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Spatial distribution, mobility and bioavailability of arsenic, lead, copper and zinc in low polluted forest ecosystem in North-western Mexico

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T



- e integral forest fleatin response at low levels of soil pollution.
- A monitoring forest ecosystem level study.
- Identification of the main mineral phases containing As, Pb, Zn and Cu.
- Chemical mobility of As, Pb, Zn and Cu and measurements of potential Z.

A R T I C L E I N F O

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ABSTRACT

A geochemical-environmental mapping was carried for a low polluted forest in North-western Mexico (Santiago Papasquiaro mining area), as part of the North American forests accounting for environmental behavior of arsenic (As), lead (Pb), zinc (Zn) and copper (Cu) in soil and tree components (stem wood and aciculums). Spectroscopic and microscopic techniques along with standard protocols were used to determine the mineralogical phases containing these elements, and their corresponding spatial distributions in soil and forests and mobility. In soil, total As, Pb, Zn and Cu ranged from 4.9 to 98.3, 19.6 to 768.6, 19.6 to 407.1, and 1.6 to 63.8 mg kg⁻¹, respectively. Ultrafine particles (<5–10 μ m) of arsenopyrite and sphalerite (and complex Zn-Fe phase) were the main As and Zn-bearing phases determined by SEM-EDS, respectively. Complex Pb-Cu-Fe and Cu-O oxide-like phases were the only ones containing Pb and Cu, respectively. Mobility was low for Pb, Zn and Cu, whereas a significant mobility was assessed for As.







Forest stands Mobile fraction Santiago Papasquiaro Forest structure Concentrations vs. depth profiles suggested progressive accumulations of As, Pb, Zn and Cu in top soil. Total As, Pb, Zn and Cu in pine stem wood varied from 11.5 to 184.5, 98.9 to 7359.8, 3242.7 to 22197.3, 689.2 to 7179.6 μ g kg⁻¹, respectively. The respective concentrations in the pine needles ranged from 50 to 624.2, 100 to 16353.1, 120 to 46440.9 and 720 to 7200 μ g kg⁻¹, indicating an active bioaccumulation of As, Pb, Zn and Cu in the low-polluted forest.

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1. Introduction

Forest plays an important role to provide environmental services, such as protection against soil erosion and water reserve, biodiversity conservation and carbon sequestration. It also offers recreational areas representing important sources of incomes for their owners and local inhabitants (Suppen et al., 2006). Occurrence of potential hazardous elements (PHE) (i.e. As, Pb, and Zn, Cu in elevated concentrations) in forest ecosystems is a serious problem since contaminants are nondegradable and often bioavailable for uptake by vegetal species (i.e. pine, oaks), and toxic to soil biota (i.e. earthworms) (Farooq et al., 2016), resulting in an enhanced distribution of these contaminants and the decrease of vegetal growth and biomass production, among others (Hobbelen et al., 2006; Vamerali et al., 2010). These PHE are commonly introduced into forest ecosystems by anthropogenic activities, which include mining industry, arsenical-based wood treatments and airborne particle deposition (Suppen et al., 2006). Studies indicate that the single estimation of metal content is a poor indicator of health risks involved in these ecosystems due to their capacities to mitigate degradation (Niklińska et al., 2005; Zehetner et al., 2009), and because environmental mobility of PHE is typically involved. Although these studies are focused on the understanding of heavy metal behavior in soil and forest stands (i.e. tree wood, tree foliage) within severely polluted forest ecosystems (i.e. Pająk et al., 2017), they do not provide comprehensive information regarding the occurrences established during initial stages of detrimental processes (Richardson et al., 2015). Additionally, geochemical processes for cationic species (i.e. Pb^{2+} , Zn^{2+} , Cu^{2+}) are different from those identified for anionic compounds (i.e. As, HAsO₄²⁻); for instance, particular occurrences in pore-water soil solution drive to different adsorption, physicochemical mechanisms limiting (i.e. precipitation-dissolution, metal complexation) and/or enhancing elemental mobility, thus, affecting the fate gradient of PHE in soil and the corresponding bioaccumulation (up-taking) processes in vegetal species (i.e. pine trees) (Kabata-Pendias and Mukherjee, 2011; Selonen and Setälä, 2015). On the other hand, some of these PHE (i.e. Zn, Cu) are also essential for vegetal (i.e. enzyme cofactors) and animals life; however, harmful effects are observed when they are excessively bioaccumulated highlighting the importance of their biomonitoring and periodical measurement in the forest ecosystems (Allahabadi et al., 2017). There is also a lack of knowledge concerning the chemical behavior of PHE (i.e. mineralogy characterization), chemical mobility and the fate of bioaccumulation in low polluted forest ecosystems (i.e. transient stages) accounting for a comprehensive environmental behavior of PHE (Shparyk and Parpan, 2004; Jana et al., 2012; Richardson et al., 2015). This assessment is necessary in order to describe fundamental geoecological relationships between mineralogy and spatial distribution of PHE in soil and the forest stands (i.e. pine trunk wood, pine aciculum or needles), particularly for the forest ecosystems with low pollution levels.

