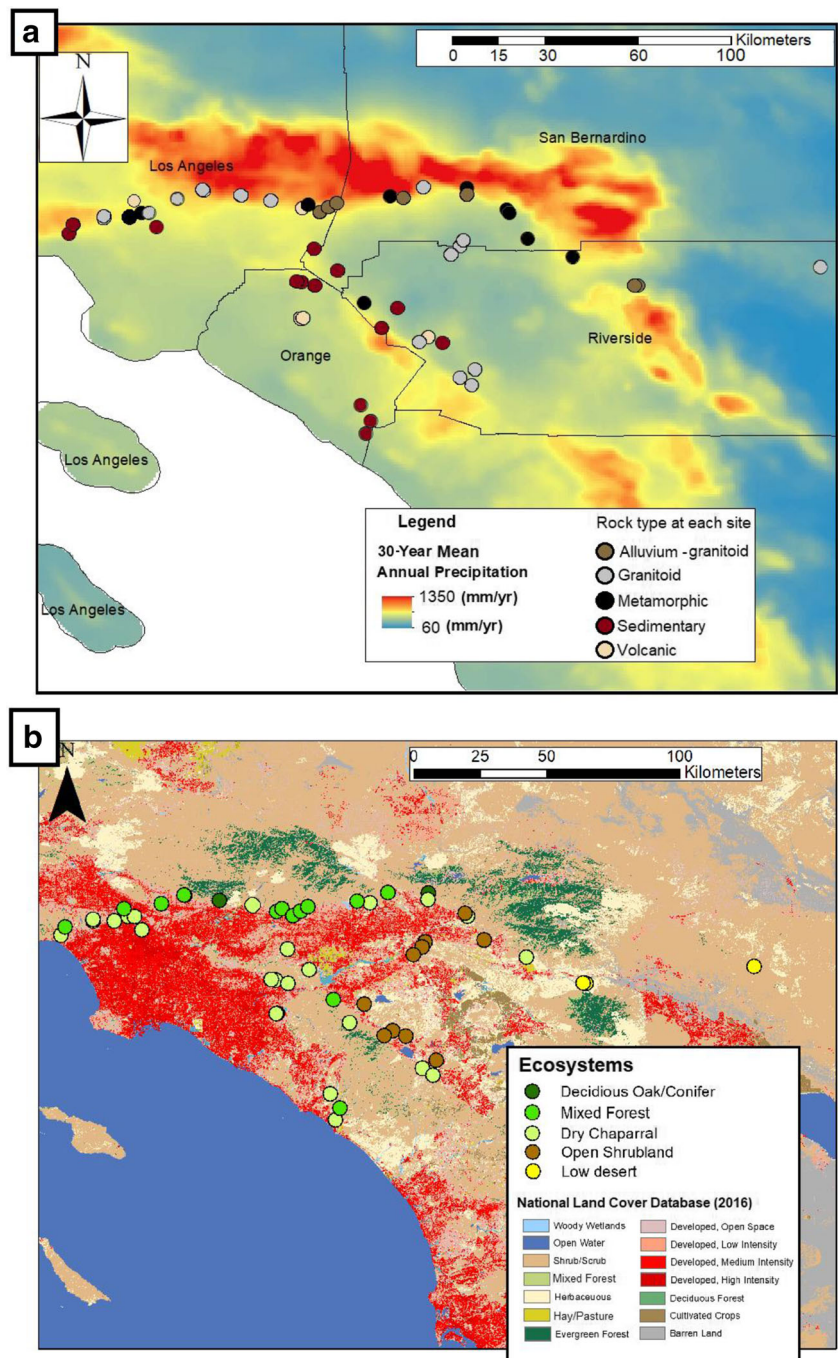
750 m above sea level (Supplemental Table 1). Sampling sites were chosen for their limited historical and current development and physical accessibility. Sites were at least 5 m from a road or impervious surface and did not show evidence of human alteration at the surface.

2.2 Bedrock and surficial geology classification for each site

The Geological Map of California (Jennings et al. 1977) was used as a guide to identify bedrock and surficial geology at

each site. Lithology/rock type was confirmed according to observations made in the field (grain size and texture, foliation, mineralogical composition). A broad range of sampling sites were needed to cover geologically diverse bedrock materials and some alluvial and sedimentary deposits were sparingly sampled but were avoided when possible. Sedimentary rocks sampled ($N = 18$ sites) included Miocene and Pliocene marine sediments in Orange County and Los Angeles Counties and Jurassic and Cretaceous marine sediments in Riverside and San Bernardino Counties (Supplemental Table 1). Granitic rocks sampled ($N = 15$ sites) included

Mesozoic granitic in Los Angeles, Riverside, and San Bernardino Counties. Metamorphic rocks samples ($N = 9$ sites) were Precambrian gneiss in Riverside and San Bernardino Counties (Supplemental Table 1). Alluvium ($N = 7$ sites) derived from Mesozoic granitic was also sampled in the foothills and outwash plains on the southern flanks of the San Bernardino mountains. Volcanic rocks ($N = 5$ sites) such as basalt flows were sampled across Los Angeles, Orange, and Riverside counties (Stanton and Alderson (2013).

2.3 Ecosystem classification for each site

Sampling sites were classified into ecosystem groups to examine covarying effect of vegetation and climate, which affects several aspects of TMM cycling from foliar fog-interception rates (e.g., Azevdeo and Morgan 1974), aboveground uptake and cycling (Gray 1983), and leaching rates (Yuan et al. 2011). Ecosystems at each sampling sites were classified with a modified Environmental Visualization (ENVI) vegetation-climate classification system devised by Anderson and Goulden (2011) for inland Southern California mountains. Precipitation and temperature for each site was interpolated from the 30-year average PRISM dataset (PRISM Climate Group, Oregon State University, data available at *https://prism.oregonstate.edu/*, 2020) and calculated to their ENVI vegetation class (Supplemental Table 1). In brief, oak forests ($N = 5$ sites) had the highest Mean Average Precipitation (MAP) 600–730 mm/year and mean average temperature (MAT) 10–13.5 °C. Mixed forest ($N = 10$ sites) had MAP 570–650 mm/year and MAT 12–13.6 °C also had high precipitation amounts. In between the wettest and driest sites were dry chaparral ($N = 23$ sites) which had MAP 420–540 mm/year and MAT 12.8–14.6 °C. The driest sites that could not support trees were open shrubland ($N = 13$ sites) had MAP 365–460 mm/year and MAT 13.5–15.6 °C and desert ($N = 3$ sites) had MAP 204–365 mm/year and MAT 15.2–19.3 °C. Vegetation at each sampling site was used to confirm the ecosystem or shift to a more correct ecosystem following vegetation communities' descriptions in Hanawalt and Whittaker (1976) and Barbour et al. (2007). Ecosystems at each site are shown in Fig. 1 and available in Supplemental Table 1.

2.4 Development intensity classification for each site

Each sampling site was classified by the highest level of urban development in close proximity using National Land Cover Database 2016 (Jin et al. 2019). To do this, a 2 km radius was extended around each site and the NLCD land-use was summed for each group. The urban development was then classified using NLCD groups of developed open space, developed low intensity, developed medium intensity, and developed high intensity. Each site was then classified by the

highest level of developed intensity that was > 5% cumulative area. This classification system follows closely to population density, with the high intensity development ($N = 8$ sites) largely in Los Angeles basin near commercial and industrial areas and large highways. Medium intensity development ($N = 13$ sites) occurred along the Peninsular range and eastern Los Angeles county as mixed commercial and industrial uses within Orange and western Riverside counties. Low intensity development ($N = 29$ sites) was primarily as single-family residential neighborhoods in the eastern part of the Peninsular range in Riverside and San Bernardino counties. Open space developments ($N = 4$ sites) occurred across all of the study areas and were typically situated near the Cleveland National Forest, San Bernardino National Forest, private conservation areas, or undeveloped steep slopes.

2.5 Rock, soil, and plant sampling

In the first sampling campaign, twenty-six of the fifty-four sampling sites were studied around the Peninsular mountain ranges in Orange County, southern San Bernardino County, and western Riverside County in January 2019, in the middle of the wet, cool season. Soil sampling sites were at shoulder or backslope geomorphic positions on hills, foothills, and terraces to study stable surfaces. Soils were exposed as road cuts, eroded gullies, or escarpments and collected by exposing a fresh surface using a tile spade to remove mixed and eroded surface soils. In this first set of sites, soils were collected by depth at 0 to ~10 cm and ~ 10 to ~20 cm using a clean stainless-steel trowel. Only one unweathered rock sample was collected at these set of sites. Unweathered rocks were defined as rocks showing very little to no signs of physical or chemical weathering and were determined in the field visually on a split sample. If unweathered bedrock was not identified in the profile, nearby outcrops of the target bedrock within 50 m were sampled instead. Unweathered bedrocks were collected from an unexposed portion of the bedrock outcrops with a rock hammer. Saprolite was collected at igneous and metamorphic sites but not collected at sites with sedimentary bedrock. Saprolite were classified as rocks showing definite signs mineral alteration (e.g., biotite to vermiculite), oxidation of Fe bearing minerals, and fissile nature with low structural integrity. Leaves and stems of the dominant native vegetation of the coastal sage scrub or dry chaparral at each site were collected. For shrubs, the previous growing season leaves were sampled and outer canopy leaves from the previous growing season were sampled on trees. Grasses and annual herbaceous plants were not sampled. Plants sampled at each site are available in Supplemental Table 1.