The North-western region of Mexico covers about 860,000 ha of

(mostly managed) natural forest ecosystems, which are comprised of a mixture of species of genera pinus and Quercus with an irregular distribution of trees with diverse sizes. These forests include about 20 pine and 43 oak species, and some of them are common in forest ecosystems in Mexico, USA and Canada conforming a forest type known as "Ponderosa pine forest" (i.e. Pinus arizonica, P. strobiformis, P. leiophylla, and P. duranguensis, P. teocote, among others) (Corral-Rivas et al., 2014). In this region, some forest stands contain important mining areas whereby soil pollution and ecological deterioration are variable (Suppen et al., 2006). Indeed, a very few of them are visually low impacted by mining industry and they contain a wide number of tree species, and relatively, low pollution levels in soil (i.e. The Santiago Papasquiaro mining area) (Suppen et al., 2006; Corral-Rivas et al., 2014), thus, these areas offer suitable environmental conditions to determine intrinsic geoecological relationships above referred (i.e. an ecosystem monitoring level). It is worth mentioning that no spatial mapping of contaminated stem wood of pine, pine foliage and soil exists for simultaneous analysis of As, Pb, Zn and Cu for the North-western region of Mexico (and virtually for the rest of the North American forests) (Miranda et al., 2003; Maas et al., 2010). To address this gap, concentrations of As, Cu, Pb and Zn in pine stem wood, pine foliage and soil were mapped and a spatial analysis was conducted. Biomonitoring methods, which are based on the measurement of selected forest health responses (i.e. biomarkers) have been successfully used in different forest ecosystems to prevent and estimate adverse effects caused by environmental (urban) pollution in advanced stages (Domingos et al., 2015). In the same direction, a multivariate geostatistical approach can be linked to chemical and mineralogical analyses to determine if the distance to pollution sources (i.e. tailing impoundments), wind flow patterns, soil chemical properties, mineralogy, topography and the PHE content, among others, can affect the spatial distribution and mobility of As, Pb, Zn and Cu concentrations in soil and tree components (i.e. stem wood and foliage) (Lin, 2002). In this context, a systematic assessment can also provide detailed information of the transitory PHE loading rates (i.e. bioaccumulation), pine health responses to external stress (i.e. biomonitoring) and PHE distribution in soil and forest structure during incipient detrimental stages of the forest pollution (i.e. from low to heavy polluted ecosystems). Thus, the aim of this research was to account for the relationships established between soil concentrations of PHE and mineralogy regarding chemical mobility and bioavailability in the low polluted forests within the Santiago Papasquiaro mining area. For these purposes, chemical analyses are conducted utilizing standard protocols (i.e. USEPA, 2007) implemented with atomic emission spectroscopy with inductively coupled plasma (ICP-AES), atomic emission spectroscopy with microwave plasma generation (MP-AES), scanning electron microscopy coupled to electron dispersion spectroscopy (SEM-EDS/WDS), X-ray diffraction patters (XRD), measurements of zeta potential and other parameters of soil samples (i.e. pH, ORP, Conductivity). It is expected that this evaluation can contribute to generate better understanding of pollution processes in forests to improve environmental policies for sustainable forestry, in order to prevent further deterioration of forest ecosystems during advanced stages of pollution due to mining.

2. Materials and methods

2.1. Study site

The Santiago Papasquiaro mining area is located within the state of Durango at approximately 2000 km from Mexico City, in the North-western region of Mexico (Santiago Papasquiaro-Canelas) (Electronic Supplementary Material, ESM, Fig. S1), Geographical coordinates are longitude 106°19'00"W and latitude 25°02'00"N (~2450 m a.s.l.). At this site, a Pb-Zn-Ag-Au skarn ore mineral deposit has been exploited over the past ~25 years (Suppen et al., 2006; PMED, 2011). As a result of mining, two tailing impoundments (one active and the other is no longer in operation) have been settled in the area. The volume of mine waste stored in the impoundments is approximately $12.3 \times 10^3 \text{ m}^3$ and the content of PHE is unknown. In addition, forestry is an important economic activity in this region, which includes the production and commercialization of diverse nationally and internationally pine species, mainly Pinus durangensis Martínez, P. arizonica Engelm., P. leiophylla Sch. et Cham., P. engelmannii Carr., P. teocote Schl. et Cham., P. strobiformis Engelm and some species of the genus Quercus (Stephens and Gill, 2005; Corral-Rivas et al., 2014). Climate is temperate-subhumid with an average rainfall of 1500 mm H₂O, soil is mainly Lithosol and Cambisol and the average temperature ranges from 12 to 18 °C (INEGI, 2004).

2.2. Sample collection and preparation

Soil samples were collected from an area of approximately 100 km² during the dry season in September, 2014 (Fig. S2). A lowdensity driven sampling was undertaken in the forest soil area impacted by the dispersion of mining waste (i.e. soil adjacent to tailing impoundments): 120 surface soil samples and 60 pine stem wood and pine needles samples were collected from each sampling point (Fig. S2). A control sample was taken at approximately 10 km to the East where no contamination was ensured, which was considered as background for soil and pine forest stands. Two more samples from the tailing impoundments were collected for comparison and reproducibility purposes. The geographic coordinates at each sampled site were determined with a Garmin eTREX-10 global positioning system (GPS). The surface mapping system ArcGis9.3 (ESRI Software Inc., US) was used to map both sampling points and PHE concentrations. Soil samples were taken with a stainless steel scoop within the first 10 cm depth on a surface area *ca.* 1 m^2 , and stored in dark polyethylene bags. Likewise, two sampling points (i.e. 10 and 37, Fig. S2) were selected to further collection of soil samples as a function of depth (i.e. 5, 10, 15, 20, 25 and 30 cm) (Fig. S4), in order to estimate if PHE are continuously accumulating or they are dispersed. Soil samples were dried at room temperature during 1 week, and sieved at <2 mm for chemical and mineralogical characterizations (USEPA, 2007; DOF, 2007). Pine stem wood samples were collected using a Pressler increment borer at 1.3 m of height. Pine needles samples were handly collected at the same pine trees. All these samples were stored in dark polyethylene bags. Pine stem wood and needles samples were washed using abundantly deionized water (mili-Q, $18 \text{ M}\Omega \text{ cm}$) to remove traces of PHE deposited via airbone transportation and/or provoked by hand manipulation. These samples were dried at 80 °C overnight and pulverized (<80 µm) to homogenize samples for chemical analyses.

2.3. Mineralogical characterization and chemical analyses

The main mineralogical phases of soil samples were analyzed with X-ray diffraction (XRD; Rigaku DMAX 2200, $10-90^{\circ}$, $\Theta = 0.02^{\circ}$) operated at 40 kV and 30 mA with a Cu K α ($\lambda_{Cu K\alpha} = 0.154$ nm) excitation source. Minor mineralogical phases were also examined using scanning electron microscopy (SEM, Philips XL30, JEOL JSM 5610) coupled with EDS (EDAX DX460) and WDS (Quantax WDS) to perform local chemical analyses and establishing chemical mapping patterns, respectively. Soil samples were gold coated using an ion sputtering chamber JFC 1100 and the SEM images were collected using 50 nA and 20 keV (Si(Li) detector EDAX4 Dix). WDS patterns were obtained after 12 h of data collection. Additionally, a colloidal Dynamics Z probe analyzer™ was employed to determine Z potential of soil samples. To conduct these measurements, a total of 14.21 g of sample (<80 μ m) were added to 270 mL of water to prepare a mineral suspension with 5 wt % of solids. Automatic titration was performed with 0.1 M HCl and 0.1 M KOH as acidic and alkaline solutions (JT Baker), respectively. This suspension was stirred during 5 min at 150 rpm to determine the Z potential measurements, and stirring was maintained during data acquisition. Validation of these data was carried out using bentonite in 0.1 M HCl to obtain a typical electrophoretic curve as a function of pH (Rao et al., 2009). Experiments were carried out at least for duplicate under room temperature. Textural composition and additional parameters of soil samples (pH, oxidation-reduction potential (ORP), Conductivity) were determined according to national and international guidelines (ASTM, 2001; DOF, 2007). ORP measurements were obtained in-situ and within the first 10 min to avoid change in oxidizing conditions. Total organic carbon (TOC) and organic matter (OM) were determined using the well-known Walkley and Black dichromate oxidation method (Nelson and Sommers, 1982). While the cation exchange capacity (CEC) was determined with typical ammonium acetate method (Sumner and Miller, 1996).

2.4. Chemical analyses, elemental determination and mobility

To determine total As, Pb, Zn and Cu concentrations in soil, 0.5 g of soil sample was digested in acid media (60% HNO₃ v/v) for 30 min under 120 psi, using a Start D-Milestone unit microwave extraction system, in agreement with national and international standards (DOF, 2007; USEPA, 2007). These elements were also determined in pine stem wood and needles samples by digesting 0.2 g of homogenized sample using 9 mL of HNO₃ and 2 mL of H₂O₂ for 15 min under 200 °C. After digestion of samples, the extracted solutions were filtered using a Whatman filter paper (0.45 µm). A blank sample was utilized during these digestion procedures for each batch of 20 soil samples. Additionally, SRM 2710A soil reference material and SRM 1575A pine needles reference material (NIST, USA) were used for elemental control in soil and pine tree components (i.e. pine stem wood, pine needles), respectively, with quality analyzed for each 20-sample batch. Recovery values were better than 90% As, 97% Pb, 100% Zn and 93% Cu for SRM 2710A; whereas 85% As, 90% Pb, 95% Zn and 90% Cu were obtained for SRM 1575A. All solutions were prepared with analytical grade reagents (JT Baker) and deionized water (mili-Q, $18M\Omega$ cm). Digested samples were maintained under refrigeration (4°C) until chemical analyses. Chemical analyses were carried out during the first week after digestion of samples.

Mobility of a chemical specie trough soil is important to assess

its environmental fate; potential dissemination and partitioning of a PHE to the forest stands (i.e. bioaccumulation) when it is in contact with acid acetic that simulate forest soil activity (i.e. leaching). Mobile elemental concentrations were determined by leaching soil samples according to national and international criteria (DOF, 2007; USEPA, 2007; method 1311). Accordingly, 5 g of soil sample (<2.0 mm) were leached in HPDE bottles using 100 mL of leaching solution (1:20 soil: solution ratio) during 18 (+2) h under magnetic stirring (30 rpm) and ambient conditions $(25 \pm 2 \circ C)$. 1 L of leaching solution was prepared with deionized water (miliQ-water, $18 M\Omega cm$) adding subsequently 5.7 mL of glacial acid acetic and 67.5 mL of NaOH 0.1 M. Final pH of organic extractant leaching solution was 4.93 (±0.05). After leaching, solutions were recovered by vacuum filtration (Whatman filter, $0.45 \,\mu\text{m}$) and maintained under refrigeration (<4 °C) until chemical analyses. As guality control, SRM 2711 (NIST, USA) was used for each 20 sample-batch. Percent recovery values were better than 90% for all PHE.

A microwave plasma atomic emission spectrometer (Agilent, MP-AES-4100) containing a hydride generation system to enhance quantification of As was utilized to determine As, Pb, Zn and Cu in soil samples. The method to establish detection limits for each element was USEPA Method 200.7 (i.e. Cauduro and Ryan, 2017). Limit of detection (LOD) was 0.15 mg L⁻¹ for Pb, Zn and Cu. While this LOD was $10 \,\mu g \, L^{-1}$ for As. Additionally, limit of quantification (LOQ) was 0.2 mg L⁻¹ for Pb, Zn and Cu, while $20 \,\mu g L^{-1}$ was obtained for As. As quality control, SRM 1643D (NIST, USA) trace element in water standard reference material was used for each batch of 50 analyses. The percent recovery values were better than 95% for all PHE analyzed. An inductively coupled plasma atomic emission spectrometer (Agilent, ICP-AES-5100) was employed to determine As, Pb, Zn and Cu in stem wood of pine samples and pine needles. As quality control, TMDW-A certified water reference materials (High Purity Standards, Charleston, South Carolina, USA) was analyzed for each batch of 50 analyses. LOD was 3.7, 0.5, 1.9 and $0.3 \,\mu g \, L^{-1}$ for As, Cu, Pb and Zn, respectively. While LOQ was 6, 5, 5 and $1 \mu g L^{-1}$ for As, Cu, Pb and Zn, respectively. The corresponding percentages recoveries were 105, 94, 102 and 105% for As, Cu, Pb and Zn, respectively. Calibration of instruments, blank correction, matrix effects; samples manipulation and operating conditions were managed according to national and/or international guidelines (APHA, 1995; DOF, 2007).

2.5. Geostatistical analysis

A geostatistical analysis was conducted to determine the relationships arising between soil and the tree components for As, Pb, Zn and Cu (Lin, 2002; Maas et al., 2010). Such methods are commonly used for analyzing concentrations of heavy metals in soils due to mining: nevertheless, few studies have been carried out to assess the concentration of these pollutants in pine stem wood and needles, and none have determined all of them (Tembo et al., 2006; Allahabadi et al., 2017). For the spatial correlation analysis, semivariograms using the kriging interpolation technique were estimated to determine the spatial dependence of PHE concentrations in soil, pine stem wood and needles (ESM, Tables S2 to S5). Semivariograms accounted for the direction of their distributions in the study area, and several interpolation models (circular, spherical, exponential, and gaussian) were tested to identify the most accurate results considering the lowest root-mean-square for estimating the spatial correlation of the PHE concentrations. To this end, the software SPSS 24.0 and the spatial analysis tool of ArcGIS were utilized. In addition, Pearson correlations were estimated in order to determine the capacity of the different type of soils and tree species to bioaccumulate PHE concentrations.

3. Results and discussion

3.1. Mineralogical characterization of forest soil samples

Quartz (SiO₂), westite (Fe_{0.94}O), ramsdellite (MnO₂) and feldspars such as kyanite (Al₂SiO₅) were primary phases found in tailings samples analyzed by XRD (Fig. S3a). Soil samples showed similar minerals, in addition to aragonite (CaCO₃), calcium phosphate (Ca₃(PO₄)₂), and Mg-Al-silicate (MgAl₂Si₃O₁₀) (Figs. S3b and S3c). The main phases identified in surface soil sampled at the control site only included quartz and feldspars. PHEs contained in mineral phases (i.e. primary and/or secondary minerals) were not identified in soil samples probably due to the detection limit of XRD technique (3–5% w/w).