In the second sampling campaign, twenty-eight of the fifty-four sampling sites were sampled along the Transverse Mountain ranges (San Gabriel and San Bernardino) at the beginning of June of 2019, during the start of the dry, hot

season. In this second set of sites, soils were collected by set depth increments. Similar to the first set of sites, soil sampling sites were at shoulder or backslope geomorphic positions on hills, foothills, and terraces and were composed of exposed road cuts, gullies, or escarpments. Soils were sampled by exposing a fresh surface using a tile spade to remove mixed and eroded surface soils, depths were demarcated using a tape measure, and sampled from top to bottom using a stainless-steel trowel. To improve resolution of TMMs with depth, four soil samples with increments of 5 cm from 0 to 20 cm were taken instead of only two soil samples in the first sampling campaign. The difference in depth sampling was to better resolve surface accumulation of TMMs. Soils and rock samples were stored in labeled polyethylene bags. Rocks collected in the second set of sites were collected from outcrops and within the soil profile, and in some circumstances as float that matched the localized mapped geologic unit. Both unweathered rocks and saprolite were collected for all of the second sampling campaign sites. Similar as the first campaign, leaves from trees and shrubs from the previous grown season were collected.

The most common soils sampled were clay-rich Mollisols (Vertic Haploxerolls and Typic Argixerolls) and Alfisols (Mollic Haploxeralfs and Typic Haploxeralfs) on stable landforms (i.e., terraces, shoulder slopes). The second most common soils were Inceptisols (Typic Xerochrepts and Typic Haploxerepts), which are mixed due to burrowing animals as well as erosion (Weitkamp et al. 1996; Soil Survey Staff 2017). Entisols (Typic Xerofluvents and Typic Xerofluvents) on hill slopes, alluvial fans, and former fluvial deposits. Lastly, two sites had Vertisols (Aridic Haploxererts) (Supplemental Table 1). At each site, dominant native vegetation of the forest groves, coastal sage scrub, dry chaparral, and desert communities were sampled (Supplemental Table 1). The most common plants sampled were *Artemisia california* Less., *Encelia farinosa* A. Gray ex Torr., *Eriogonum* spp, *Malosma luarina* Nutt., and *Quercus agrifolia* Née. Grasses and annual herbaceous plants were not sampled due to their limited life histories and many are exotic species.

2.6 Sample preparation and analyses

All collected samples were oven dried and shipped from California to the University of Massachusetts Amherst. Soils and saprolite rock samples were then placed in an oven at 70 °C for 48 h to remove remaining moisture. Dried soil samples were then sieved using a hand sieve to < 2 mm to remove large organic debris (e.g., roots > 2 mm diameter) and rock fragments. For rock processing, 100 g of unweathered rock and saprolite were first crushed to < 0.5 cm in diameter using a tungsten mortar and pestle then were placed in a tungsten ring mill. Crushed rock samples were ran for at least 60 seconds

and sieved to < 0.05 mm. Powdered rock was collected from the ring mill, in between samples the ring mill and mortar/ pestle was washed and dried to prevent cross contamination of samples. Plant samples were oven dried at 70 °C for 24–48 hour prior to shipping to prevent decomposition. Plants were identified to genera, and species when possible. Foliage was not washed prior to preparation for analysis as roots are the dominant source of TMMs to plants (Clemens 2006). While washing can prevent dust from enriching samples, washing can also leach metals from the surface and within leaves (e.g., Tukey Jr 1970; Álvarez-Fernández et al. 2001). Leaves were separated from stems and petioles and ground in a stainless-steel coffee grinder.

2.7 Physicochemical soil property measurements

Soil pH was measured using a 2:5 soil−0.1 M $CaCl_2$ slurry. Slurries were shaken for 1 h using an Eberbach table shaker and filtered through a Whatman 40 filter. The pH of the supernatant extract was measured with a pH meter (8015 VWR). Loss on ignition (LOI) was used to estimate % soil organic matter (SOM) and measured by combusting a 4-g oven-dried subsample at 550 °C for 8 h. Every 20 samples included one blank and duplicate. Soil texture was determined using sedimentation column method. In brief, ~30 g of dried soil was weighed into 250 mL glass beaker. For organic rich soils, organic matter was removed using loss on ignition. Soil aggregates were dispersed using 100 mL of 1 M sodium hexametaphosphate (HMP) solution to the soil for at least 12 h. The HMP-soil slurry was washed out into a 1000 mL graduated cylinder with deionized (DI) water. We utilized a modified Bouyoucos hydrometer method with hydrometer readings at 60 s and 1.5 h after mixing, with readings taken to the closest 0.5 g L^{-1} (Gee and Bauder 1986).

2.8 Total soil, plant and rock digestions and analytical measurements

Plants, soils, and rocks were digested using two total digestion methods. Plant samples were thermally oxidized at 550 °C and the ashes were digested in sealed 50 mL polypropylene tubes using 5 mL of reverse aqua regia at 70 °C using a ThermoFisher hotplate. Every 20 samples included a blank, a standard reference material of NIST 1547 Certified Peach leaves, and a duplicate. Recoveries for digests were As (89%), Cd (89%), Cr (97%), Co (92%), Cu (83%), Ni (102%), Pb (97%), U (93%), V (83%), and Zn (103%) of the certified values for NIST SRM 1547 and duplicates had coefficient of variation < 8%. Rock and soil samples were digested using an HNO_3-HF total digestion method. In brief, a 50 mg homogeneous subsample of rock was placed in a 30 mL perfluoroalkoxy alkane (PFA) vial with 2.5 mL of 70% HNO_3 and 2.5 mL of 35% HF and heated to 170 °C for 48

h. The digest was dried to a moist paste and resuspended with 2 mL of HNO$_3$ and dried down again to a paste. The final paste was digested with 5 mL of 35% HNO$_3$ at 170 °C for 48 h and diluted to 50 mL with DI water. Diluted sample aliquots were then analyzed using an Agilent 7700x Inductively Coupled Plasma Mass Spectrometer (Agilent Technology, Santa Clara, California, USA). Recoveries for digests were As (81%), Cd (106%), Cr (105%), Co (96%), Cu (73%), Ni (81%), Pb (85%), U (106%), V (87%), and Zn (84%) of the certified values for NIST SRM 2711A. The TMM concentrations coefficient of variations (CV) between intra-sample duplicates was < 11 % and metal concentrations in the preparation blank samples were < 0.05 ng/g.

2.9 Data analyses

Descriptive statistics for soil trace metal concentrations, soil chemical properties, foliar trace metal concentrations were calculated in Matlab (Mathworks, Natick, MA, USA). To harmonize soil samples with varying depths between the two sampling campaigns, soils from the first sampling campaign for the 0 to ~10 cm depths were included in both the 0 to 5 cm depth interval and 5 to 10 cm depth interval and ~10 to ~20 were included as part of the 10 to 15 cm depth interval and 15 to 20 cm depth intervals. While this approach negatively affects the study design through double counting soils with depth, it more accurately conveys the soils material was homogenized across depths, avoids sample size bias with depth if samples were only counted for one depth, and allows for preserving the greater resolution in the second soil sampling campaign.

To estimate the amount of added TMMs, enrichment factors were calculated for each soil sample at all sampling sites using Eq. 1. Enrichment factors utilized Ti as an index element due to its insolubility and recalcitrance in soils and abundance in silicates compared to other common index elements like Zr and Nb.

$$Soil\ Metal\ EF = \frac{[Metal\ soil \div Ti\ soil]}{[Metal\ rock \div Ti\ rock]} \quad (1)$$

For interpretation of EF values, we leveraged the system developed by Chen et al. (2007) and leveraged by many other studies (e.g., Çevik et al. 2009), in which EF 0 to < 1 indicates net depletion with respect to background geologic materials, EF ~1 suggests TMMs were retention from bedrock or minimal addition of new TMM, EF >1 to 3 suggest net minor accumulation of TMMs, EF = 3 to 5 is moderate accumulation of added TMMs, EF = 5 to 10 is moderately severe accumulation of TMMs, and EF = 10 to >25 is severe enrichment.