Fig. 1 depicts SEM images of soil samples collected from the study site (i.e. sampling points 10, 37, 41 and 48). Irregular grains of primary As-bearing and Zn-bearing sulfides in the soils such as arsenopyrite (FeAsS) (Fig. 1a) and sphalerite (ZnS) (Fig. 1b) were clearly observed as inclusions. Additionally, the presence of complex Pb-Cu-Fe bearing and Zn-Fe bearing phases were identified in these soils (Fig. 1c and e, respectively). A copper oxide-like phase was also identified in soil samples as the only Cu-bearing compound (Fig. 1d). The size of these PHE bearing phases was in general $<5-10 \mu m$, thus, mineral phases are potentially prone to chemical weathering and/or biological oxidation (i.e. alteration of edges, Fig. 1a) revealing that concentrations of PHE can be potentially enhanced through surface soil (Mitchell and Santamarina, 2005: Kögel-Knabner et al., 2008). The occurrence and dissemination of As, Pb, Zn and Cu in the forest soil matrix (i.e. adsorbed, complexed or precipitated) was further corroborated by SEM-WDS chemical mapping patterns (Fig. 1a', b', c' and d', respectively). These phases were not found in the control soil (Fig. 1h). However, free sub-micro structures of arsenopyrite, sphalerite and galena (PbS) were observed in tailings impoundments (Figs. 1f and 1g, respectively), suggesting that the presence of these elements in the study site was mainly due to soil impact.

According to Fig. 1, two main observations can be made: (1) Disposal of fine and/or ultrafine non-rimmed grains of arsenopyrite and sphalerite occurred in surface soil from tailing impoundments (i.e. Fig. 1f and g), and (2) the occurrence of the complex Pb-Cu-Febearing phase, CuO-like phase and Zn-Fe-bearing phase suggested that primary sulfides undergo potential weathering processes highlighting forest health risk factors in low-polluted forest ecosystems. Note that the identification of mineral phases containing these PHE (i.e. As, Pb, Zn and Cu, Fig. 1) can aid to identify more efficient extractants (i.e. EDTA, DSFA, DEHPA) or stabilizers, and helping to obtain better results in the application of phytoremediation procedures, where typically these mechanisms are applied without an integral understanding of the geochemical behavior of the PHE (i.e. mineralogy) in heavily polluted forest soil ecosystems (Bhargava et al., 2012; Jana et al., 2012; Ali et al., 2013).

3.2. Potential hazardous elements in surface soil

Fig. 2 shows the corresponding concentrations of As, Pb, Zn and Cu in order to visualize the distributions of PHE in the study site. Additionally, Fig. S4 describes total As, Pb, Zn and Cu concentrations vs. depth profiles (i.e. sampling points 10 and 37, Fig. S2), to infer potential accumulation of these elements as a function of depth position. Soil As and Pb concentrations above 260 mg kg⁻¹ and 800 mg kg⁻¹are typical trigger levels after which a polluted industrial soil (i.e. mining area) requires prompt attention to avoid human health risks, respectively (USEPA, 2008; DOF, 2007). However, minor soil concentrations of As and heavy metals are often required to provoke progressive forest health detriment (Table 2).



Fig. 1. SEM images to identify main minerals containing As, Pb, Zn and Cu in surface soil: (a) As-bearing phases, (b, c, e) Zn-bearing phases, (c) Pb-bearing phases, and (c, d) Cubearing phases, and tailing impoundment (f, g) samples. This figure also shows WDS chemical mapping images for further characterization of soil samples indicating the occurrence of As, Zn, Pb and Cu (a', b', c', d', respectively). Images for control samples are also presented (h). Aspy = Arsenopyrite (FeASS); Sph = Sphalerite (ZnS); Pb-Cu-Fe = complex secondary/tertiary mineral containing Pb and Cu, among others; CuO = cooper-like oxide phase; Quartz = SiO₂; Felds = Feldspars (i.e. Na(Si₃Al)O₈ and (Na, K)AlSi₃O₈). Identified phases were proposed under EDS basis (data, n = 10).

Note that 100 mg kg⁻¹ Pb and 10 mg kg⁻¹ As are typical background values whereby higher concentrations were indicative of soil pollution (Kabata-Pendias and Mukherjee, 2011). Accordingly, Fig. 2a and b exhibit respectively As and Pb concentrations in soil that represent a potential forest health risk (in the current state of pollution), instead of human health risk since soil concentrations are lower than that depicted by trigger concentration values. Indeed, As and Pb in soil concentrations can progressively accumulate in top soil until involve a serious forest health risk factor (Fig. 3a and b, respectively; Fig. S4) (i.e. Dovletyarova et al., 2018), as occur in several forest regions that require phytoremediation

strategies to reduce heavy soil pollution (Table 2) (Vamerali et al., 2010; Możdżeń et al., 2017). These strategies (i.e. phytoremediation) can be certainly improved by considering intrinsic geoecological PHE behavior, as indicated in Fig. 1.

In contrast to As and Pb, there are not available national and/or international criteria for estimating trigger levels of Zn and Cu representing a polluted industrial soil with potential human and/or forest health risks. However, typical Zn and Cu average background concentrations in soil above 125 and 24 mg kg⁻¹ can be attributed to pollution with potential toxicity to vegetal species and biota (i.e. background levels) (Kabata-Pendias and Mukherjee, 2011).



Fig. 2. Total As, Pb, Zn and Cu concentrations in surface soil and spatial trends in the study site (a, b, c, d, respectively). Corresponding range of concentrations were established according to geostatistical results.

Table 1

Total As, Pb, Zn and Cu concentrations ($\mu g kg^{-1} \pm S.D.$) determined in the forest stands for the forest stand structure in the study site. S.D. = deviation standard.

Pine specie	Average pine ti	runk wood concentra	ation (µg kg $^{-1}$)		Average pine aciculum concentration ($\mu g \ kg^{-1}$)						
	Pb	Zn	Cu	As	Pb	Zn	Cu	As			
P. arizonica	184.8 ± 12	15583.8 ± 37	2015.3 ± 11	30.06 ± 2	16353.1 ± 45	46438.1 ± 41	6078.2 ± 23	13.1 ± 2			
P. leiophylla	158.2 ± 4	8491.1 ± 36	1023.8 ± 8	19.72 ± 3	7479.6 ± 12	46440.9 ± 23	5264.5 ± 44	176.7 ± 4			
P. strombiformis	1119.5 ± 23	7294.5 ± 28	2068.1 ± 25	35.16 ± 4	2010.9 ± 23	22623.7 ± 65	3124.3 ± 23	221.9 ± 12			
P. teocote	1130.2 ± 24	10611.1 ± 31	2296.3 ± 22	24.61 ± 6	3372.2 ± 22	20246.4 ± 23	4177.3 ± 22	194.8 ± 10			
P. durangensis	363.3 ± 9	10741.8 ± 6	1252.1 ± 13	29.88 ± 8	2610.6 ± 39	22855.2 ± 45	3537.8 ± 18	173.1 ± 6			

Accordingly, Figs. 2c and 2d show respectively Zn and Cu concentrations found in soil that represent a potential forest health risk in most sampling points. Additionally, Figs. S4c and S4d reveal that Zn and Cu concentrations undergo scant depth-soil variations, respectively, whereby these PHE can further accumulate in top soil due to primary sulfides and/or secondary PHE-bearing phases scattering and alteration (Fig. 1) (Kabata-Pendias and Mukherjee, 2011). It has been demonstrated the importance of mechanisms for dissemination of PHE from mine waste to surface soil, which depend on size, mineralogy, reactivity and environmental conditions and processes, among others, and can include long range shooting areas in forest soil ecosystems (Hernandez et al., 2003; Zehetner et al., 2009; Jana et al., 2012, Table 2). PHE accumulate in surface organic layers and affect the biological activity of forest soils, whence a general trend is their progressive accumulation in top soil (Hernandez et al., 2003; Ettler et al., 2005; Bednářová et al., 2016; Martin et al., 2017; Chakraborty et al., 2017), in agreement with Fig. 2 and Fig. S4.

3.3. Potential hazardous elements in the forest stands

Figs. 3 and 4 show the corresponding total As, Pb, Zn and Cu concentrations in pine stem wood samples (Fig. 3a–d, respectively), and pine needles samples (Fig. 4a–d, respectively), in order to illustrate the spatial distribution trend observed in the forest stands structure of the studied stands. Additionally, Tables 1 and 2 depict total As, Pb, Zn and Cu concentrations for the different pine species sampled and metal contain in different pine (or tree) species, respectively. Most of pine samples contain As concentrations in stem wood and needles ranging from 11.4 to 185.51 and 50 to

Table 2				
Content of heavy metals in soil,	needles and roots,	determined in	contaminated are	eas.

Pinus	Needles/leav	ves (mg kg ⁻¹)			Soil (mg kg ⁻¹) R						kg^{-1}				Place	
specie	Cu	Zn	Pb	Cd	As	Cu	Zn	Pb	Cd	As	Cu	Zn	Pb	Cd	As		
Sylvestris	0.81 (±0,68)	1.29 (0.17)	4.31 (±1,6)	1.46 (±0.18)	_	7.0 (±2)	47.0 (±3)	35.0 (±4)	0.6 (±0.4)	_	11.0 (±1)	188.0 (±48)	28.0 (±5)	1.0 (±0.3)	_	Mining oil shale. Estonia. Soil pH 3–5.2. Napa et al., 2017	
Sylvestris	_	12.0-393.5	2.35 -256.49	0.02-6.15	-	_	_	_	_	-	_	_	_	~ ,	-	Power plant. Poland. Kandziora-Ciupa et al., 2016	
Sylvestris	5.1-15.5	152.5409.5	13.0 166.0	0.1-2.4	-	_	_	-	-	-	-	-	-	-	-	Mining and metallurgic plant Poland. Pajak et al., 2016	
Sylvestris	3.0-27.9	32.9–113.5	0.8-10.9	0.1-1.1	-	1.0-17.0	6.5-280.0	0.15-107.4	0.5-4.0	-	-	-	-	_	-	Mine soils. Poland. Pietrzykowski et al., 2014	
Sylvestris	2.17-18.20	4.09-44.47	0.32-0.64	0.02-0.15	-	3.6-6.7	14.1-29.8	10.9-20.4	0.4–0.5	-	-	-	_	-	-	Cement Plant. Soil pH 4.0–7.9. Estonia, Ots and Mandre, 2012	
Sylvestris	_	_	-	-	48.0 (±16)	1.1-64.0	8.0-158.0	_	-	101.0 852.0	-	-	-	-	63.0 (±22)	Mining site. Soil pH 2.4–3.9. Cantal, France. Jana et al., 2012.	
Eldarica	3.08 (±1.35)	42.57 (±2.7)	3.71 (±1.8)	0.62 (±0.09)	-	_	_	_	-	-	-	_	-	-	-	Urban area. Sabzevar, Iran. Allahabadi et al., 2017	
Eldarica		2.72	9.68	6.66								0.87	3.07	2.13		Urban area. Isfahan, Iran. Fatemitalab et al., 2016	
Nigra	(10.0 -200.0) 1000	(10.0–50.0) 1000) (1.0–47.0) 1000	(0.25 -0.63) 1000	(0.5–45.0) 1000) (10.0 -3600.0) 1000	(60.0 -420.0) 1000	(5.0 -450.0) 1000	(0.2–7.0) 1000	(10 -350.0) 1000	_	-	_	_	-	Copper smelter and the tailings ponds of open pit mines. Bor, Serbia. Kalinovic et al., 2016	
Nigra	1.6-7.1	_	0.7-3056	32.0-126.0	-	12.0-38.0	_	17.0-602.0	142.0 656.0	-	-	-	-	-	-	Cement Plant and Lead battery production Plant, Gaziantep, Turkey.	
Nigra	1.55-10.2	8.69-54.3	0.30-12.5	0.01-0.24	0.01-1.7	-	_	-	-	-	-	-	-	-	-	Industrial and agricultural activities. Canakkale, Turkey. Coskun, 2006	
Halepensis	1.7-3.5	28.0-130	4.0-20.0	0.1-0.4	0.3–2.8	42.0-112.0	264.0 10,715	398.0 11,854	6.0-27.0	18.0 657.0	-	-	-	-	-	Tailing of mine areas, pH 7–8. Cartagena, Spain. Párraga-Aguado et al., 2013	
Halepensis	(5.3–29.5) 1000	(10.0 -262.0) 1000	(11.0 -196.0) 1000	(0.12–3.5) 1000	_	(40.0) 1000 (±5)	(1210.0) 1000 (±60)	(160.0) 1000 (±16)	(10.0) 1000 (±0.6)	-	_	-	_	_	-	Industrial and residential área. Amman City, Jordan. Al-Alawi and Mandiwana, 2007.	
Massoniand	a 3.37–5.85	16.52 76.46	0.41 10.47	0.0-0.50	-	_	_	-	-	-	7.45 25.13	0.30 0.46	2.98 16.27	20.65 80.86	-	Report available fraction, Guangzhou, China. Sun et al., 2009	
Banksiana	3.1-28.6	10.4–66.4	0.5–5.9	0.05-0.31	-	7.0-866.0	15.0–95.0	8.0-202.0	0.02 -1.29	-	-	-	-	-	-	Mining and smelting of high ores. Ontario, Canada. Gratton et al., 2000	