The accumulation of TMMs in plant leaves was assessed using the bioaccumulation factor (BAF) using Eq. 2, which is synonymous with bioconcentration factor (BCF). In this

system, BAF values < 1.0 indicate concentrations in foliage are lower than soil concentrations, meaning limited bioaccumulation while BAF values > 1.0 indicate net bioaccumulation with respect to soil concentrations.

$$Foliar\ Metal\ BAF = \frac{[Metal\ Foliar]}{[Metal\ Soil]} \quad (2)$$

Due to the limited replication for some of the rock types (e.g., volcanic $N = 4$ sampling sites), ecosystems (e.g., desert $N = 3$ sampling sites), and development intensities (e.g., open space $N = 4$ sampling sites), non-parametric statistics were used compare across groups. We tested differences in soil TMM concentrations, TMM EFs, chemical properties (pH, SOM, %clay), and foliar trace metal concentrations across geologic materials, development intensity, and ecosystems using the non-parametric Kruskal-Wallis Test with post hoc Wilcoxon Rank Sum Tests. We further explored relationships among the TMMs, soil properties, and sampling site properties (ecosystems, development intensity) using a normalized principal component analysis. In the principal component analysis, data were normalized with their respective standard deviations to remove the weighted effect of data with larger numerical values. Lastly, Pearson linear regressions were used to determine linear relationships among soil TMM, plant TMM, and soil properties.

3 Results and discussion

3.1 Soil TMM concentrations at the peri-urban sites

At our sampling sites, soil TMM concentrations were at or below ranges reported in other urban or contaminated areas of the United States and globally. The soil TMM concentrations observed in our study were comparable to global noncontaminated soil concentrations in Adriano (2001) of As 0.1–30 mg/kg, Cd 0.01–2.0 mg/kg, Co 2–40 mg/kg, Cr 10–150 mg/kg, Cu 2–250 mg/kg, Ni 17–50 mg/kg, Pb 5–70 mg/kg, V 3–230 mg/kg, and Zn 1–900 mg/kg for. Our soil U concentrations were comparable to the lower end of uncontaminated soil U concentrations 0.4–96 mg/kg reported by Kabata-Pendias and Szteke (2015). Regionally, our soil TMM concentrations were comparable for Co, Cr, Ni, U, V, and Zn background soil concentrations but exceeded for As, Cd, Cu, and Pb background soil concentrations across California (Bradford et al. 1996). To generate an estimate for the background soil concentrations for the state of California, Bradford et al. (1996) quantified background concentrations in 50 benchmark soil series, which includes regions beyond Southern California. Bradford et al. (1996) reported mean background concentrations with standard deviations to be: As 3.5 ± 2.5 mg/kg, Cd 0.36 ± 0.31 mg/kg, Co

14.9 ± 9.2 mg/kg, Cr 122 ± 223 mg/kg, Cu 28.7 ± 19.3 mg/kg, Ni 57 ± 80 mg/kg, Pb 23.9 ± 13.8 mg/kg, U 4.7 ± 3.9 mg/kg, V 112 ± 53 mg/kg, and Zn 93 ± 90 mg/kg. These broad interpretations already demonstrate that some soil TMMs concentrations in our study are elevated.

Our results show that foothill soil TMM concentrations were elevated above regional background assessments, but did not attain severely elevated TMM concentrations like other urban and contaminated areas in the UK (e.g., Morgan and Morgan 1990; Zia et al. 2018), Spain (e.g., García-Sánchez et al. 2010), Italy (e.g., Imperato et al. 2003; Bretzel and Calderisi 2006; Cicchella et al. 2020), Norway (Steinnes 2001; Steinnes and Friedland 2006; Flem et al. 2018), and China (Li et al. 2014; Yang et al. 2018). Soil concentrations at all sites were below US EPA Ecological Soil Screening levels for mammals for As (46 mg/kg), Co (230 mg/kg), Ni (130 mg/kg), and V (280 mg/kg). However, soil concentrations at some sites exceeded interim final Ecological Soil Screening levels for mammals for Cd (0.36 mg/kg), Cr (34 mg/kg for Cr^{+3}), Cu (49 mg/kg), Pb (56 mg/kg), and Zn (79 mg/kg). Soil Cd and As concentrations in our study were comparable to Cd (0.5–1.5 mg/kg) and As (2.5–17 mg/kg) soil concentrations observed in urban soils in Los Angeles observed by Clarke et al. (2015). However, our average Pb concentrations were lower than their observed concentrations which exceeded 200 mg/kg. This is to be expected as their sampling locations were near the urban center of Los Angeles and have longer historical land-uses before 1940 (Clarke et al. 2015). Only six of our fifty-four sites had Pb concentrations exceeding the 200 mg/kg concentration and were distributed across Los Angeles, San Bernardino, and Orange Counties as opposed to aggregated in a specific area.

3.2 TMMs in rocks and soils across geologic materials

We investigated TMMs concentrations in rocks and soils to assess if TMM retention from their parent geologic sources drove higher TMM concentrations in their overlying soils. In other words, if unweathered rocks and saprolite of a specific rock type were associated with higher TMM concentrations in their soils. Our results show there were some significant differences in TMM concentrations among lithologies for unweathered rocks (Fig. 2). Unweathered rocks were generally comparable across lithologies for Cd, Cr, Cu, and Zn. For unweathered rock samples, As, Co, Ni, and V concentrations were greater in volcanic rocks than sedimentary rocks ($p <$ 0.05; Fig. 2). Unweathered metamorphic rock Pb concentrations were significantly higher than granitic rocks sampled (p < 0.05). On the other hand, saprolite (highly weathered, oxidized but still cohesive rock) TMM concentrations were comparable across lithologies for Cd, Cr, Cu, Pb, U, V, and Zn (p > 0.05; Fig. 2).

Soil concentrations of Cd, Cr, Co, Ni, U, V, and Zn were comparable or lower than their respective rock concentrations, suggesting minimal TMM accumulation and net losses during pedogenesis. We observed some significant differences in soil TMM concentrations across geologic materials. Soils derived from sedimentary rocks had significantly higher As and Cd than the other rock types (Fig. 2). Soils derived from volcanic rocks had higher Cr than granitic, and metamorphic rocks (Fig. 2). However, we did not observe a consistent control on TMM concentrations by geologic material, thus, other factors are likely more important for TMM accumulation or retention in soils than the bedrock or deposits they are derived from. Considering changes with depth, sedimentary As and Cd concentrations were higher in their soils than rock samples. Similarly, soil Cu and Pb concentrations were greater than their respective rock concentrations in the 0 to 5 cm depth, indicating net accumulation at the surface across all rock types. This surficial accumulation is discussed later in Section 3.3 regarding human development intensity.