Fig. 3. Total As, Pb, Zn and Cu concentrations in pine stem wood and spatial trends in the study site (a, b, c, d, respectively). Corresponding range of concentrations were established according to geostatistical results.

 $624.25 \,\mu g \, kg^{-1}$, respectively, whence *P. arizonica* obtain the highest pine stem wood concentrations (Table 1, Fig. 3a) and P. strobiformis involved the highest pine needles concentrations (Table 1). These concentrations were in general lower than those observed in surface soil (Fig. 2a), and therefore, the corresponding bioaccumulation factors (BAC) for soil-pine stem wood and soil-pine needles were in general lower than 1.0, suggesting that pine studied species are potential As bioaccumulators (Vamerali et al., 2010; Ali et al., 2013) (Table 2). Note that higher As concentrations occurred in pine needles samples compared to pine stem wood (Figs. 3a and 4a, respectively), indicating the potential translocation of this metalloid in the aerial pine tissues, whence As concentrations were reported between $400 \,\mu g \, kg^{-1}$ and 116 mg kg^{-1} in tree stem wood (i.e. Quercus pubescens), up to $480 \,\mu g \, kg^{-1}$ for pine needles (i.e. *Pinus sylvestris*), and up to 31 mg kg^{-1} in tree leaves (i.e. *Quercus pubescens*) involving in general BAC soil-tissue factors <1.0 (Jana et al., 2012; Salas-Luévano et al., 2017), among other tree pine species (Table 2).

Figs. 3b and 4b show total Pb concentrations in pine stem wood and pine needles samples, respectively. Most pine stem wood samples exhibited Pb concentrations ranging from 98.93 to 7359.83 μ g kg⁻¹, whereas those from 100 to 16353.11 μ g kg⁻¹ were identified in the pine needles samples. Similarly, all sampling points showed BAC soil to pine stem wood and BAC soil to pine needles lower than 1.0, indicating bioaccumulation of Pb in the forest stand structure, where the highest pine species accumulating this element is *P. strobiformis* (Table 1, Figs. 3b and 4b). The traslocation of Pb from pine stem wood to pine needles was suggested since pine needles concentrations were higher than those for pine stem wood (Figs. 3b and 4b, respectively). In contrast with As, pine needles can accumulate several hundreds of mg kg⁻¹ of Pb, which were even higher than those reported for other pine species (i.e. *P. sylvestris* L.) (Table 2), whereby pine needles were considered typical biomonitors for assessment of the local soil contamination even in low-polluted forest regions (Celik et al., 2005; Borgna et al., 2009; Pajak et al., 2017) (Table 2). These findings suggested that determining spatial distribution PHE in the forest stand structure was relevant to define the areas at risk, the factors that affect the As and Pb concentrations in the forest stand structure and the remediation efforts needed during different detrimental stages.

Figs. 3c and 4c, 3d and 4d exhibit total Zn and Cu concentrations in pine stem wood samples and pine needles samples, respectively. Although BAC soil to pine stem wood and/or BAC soil to pine needles samples was also <1.0, a higher potential for the progressive Zn and Cu bioaccumulation in pine stem wood, and particularly in pine foliage was measured regarding bioaccumulation of As and Pb (see above). The highest bioaccumulation was suggested for Cu indicating significant bioavailability of this element in low-polluted forest soil studied (i.e. <4000 µg kg⁻¹, Fig. 1c and d), which was similar to other forest stands behavior heavily polluted with Cu (i.e. *P. sylvestris*) (Możdżeń et al., 2017, Table 2). The highest bioaccumulation of Cu was determined for *P. teocote* in stem wood



Fig. 4. Total As, Pb, Zn and Cu concentrations in pine needles and spatial trends in the study site (a, b, c, d, respectively). Corresponding range of concentrations were established according to geostatistical results.

samples, while *P. arizonica* involved highest contain in needles samples (Table 1, Figs. 3d and 4d). Similarly, bioavailability of Zn was also prominent to obtain progressively BAC >1.0 in the study site, according to Figs. 3c and 4c (i.e. >23,220.48 μ g kg⁻¹). Zn and Pb pine needles concentrations $>100 \text{ mg kg}^{-1}$ and 30 mg kg^{-1} , respectively, are enough to promote growth inhibition and damage for tree development in heavily polluted forest ecosystems (Celik et al., 2005; Borgna et al., 2009; Kabata-Pendias and Mukherjee, 2011; Pajak et al., 2017), whereby the trend observed in Figs. 3c-d and 4c-d suggested rapid bioaccumulation of these elements in the study site. Moreover, Zn concentrations in pine needles were also observed >400 mg kg⁻¹ in forest soil, where Zn concentrations in soil were also low (i.e. $<50 \text{ mg kg}^{-1}$) (Dmuchowski et al., 2013, 2014, Table 2). The findings presented in Figs. 3 and 4 and Tables 1 and 2 illustrated the rapid bioaccumulation of As, Pb, Zn and Cu in low-polluted forest ecosystem helping to understand the fate of PHE loading in heavily polluted forest ecosystems and suggested that the PHE gradient observed in these conditions was established since the early stages of soil pollution (Table 2). The foliage of tree species from contaminated regions can be considered as monitor for bioaccumulation process in situations where significant amounts of PHE tend to accumulate on forest stands via airbone deposition (Celik et al., 2005). The findings presented in Fig. 4 and Table 1 provided better documentation of specific PHE loading rates (from soil to biomass) which can be useful to predict forest health sensitivity factors (i.e. monitoring ecosystem level) complementary to biomonitoring of airbone particles deposition on pine needles. Bioavailability of metals in trees (i.e. pines, oaks) and subsequent PHE accumulation in tree tissues can enormously vary according to the source of metal contamination and site conditions (Table 2). The findings presented in Table 1 (and Figs. 1–4) provided, in general, an incipient overview of the North American forest stand structure behavior during managements of PHE and towards a suitable ecological and bioaccumulation occurrences.

Heavy metals introduced into the bio-geochemical cycle can accumulate in the soil as well as in plant and animal tissues (Gruszecka and Wdowin, 2013; Ciarkowska et al., 2016). Zinc and Cu play an important role in biosynthesis and they are essential elements for all organisms, but their continuous uptakes can progressively drive to biota and forest health problems at relatively high levels in the range of tens and even hundreds of mg kg^{-1} (Table 2, Serbula et al., 2012). It is known that the content of heavy metals in pine needles and birch leaves can be high and the response of trees is variable depending on its individual vulnerability, the duration of exposure, the intensity of stress, and the form in which the metals are accessible, among others (Pajak et al., 2017). As introduced by Kabata-Pendias (2009), the content of trace elements (i.e. Zn, Pb) in needles of Scots pine should not exceed a certain maximum value ($Zn > 100 \text{ mg kg}^{-1}$, $Pb > 30 \text{ mg kg}^{-1}$), since this could result in the growth inhibition of tree. According to Figs. 2b-c, 3b-c and 4b-c, the bioaccumulation of Pb and Zn seems to be influenced by the exposition rate of trees to soil concentrations, and the corresponding up-taking response of trees, instead of distribution of these elements in high concentrated areas. Additionally, there are some points where Pb and Zn needles concentrations are 16353.1 and 46441 μ g kg⁻¹, respectively, whence chemical mobilities for these elements are negligible (Table 3). According to Dmuchowski and Sołtykiewicz (2007) and Dmuchowski et al. (2013), silver birch belongs to a group of species that may gather large amounts of Zn (hyper-accumulating plants): they can accumulate up to 400 mg kg⁻¹ Zn in the leaves originated from a low-contaminated soil, and up to 2000 mg kg⁻¹ in a case of significant pollution. In the present study, none of pine species present Zn and Pb concentrations beyond the normal range (i.e. P. scot) (Figs. 3 and 4, Table 1). These findings suggested that even when there is not a significant forest health risk at the present levels of Pb and Zn in pine needles (Table 1), the geospatial and mobile trends indicated the progressive (active) bioaccumulation process of these PHE, as observed for different pine specimens under varied soil pollution degree (Table 2). The corresponding high concentrated areas illustrated in Figs. 3 and 4 are then mostly driven by the pollution gradient of these contaminants and the accumulation capacity of pine specimens to manage concentrations of heavy metals, as they accumulates mainly in aerial tissues (i.e. needles) (Selonen and Setälä, 2015).

Most plant species can accumulate considerable amounts of Cu under natural and anthropogenic conditions (Padmavathiamma and Li, 2007; Serbula et al., 2012). The normal (typical) range of Cu concentrations in the plants (including pine and Oak species) is from 3 to 30 mg kg⁻¹ (Kabata-Pendias and Mukherjee, 2011), but its phytotoxic concentration range varies from ~30 to 100 mg kg⁻¹ (Padmavathiamma and Li, 2007). In the present study, the concentrations of Cu in the pine specimens were in safe range since stem wood and needles concentrations were up to 7179 and 7200 μ g kg⁻¹, respectively (Figs. 3d and 4d, Table 1). The high concentrated areas of Cu in pine stem wood and pine needles seem

to be mostly influenced by pine accumulating capacity since highest Cu values are heterogeneously distributed. Note that mineralogical observations indicated the occurrence of CuO-like compounds (Fig. 1d and d'). It was found that solubility of CuO (i.e. LogKps = 7.62) is considerably higher than other copper sulfides (i.e. LogKpsCuS = -22.27, LogKpsCu2S = -34.61, LogKps-CuFeS2 = -35.27) (Stumm and Morgan, 2012), indicating a higher available concentration of Cu to migrate or to be absorbed by plants and pine specimens in the case of the oxide (Możdżeń et al., 2017). Additionally, Figs. S4c and S4d suggested some migration of Zn (i.e. Zn-Fe complex bearing phase, Fig. 1e) and Cu, respectively, at larger depths of soil profile (i.e. concentration vs. depth profiles); which could be associated with the progressive formation of secondary phases with higher solubility as above mentioned. However, mechanic mobility is also possible enhancing continuous distribution of ultrafine Cu-O-like compounds throughout coarse soil particles in depth soil profiles. Similarly to Zn, Cu trend behavior suggested the continuous (i.e. sluggish) bioaccumulation in the forest stands of the study site, thus, increasing environmental health risks for the North-American forests. Regarding the As in the pine stem wood and pine needles, all pine specimens were negligible contaminated with As, whence the highest concentrations for pine stem wood and pine needles were 185.5 and 624.2 $\mu g\,kg^{-1}$, respectively (Figs. 3 and 4, Table 1). However, As concentrations in stem wood were similar to those found for other pine specimens within heavily polluted forests (i.e. 400 µg kg⁻¹, *Pinus sylvestris* L.) (Jana et al., 2012, Table 2). Additionally, Fig. 4a indicated a low bioaccumulation stage of this metalloid in the pine needles (Table 1). These findings suggested that pine specimens bioaccumulate As mainly in needles. instead of stem wood, and therefore, the progressive bioaccumulation of As in the study site would occur long-term (Table 2), since detrimental effects are identified in trees in the range from 27 to 2740 mg kg $^{-1}$ in needles (i.e. excess of metalloid) (Kabata-Pendias and Mukherjee, 2011). The most common forms of As available for plant uptake in the soil solutions are arsenate (AsV),

Table 3

Mobility and total concentrations of As, Pb, Zn and Cu in forest surface soil samples collected in the Santiago Papasquiaro mining area at the North-western region of Mexico. Sampling points were randomly selected to determine chemical mobility.