To investigate if TMMs were retained during pedogenesis or added from exogeneous sources (such as pollution or dust), we utilized enrichment factors (EF) normalized to soil and bedrock Ti (see Eq. 1). In principle, Al, Fe, and Si are lost during pedogenesis but insoluble refractory elements such as Ti are retained. Here, we normalized TMM concentrations to Ti in soils and unweathered bedrock to determine net additions or losses. Our calculated EFs suggest depletion or limited additions for most elements, especially on granitic and metamorphic rocks (Table 1). Only Cr and Cu were consistently enriched across rock types. However, EF values were > 1 for soils on sedimentary and volcanic rocks, suggesting enrichment was likely affected by rock type. EF values were greater for sedimentary rocks for As, Cd, Cr, Pb, and V than granitic and metamorphic rock types (Table 1). EF values were greater for volcanic rocks for As, Cr, and Pb than granitic and metamorphic rock types (Table 1). We hypothesize that instead of rock TMM concentrations controlling TMM through retention in soils, the inheritance of clays and ability for organic matter accumulation may be important drivers. Sedimentary rocks (varying from argillite to slate in this study) have clay minerals and clay-sized particles which can promote sorption and organo-mineral complexes (Sarkar et al. 2018). Sedimentary-derived soils had nearly double the %clay and %LOI than granitic and metamorphic soils and had higher As, Cd, and Pb (Supplemental Figure 1). Thus, the higher surface areas on clay, charge sites on clays, and organic matter for complexation likely resulted in greater accumulation of added or retention of inherited TMMs (Saidy et al. 2013; Rasmussen et al. 2010). Volcanic rocks (primarily basalt in this study) have abundant Fe bearing minerals that can form Fe oxides for retaining TMMs (e.g., Weitkamp et al. 1996; Rasmussen et al. 2010). However, volcanic soils did not have significantly higher %clay or %LOI than the other rock types
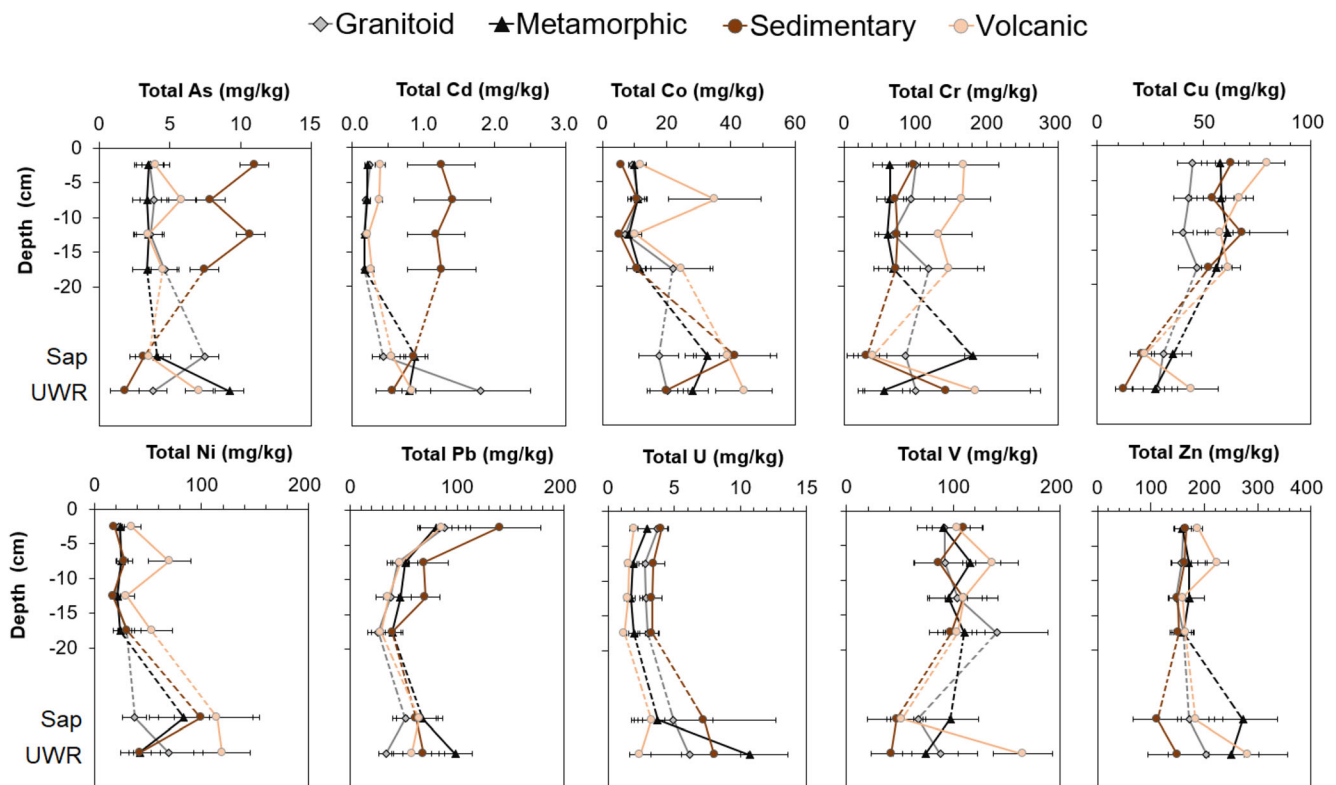
Fig. 2 Trace metal and metalloid concentrations in soil profiles and rock samples (Sap, saprolite; UWR, unweathered rock) among geologic materials across all sampling sites. Saprolite and unweathered rock samples were collected at much greater depths or from nearby outcrops. Error bars are ± 1 standard error across sampling sites

but we lack quantitative data on Fe oxide abundance across the soils. By examining soil TMM concentrations and EF with respect to geologic material, we observed that soils derived from volcanic and sedimentary rocks had some higher TMM concentrations than other geologic materials but consistent EF values indicating accumulation for most TMMs.

3.3 Soil TMM across ecosystems and land-use intensity

We assessed the variation in soil TMMs from the cumulative effect of plant community and climate by grouping sites by ecosystem and also grouping sites by development intensity as a comparison of localized pollution exposure. Soil As, Cd, Ni, U, and V concentrations did not vary significantly among ecosystem groups (Supplemental Figure 2). Soil Cu, Cr, and Zn concentrations were significantly lower for desert soils than the other ecosystems for most the soil depths. Soil Co, Cu, Cr, and Zn concentrations were higher for dry chaparral than open shrubland and mixed forest for some of the soil depths (Supplemental Figure 2). Soil Pb concentrations were greater for mixed forests in the 0 to 5 and 5 to 10 cm depths than the other ecosystems but not deeper soil depths (Supplemental Figure 2). Further, soil properties exhibited limited significant differences, with %LOI lowest at desert

and %clay significantly higher at open shrublands (Supplemental Figure 3). Due to the inconsistent nature of the few significant TMMs differences, these results suggest that plants communities and precipitation had limited control on soil TMM concentrations.

Soil TMM concentrations were investigated by land-use development intensity, which was examined as the highest level of urban development in 2 km radius at each site using National Land Cover Database 2016 (Jin et al. 2019). Soil As, Co, Cu, Ni, U, V, and Zn concentrations did not vary significantly among land-use development intensities (Supplemental Figure 4). However, high developed sites generally had higher soil Cd, Cr, Ni, and Pb concentrations than open developed areas. This result suggests that developed areas are increasing soil TMM concentrations and agree with findings of higher soil TMMs in urban areas of Los Angeles county by Clarke et al. (2015) and Hung et al. (2018). The enrichment of Cd, Cr, Ni, and Pb in and near large metropolitan urban areas appears to be common with additional examples of these TMMs elevated in urban soils of Nanjing, China (Ding and Hu 2014) and Sydney, Australia (Markus and McBratney (1996). As described by Charlesworth et al. (2011), municipal activities (e.g., automobiles and fuel combustion) and industrial activities (incineration, combustion) generate aerosols containing TMMs that can enrich soils and negatively impact air quality.

Table 1 Enrichment factors across rock types

	Depth (cm)	As	Cd	Co	Cr	Cu	Ni	Pb	U	V	Zn
Granitic	0 − 5	0.8	0.3	0.8	2.0	1.5	0.7	1.5	2.4	1.1	0.6
	5 − 10	0.8	0.5	0.8	2.0	1.2	0.6	1.3	1.7	1.6	0.7
	10 − 15	0.9	0.3	0.7	2.2	1.8	0.6	0.8	1.8	1.3	0.7
	15 − 20	0.9	0.5	0.7	1.5	1.2	0.5	0.9	2.0	1.3	0.7
Metamorphic	0 − 5	0.8	0.2	0.5	2.0	1.8	0.4	0.7	0.4	1.1	0.5
	5 − 10	0.8	0.2	0.5	1.9	1.6	0.4	0.6	0.3	1.3	0.5
	10 − 15	1.0	0.2	0.4	2.1	2.0	0.4	0.7	0.4	1.4	0.6
	15 − 20	0.8	0.2	0.5	2.0	1.5	0.4	0.5	0.4	1.3	0.5
Sedimentary	0 − 5	3.9	2.5	0.2	10.4	3.8	0.4	2.4	0.4	2.1	0.7
	5 − 10	1.7	2.3	0.3	3.7	1.7	0.5	1.3	0.6	2.0	0.9
	10 − 15	4.9	2.0	0.2	9.4	4.8	0.4	0.9	0.4	2.7	0.7
	15 − 20	2.1	2.5	0.3	4.4	1.7	0.5	0.7	0.5	2.5	0.8
Volcanic	0 − 5	1.9	0.6	0.5	8.3	3.2	0.5	4.6	1.1	0.8	0.7
	5 − 10	2.0	1.4	0.9	3.9	1.8	0.7	7.0	3.0	1.0	1.0
	10 − 15	2.1	0.4	0.6	6.7	2.7	0.6	2.6	1.3	1.2	0.7
	15 − 20	1.7	0.7	0.6	5.9	2.5	0.5	2.2	1.2	1.0	0.8

We re-assessed soil TMMs across ecosystems and development intensities groups using EF to determine relative addition or losses of TMMs with bedrock Ti-normalized ratios at each site. EF values were ≤ 1 for Co, Ni, U, Zn across all ecosystem groups, suggesting minimal retention or net depletion with respect to their original geologic composition (Fig. 3). EF values were between 0.7 to 3 for As, Cd, Cu, and V, demonstrating either minor accumulation or consistent retention across all ecosystems (Chen et al. 2007). Chromium had EF values above 3, indicating moderate accumulation across all ecosystems (Fig. 3). Lead had EF values above 1 for the two dried ecosystems, open shrublands and deserts. Mixed forests had higher As than other ecosystems, open shrublands had higher Cr and V than dry chaparral and oak forests (Fig. 3). These results suggest that ecosystems did not significantly affect the accumulation of TMMs in soils. Furthermore, the wettest sites did not have higher TMM concentrations, suggesting precipitation, foliar fog interception, and wet deposition may not be primary drivers of soil TMM accumulation. This is most evident for Pb, which was most enriched in the driest ecosystems. These results largely refute our hypothesis that plant communities and climate exert control on soil TMM concentrations.

When TMMs EFs were re-examined by development intensity groups, we observe a different story than with the ecosystem comparison. Open and Low development intensities had EF values < 3 for all TMMs and depths (Fig. 4). However, medium and high development intensities had EF values 1 to 9 for As, Cr, Cu, Pb, and V (Fig. 4). Further, medium and high development intensities had significantly higher EF values for As, Cr, and Pb than Open and Low development intensities. Our soil TMM EF results suggest

development intensity was an important factor controlling the addition of several TMMs in the peri-urban soils. Thus, TMM concentrations are not elevated to levels observed in contaminated or urban areas elsewhere, but we can observe humans have impacted these undeveloped foothills and terrace soils. These results partially support our hypothesis human activities have altered soil TMMs but highlight the contamination was generally not at levels considered harmful to plants as a growth media nor at elevated concentrations to harm animals or humans if ingested. Only one outlier site had Pb concentrations above the EPA limit of 400 mg/kg. The enrichment of Pb in the more human developed areas may be attributable to the combustion of leaded gasoline (Chow et al. 1994; Laxen and Harrison 1977; Nriagu 1978). Soil enrichment of Cr, Cu, and V may be due to smelting and metal refining, fuel combustion, waste disposal, or vehicle exhaust (Cloquet et al. 2006; Wang et al. 2015). Soil enrichment of As may be due to its use as a pesticide or long range transport of As rich dust from mines or agricultural areas (e.g., Manning and Goldberg 1997; Charlesworth et al. 2011; Kim et al. 2014). Lastly, these results highlight that peri-urban sites that exist on the periphery of urban developments can have their geochemistry altered by municipal and industrial activities (automobiles, incineration, fuel combustion) generate TMM-rich aerosols and agrees within findings in other metropolitan areas such as Beijing, China (Man-Zhi et al. 2006), Cosenza, Italy (Guagliardi et al. 2015), and Villavicencio, Colombia (Trujillo-González et al. 2018).

We observed that soil Cd, Co, Cr, Ni, V, and Zn concentrations were largely correlated with each other (Supplemental Table 2). The strongest correlations in soils were between Ni
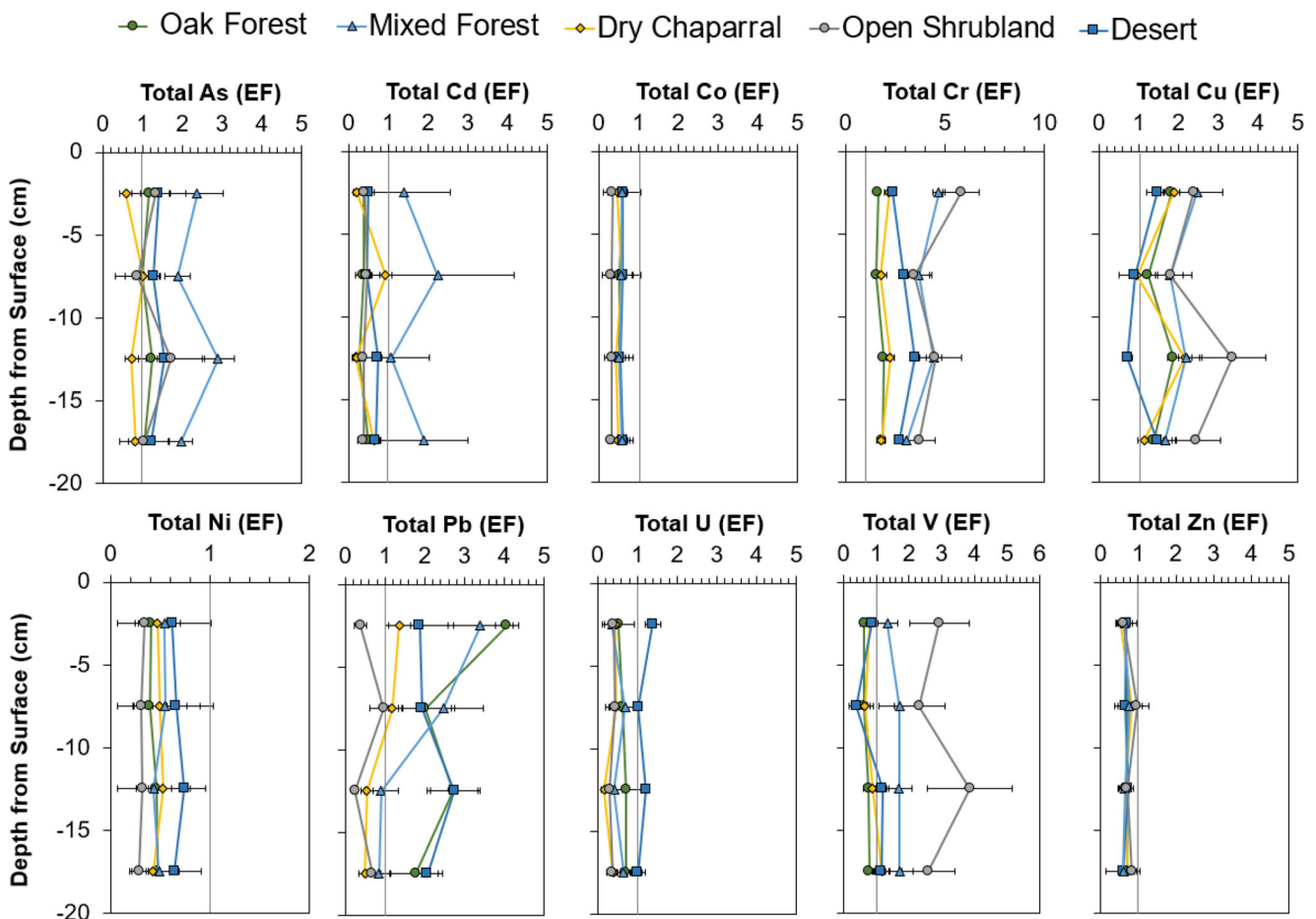
Fig. 3 Soil trace metal and metalloid enrichment factors (EF) across ecosystems groups across all sampling sites. Error bars are ± 1 standard error across sampling sites

and Co ($R > 0.7$) and Cu and Zn ($R > 0.8$), suggesting similar sourcing and biogeochemistry. No TMM was significantly correlated with soil pH. Soil LOI was positively correlated with Cd and Pb and soil clay content was positively correlated with Cd and LOI (Supplemental Table 2). This agrees with earlier finding that soils on sedimentary rocks had higher %LOI and %clay and had higher Cd and Pb concentrations. Organic matter and clay increase soil sorption capacity of TMMs by increasing surface area and charge sites for adsorption (Adriano 2001; Saidy et al. 2013; Sarkar et al. 2018). Examining our principal component analysis of soil TMM concentrations, we observe that only a small amount of the variance can be explained by the PC1 (22%) and PC2 (16%) (Fig. 5). However, PC1 shows that most of the TMMs (As, Co, Cr, Cu, Ni, V and Zn) have similar aligning variance, while only a portion of the variance is shared by soil properties such as LOI, pH, and %clay or site ecosystem or development intensity (Fig. 5). On the other hand, Pb, Cd, U share similar variance as the LOI and ecosystem and development intensity. We hypothesize that Cd and Pb were positively associated with land-use intensity and positively associated with precipitation likely from pollution, which is in agreement with Figs. 3 and 4. Uranium was also associated with development

intensity and precipitation but we interpret that U was most abundant at in the sparsely populated, desert sites (Fig. 3, Fig. 4, Supplemental Figure 2).

3.4 Foliar TMM concentrations across geologic materials

Across all sampling sites, overall foliar TMM concentrations were lower than foliar concentrations obtained by urban shrubs in Turkey (Banu Doganlar et al. 2012), urban shrubs in Tuscany Italy (Mori et al. 2015), and roadside shrubs in Nigeria (Ndiokwere 1984). Thus, our foliar concentrations do not explicitly show elevated TMM concentrations found in more polluted areas. One factor that affected foliar concentrations was the differences among species and genera (Table 2). *Adenostoma fasciculatum* and *Baccharis Salicifolia* had significantly lower foliar Cd concentrations than the other species (Table 2). *Adenostoma fasciculatum* had significantly lower foliar Cu concentrations than the other shrub and tree species (Table 2). Further, *Artemisia californica* and *Baccharis Salicifolia* had significantly lower Cr and V than all other shrubs and trees (Table 2).
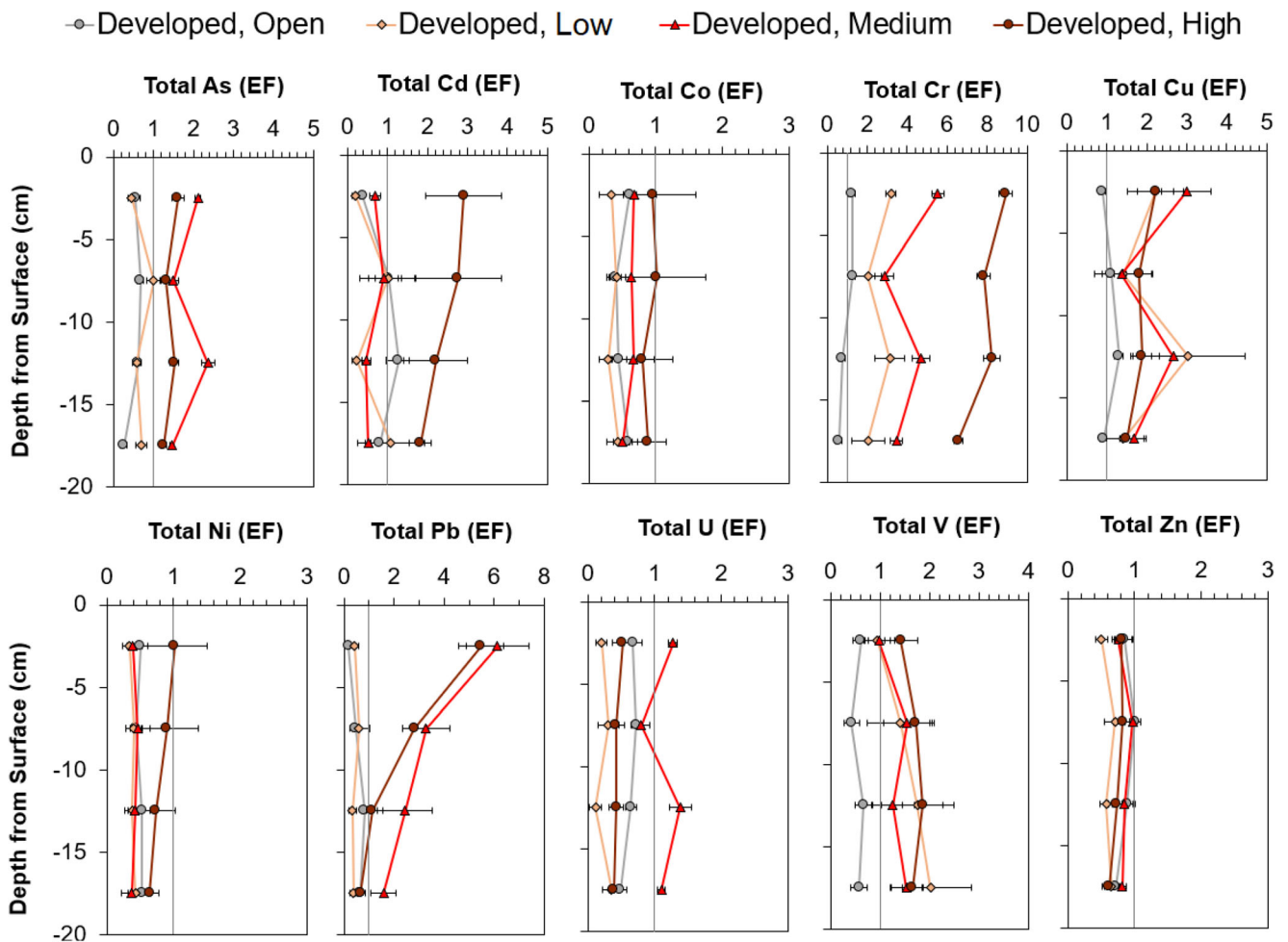
Fig. 4 Soil trace metal and metalloid enrichment factors (EF) across land-use intensity groups, which are based upon NLCD 2016 land-cover data in 2 km proximity of each sampling site. Error bars are ± 1 standard error across sampling sites

We investigated relationships among foliar TMMs concentrations with linear regressions. The strongest correlations in foliage were between Cr, U, and V ($R > 0.8$; Supplemental Table 3), which were all oxyanions and can have greater mobility than TMM cations. No foliar TMMs were significantly correlated with soil pH or LOI (Supplemental Table 3). Soil clay content was positively correlated with foliar Cd, Cr, Cu, Ni, Pb, U, and V concentrations, potentially indicating clay may retain and allow for greater TMM uptake by shrubs and trees. We observed that Cd, Co, Cr, Cu, Ni, Pb, U, V, and Zn were all largely correlated with each other (Supplemental Table 3). This suggests that dilution by specific plant materials (such as lignin and cellulose) likely influenced foliar TMM concentrations (e.g., Šućur et al. 2010; De Nicola et al. 2008). For example, lignin and cellulose can vary across plant species and plant materials, with the potential effect of diluting measured or perceived nutrient concentrations from higher concentrations of C than other elements (e.g., Hooper and Vitousek 1998).

Relationships between foliar TMM and soil TMM concentrations were investigated with linear regressions (Supplemental Table 4). Soil TMM concentrations at 10 to 15 cm depth as shrubs and some trees have shallow root systems for rapid uptake of precipitation (see Miller 1982). We observed that soil and plant TMM concentrations were not correlated (Supplemental Table 4), except for Cd, which was weakly, positively correlated ($R = 0.3$, $p < 0.05$). These results highlight that foliar and soil TMM concentrations are not connected. First, plants are able to actively discriminate for nutrients and against toxicants through casparian strip and suberin block diffusion into the vascular tissue (Ricachenevsky et al. 2018) and proteins limit intercellular transport of TMMs into the vascular tissue and to foliage (Clemens 2006; Page and Feller 2015).

3.5 Foliar TMM across geologic materials, ecosystems, and land-use intensities

In our first hypothesis, we expected significant differences across geologic materials. Foliar trace metal concentrations exhibited some differences but were largely similar. Foliar As and V were significantly higher at volcanic rock sampling sites compared to

Fig. 5 Soil TMM concentrations, soil properties, and sampling site groups (ecosystem and development intensity) variance explored through principal component analysis. Data were normalized with their respective standard deviation to remove the weighted effect of data with larger numerical values. PC1 explained 22% of the variance of the data while PC2 explained 16% of the variance in the data
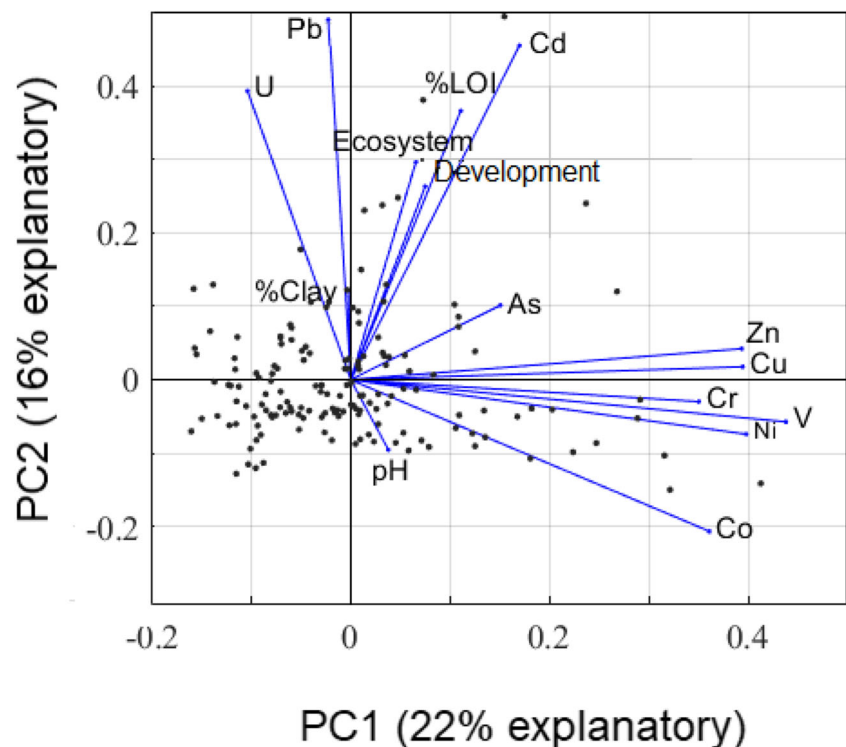
other rock types (Fig. 6). Foliar Cd and Ni were significantly higher at sedimentary rock sampling sites than other rock types (Fig. 6). Similar to EF in soils, we assessed the variation in foliar TMM concentrations across ecosystems and again by development intensity using bioaccumulation factors (BAF) instead of total concentrations to take into account variations in the soil. BAF values were all << 1.0 indicating that plants did not bioaccumulate any TMM).

We observed limited significant differences in BAF values across ecosystems. In foliar Cd, Cr, Cu, Pb, and V EF values, there were instances where oak forest, desert, or mixed forest had lowest BAF values than the other ecosystem groups ($p <$ 0.05; Fig. 7). Overall, there were no consistent trends in BAF values for TMMs across ecosystem groups and BAF values did not vary significantly among ecosystems for As, Co, Ni, U, and Zn ($p >$ 0.1; Fig. 7). TMM concentrations did not vary among ecosystem groups as well (Supplemental Table 5). This refutes our hypothesis that ecosystems parameters such as mean annual precipitation or type of vegetation present controlled foliar concentrations. BAF values were re-examined by development intensity at each site and observed that open development intensity had the highest BAF values for Cd, Co, Cr, Cu, Pb, U, V, and Zn, many of which were statistically higher ($p <$ 0.05; Fig. 8).

Foliar TMM concentrations were significantly lower for developed, open sites than developed high for only As. Conversely, developed open and light sites were significantly higher than developed, high sites for Cd, Co, Cr, Cu, Ni, and Zn (Supplemental Table 6). Our findings suggest that either plant

growth at medium and high intensity developments is higher than in open areas leading to diluted BAF values in the plants or plants in open areas have leaves that live longer than in more developed areas leading to higher TMM accumulation. For example, shrubs in drier, nutrient poor soils in the open areas outside of the city can have older leaves which can bioaccumulate TMMs over several seasons (e.g., Fernandez-Escobar et al. 1999). Further, the wetter areas near Los Angeles can have greater photosynthesis and growth rates, causing a carbon dilution effect (Jarrell and Beverly 1981; Miller 1982; Anderson and Goulden 2011). But these results highlight that localized TMM pollution may not drive foliar bioaccumulation of TMMs.

Lastly, we investigated the relationship among foliar TMM concentrations with soil properties and groups (ecosystems and development intensities). Our principal component analysis of foliar TMM concentrations with soil properties and site characteristics can explain 34% of the variance in PC1 alone (Fig. 9). In PC1, we observe that nearly all of the TMMs are closely related and vary with soil clay content. Considering PC2 which only explains 12% of the variance, ecosystems and development intensities variances were related to soil LOI, Cd, Ni, and soil clay variance, but not most TMM concentrations (Fig. 9). Our PCA suggests that presence or availability of soil TMM nor soil variables of pH and LOI drove TMM concentrations or bioaccumulation in the shrubs and trees. Further, foliar TMM bioaccumulation was not dependent on their ecosystems (plants present or annual precipitation) nor development intensity. Instead, plant uptake from soil and internal regulation of vascular tissue chemistry likely

Table 2 Average total foliar TMM concentrations across all sampling sites. Standard error is provided in parentheses

| Averages	T or S†	N	As mg/kg	Cd mg/kg	Co mg/kg	Cr mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	U mg/kg	V mg/kg	Zn mg/kg
Adenostoma fasciculatum	S	7	0.02 (0.00)	0.04 (0.01)	0.20 (0.06)	0.28 (0.10)	2.3 (0.3)	0.7 (0.1)	0.17 (0.08)	0.01 (0.00)	0.7 (0.2)	20 (3)
Artemisia californica	S	22	0.01 (0.00)	0.07 (0.02)	0.10 (0.02)	0.13 (0.01)	3.4 (0.5)	0.7 (0.1)	0.16 (0.01)	0.01 (0.00)	0.4 (0.0)	16 (1)
Baccharis salicifolia	S	7	0.02 (0.01)	0.02 (0.00)	0.09 (0.02)	0.14 (0.02)	3.8 (0.7)	0.6 (0.1)	0.22 (0.03)	0.01 (0.00)	0.4 (0.0)	13 (3)
Encelia farinosa	S	22	0.02 (0.00)	0.07 (0.02)	0.16 (0.03)	0.18 (0.02)	4.2 (1.2)	0.8 (0.1)	0.20 (0.02)	0.01 (0.00)	0.6 (0.1)	20 (3)
Eriogonum spp.	S	21	0.02 (0.00)	0.05 (0.02)	0.13 (0.03)	0.17 (0.03)	3.8 (0.6)	0.6 (0.1)	0.23 (0.03)	0.01 (0.00)	0.7 (0.1)	20 (4)
Heteromeles arbutifolia	T	11	0.02 (0.01)	0.25 (0.24)	0.17 (0.03)	0.35 (0.14)	4.4 (0.9)	0.6 (0.1)	0.42 (0.17)	0.02 (0.01)	1.0 (0.3)	31 (11)
Malosma laurina	T	17	0.01 (0.00)	0.38 (0.23)	0.18 (0.04)	0.32 (0.08)	5.6 (1.0)	1.4 (0.4)	0.38 (0.06)	0.01 (0.00)	1.3 (0.2)	25 (3)
Quercus agrifolia	T	22	0.01 (0.00)	0.12 (0.04)	0.11 (0.01)	0.20 (0.02)	3.7 (0.6)	0.9 (0.2)	0.29 (0.04)	0.01 (0.00)	1.1 (0.1)	17 (2)

† S, woody shrub; T, tree

controlled the foliar TMM concentrations, as roots can prevent uptake of TMMs (Ricachenevsky et al. 2018) and additional proteins limit TMM transport in the phloem to shoots and leaves (Page and Feller 2015).

3.6 Study limitations and research needs

While our study design of 54 sites aimed to separate the effects of geologic materials, ecosystems, and development intensities, there were unavoidable covariances that affected our results. Desert and dry shrubland ecosystems were only present in open areas away from the heavily urbanized areas near Los Angeles. This caused there to be zero sites with both desert or open shrubland ecosystems and high development intensity. Sedimentary and volcanic rock units sampled did span several ecosystems but were not as abundant for open shrublands and desert ecosystems as granitic and metamorphic rocks. Further, volcanic rock types were limited to only five sites. This is partly due to the geology of Southern California and the greater igneous plutons and metamorphic rocks in the transverse range. The other reason is due to constraints on access to property, geomorphic position limitations, and development onto of the volcanic rocks. The use of NLCD database as a proxy for development was useful for quantitatively approaching the extent of human development of land, but has drawbacks as point-source polluters can disproportionately affect the emissions of TMMs. In spite of these drawbacks, our approach is one of the few studies to link dimensions of geology and land-use on TMMs in the environment for this region.

Although many plant species were sampled with numerous replicates, variations in foliar TMM concentrations among shrub and tree species within each site were significant. Grouping together different shrubs and trees for each site may have decreased detection of differences among sites but sample sizes for individual plant species were not extensive enough to tease apart variation across development intensity or geologic materials. Further, the age of the plants would need to be quantified to better limit differences in age-influenced ecophysiology, such as spatial extent of root system, rooting depth, and aboveground biomass. Despite these limitations, our study shows that soils and foliage in the foothills across Southern California are not severely impacted as soils surrounding other metropolitan areas (e.g., New York City—Richardson et al. 2015) but have received minor to moderate levels of TMM contamination.

Future studies are needed to better characterize how TMMs are stored in soils along the gradient from the undisturbed soils in this study to the human-constructed technosols found in urban areas. The peri-urban and suburban soils of Southern California remain largely understudied with respect to trace elements. The management practices of home and landowners in peri-urban and suburban areas can collectively affect the generation and transport of TMMs in dust. Landowners can also force the introduction of exotic shrubs and trees. Future studies are needed
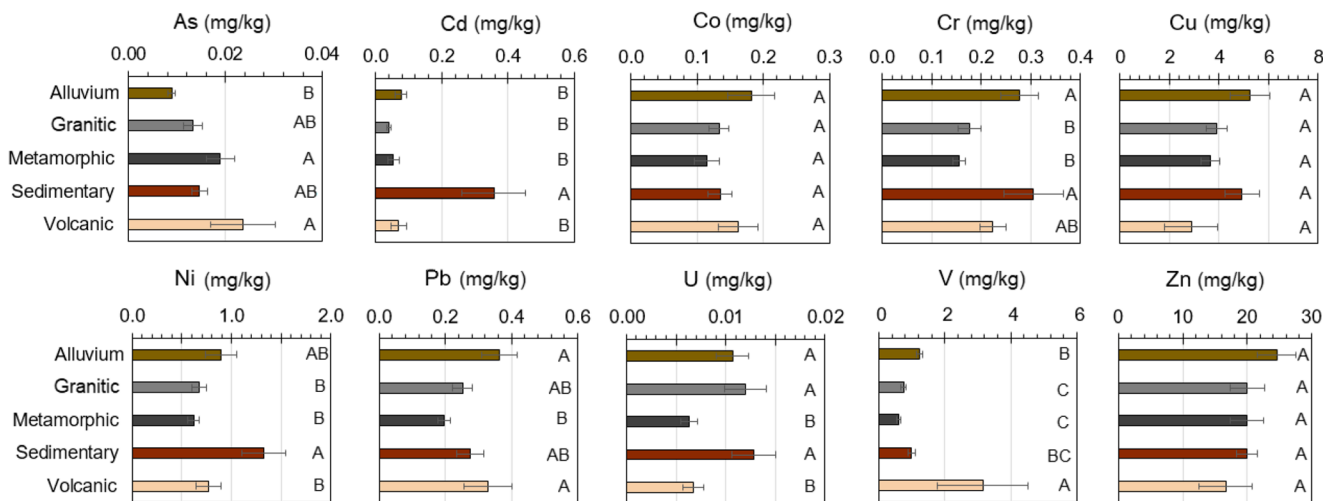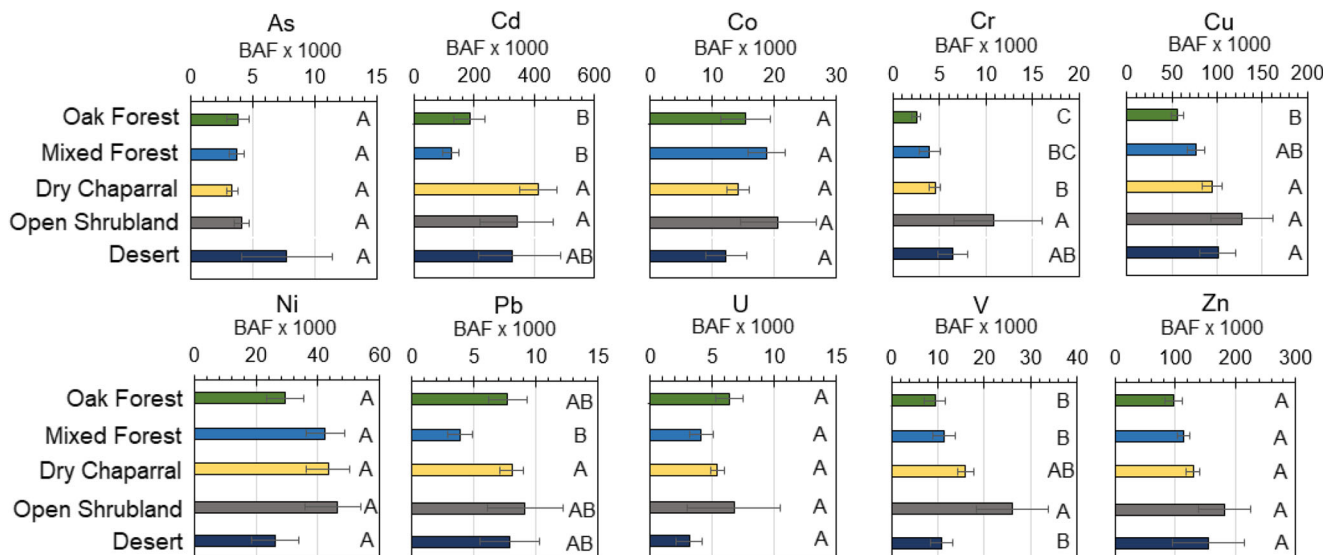
Fig. 6 Foliar trace metal and metalloid concentrations across geologic materials. Letters indicate grouping by significant differences ($p < 0.05$). Error bars are ± 1 standard error

to explore how TMM pollution impacts native versus introduced shrubs and trees. The majority of pollution work in Southern California centers around the massive issues of ozone, PM10, and nitrogen but our study has shown TMMs can be elevated in the region. Thus, further characterization is warranted to continue understanding the extent of human actions on TMMs and its environmental impact.

4 Conclusions

The results from this study show that soils and foliage across foothills of Southern California have not attained elevated TMM concentrations as observed in other urban

and contaminated sites. However, some soils have attained concentrations potentially toxic to plants or mammals according to the US EPA interim final soil screening guidelines but their toxicity is dependent on exposure route. Considering our original set of hypotheses, variations in soil TMM concentrations and EF values were partially explained by rock type present, as sedimentary rocks and to an extent volcanic rocks had overlying soils with elevated As, Cd, and Cr. Our results suggest that it may not inheritance of TMMs from sedimentary and volcanic rocks, but rather their clays and ability to stabilize organic matter may promote the accumulation of added TMMs. There were some variations among ecosystems (the combined effect of vegetation and climate), but development intensity

Fig. 7 Foliar trace metal and metalloid bioaccumulation factors (BAF) across ecosystems, which are based upon their mean annual precipitation and species composi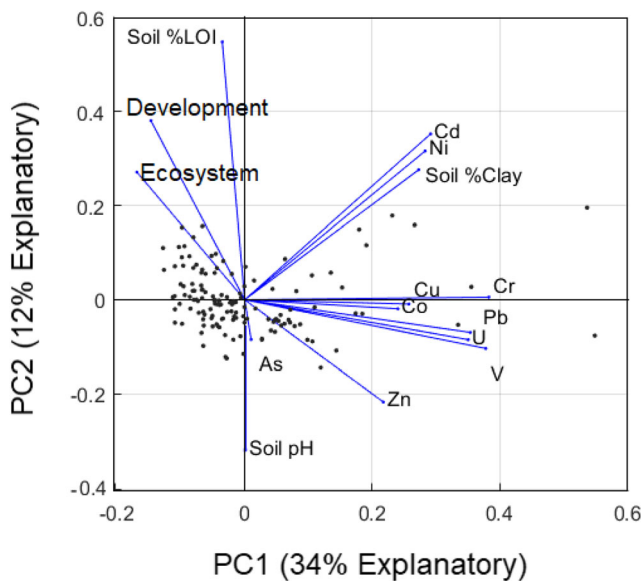tion. Note that BAF values are multiplied by 1000 because they were << 1. Letters indicate grouping by significant differences ($p < 0.05$). Error bars are ± 1 standard error
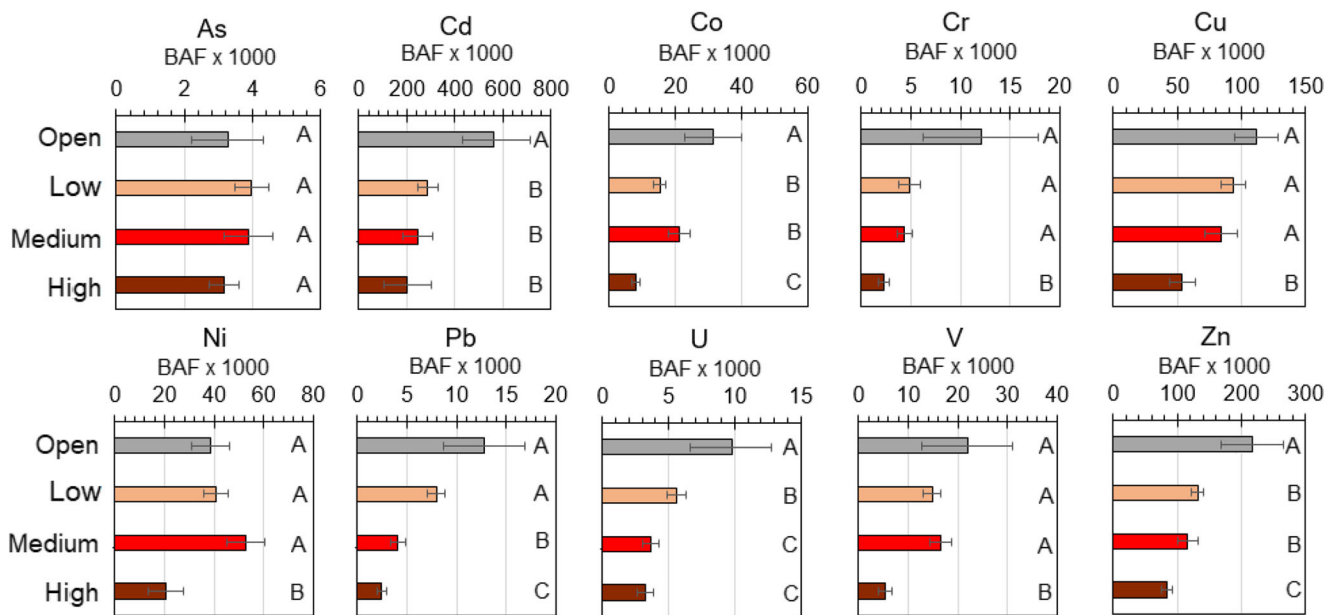
Fig. 8 Foliar trace metal and metalloid bioaccumulation factors across the four land-use development intensity, which are based upon NLCD 2016 land-cover data in 2 km proximity of each sampling site. Letters indicate grouping by significant differences ($p < 0.05$). Error bars are ± 1 standard error

demonstrated Cr, Cu, and Pb pollution has occurred. The variation in foliage TMM concentrations and BAF values were only partially explained by rock type and ecosystem,

Fig. 9 Foliar TMM concentrations, soil properties, and sampling site groups (ecosystem and development intensity) variance explored through principal component analysis. Data were normalized with their respective standard deviation to remove the weighted effect of data with larger numerical values. PC1 explained 34% of the variance of the data while PC2 explained 12% of the variance in the data

but development intensity and soil clay content explained the most variation. We hypothesize the TMM uptake regulation and plant ecophysiology were responsible for the variation in foliar TMM concentrations and BAF values rather than soils, geologic material, or ecosystems. Our study provides further evidence that lithology and human development are important factors shaping soil biogeochemistry of TMMs, which is commonly under characterized in ecological and environmental assessments.

Author contribution Trevor Mackowiak designed the experiment, conducted sampling, generated and interpreted data, generated maps with ArcGIS, and wrote the rough draft.

Mark Butler and Ivan Mischenko aided with experimental design, conducted sampling, generated, and interpreted data.

Justin Richardson came up with the study idea, helped with study design, conducted sampling, generated and interpreted data, generated maps with ArcGIS, and edited the final draft.

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