Sampling point	Total mo	obile concer	ntration (mg	kg^{-1})	Total soil	concentration	$(mg kg^{-1})$	Mobility (%)				
	As	Pb	Zn	Cu	As	Pb	Zn	Cu	As	Pb	Zn	Cu
2	21.3	1.7	0.6	0.2	43.7	349.5	90.8	7.9	48.8	0.4	0.6	2.6
4	13.6	2.4	0.4	0.1	23.0	297.2	118.8	4.7	59.1	0.8	0.3	3.1
6	9.5	2.1	0.1	0.1	15.9	264.8	117.6	4.2	59.5	0.8	0.1	3.1
10	12.6	1.6	0.3	0.1	63.1	269.2	30.9	5.8	19.9	0.9	1.1	1.8
12	22.4	1.6	0.9	0.1	27.3	349.5	63.9	7.2	82.1	0.4	1.4	0.7
13	16.3	1.7	0.1	0.1	21.9	310.9	43.1	5.6	74.5	0.5	0.4	1.4
14	11.9	0.9	1.6	0.11	22.3	154.7	84.8	9.1	51.3	0.6	1.9	1.2
29	9.7	1.1	0.6	0.2	18.1	243.3	149.1	8.7	54.1	0.4	0.4	2.2
30	23.2	2.1	0.4	0.2	32.8	211.2	245.6	14.9	70.8	0.9	0.1	1.5
32	79.4	2.3	1.1	0.1	95.2	768.9	984.6	55.1	83.4	0.3	0.1	0.1
34	33.3	1.6	0.2	0.1	57.8	112.8	132.5	18.1	57.7	1.4	0.1	0.4
35	4.9	2.3	0.7	0.1	62.7	100.1	175.1	13.2	7.9	2.2	0.4	0.6
36	29.6	0.5	0.3	0.1	65.4	128.3	123.4	7.2	45.3	0.4	0.2	1.1
37	23.6	0.7	0.5	0.1	74.6	254.2	139.5	10.5	31.6	0.2	0.4	1.1
38	8.1	1.2	0.3	0.1	63.8	233.1	198.3	17.5	12.6	0.5	0.1	0.5
39	26.8	1.5	0.7	0.1	91.8	243.3	407.1	13.5	29.2	0.6	0.2	0.8
42	10.5	1.3	0.4	0.1	40.7	98.5	128.1	4.9	25.7	1.3	0.3	2.1
48	9.5	1.1	0.8	0.1	19.7	26.5	92.5	5.8	48.4	4.2	0.8	2.1
52	14.3	1.1	0.2	0.1	20.8	251.5	118.3	8.7	68.8	0.4	0.2	1.1
57	9.1	0.9	0.1	0.1	58.3	157.5	108.3	7.4	15.6	0.6	0.2	1.2
62	7.2	0.9	0.7	0.1	69.4	443.2	98.5	8.3	10.4	0.2	0.7	0.9
65	1.4	2.9	14.9	0.2	24.2	295.5	344.8	24.1	6.1	0.1	4.3	1.1
69	0.9	1.6	1.8	0.1	40.28	71.68	58.74	4.68	2.2	2.2	3.1	2.5
84	13.1	2.1	2.6	0.2	48.47	629.83	20.32	32.61	26.8	0.3	12.8	0.6
91	31.6	1.5	0.3	0.1	37.43	154.63	75.82	8.38	84.6	0.9	0.5	1.1
Control	1.3	0.2	0.1	0.1	4.67	10.60	3.23	1.19	<1	<1	<1.0	<1

arsenite (AsIII) and methylated As (Monometilarsonic acid, MMA and dimetilarsonic acid, DMA). These forms exist simultaneously in organic soil enhancing the corresponding mobility of As (Farooq et al., 2016), in agreement with (Table 3). Accordingly, As bioavailability to plants (i.e. pine specimens) is governed by soil physical and chemical characteristics, environmental conditions, kinetics of bioaccumulation and modifications to the rhizsosphere soil, whence determining soil parameters (Table S1) are useful to infer potential conditions for As bioaccumulation or up-taking. The high concentrated areas of this metalloid in pine needles (Fig. 4a) were consistent with higher concentration in soils (Fig. 2a), whence the progressive accumulation of As is expected in long term and in a more predictable form regarding Pb, Zn and Cu, due to mobility of this element in surface soil (Table 1 and Table S1). Finally, the effects of heavy metals on soil organisms depend on exposure to concentrations that are available for up-take (Hobbelen et al., 2006). It is important to know which metal species can be taken up by organisms and to determine the relative importance of different up-take routes. Earthworms as metal pool indicators (i.e. Lumbricus rubellus, Aporrectodea caliginosa) can be exposed by direct dermal contact with heavy metals in the soil solution (i.e. pore water) or by ingestion of pore water, polluted food and/or soil particles whereby bioaccumulated PHE is typical indicative of metals bioavailability to plants (Hobbelen et al., 2006). In the present paper, there are high enough soil PHE concentrations heterogeneously distributed in surface soil (Fig. 2), together with significant As mobility and/or negligible Pb, Zn and Cu mobility (Table 1). These findings suggested the potential bioaccumulation of Pb. Zn and Cu but mainly for As in the study site, whereby the content of PHE in earthworms should be further determined in relation to total and available metal concentrations available in forest stands.

3.4. Mobility

Table 3 depicts results of the chemical mobilities for As, Pb, Zn and Cu in soil samples. Additionally, Table S1 exhibits soil parameters obtained during soil samples characterization. In general, a negligible/low mobility for Pb, Zn and Cu was assessed in all sampling points (i.e. up to 3.15%), thus, suggesting that dissemination of these elements was in general sluggish probably due to their great reactivity to form stable metal-organic complexes (Huang and Matzner, 2007). Quenea et al. (2009) conducted a study of soil characterization; whence results suggest that metals influence the dissolved organic matter dynamics highlighting metal speciation and occurrence of metal complexes in soil system. Additionally, Kumpiene et al. (2008) reported the decrease of trace elements leaching and their bioavailability by inducing various sorption processes: adsorption to mineral surfaces, formation of stable complexes with organic ligands, ion exchange, and surface precipitation as salts and co-precipitation contributing to reduce contaminant mobility in acidified soils. Our results indicated that the fate gradient for Pb, Zn and Cu was mainly limited by the progressive accumulation of these elements in top soil (Fig. 2 and Fig. S4), principally precipitated as salts and/or co-precipitated as secondary/tertiary compounds, among others (Fig. 1). In contrast, a significant As mobility was assessed in soil samples (i.e. up to 84.63%, Table 3), suggesting that this metalloid can be progressively enhanced by numerous factors, such as chemical mobility. Note that As can be as anionic specie (i.e. $HAsO_4^{2-}$) in interstitial porewater solution, thus, increasing its particular mobility in the soil system, in agreement with Table 3. The complex anions AsO_2^- , AsO₄³⁻, HAsO₄²⁻ and H₂AsO₃⁻ are the most common mobile forms of As, being sorbed (by typical soil constituents) at the pH range from 7 to 9 (Kabata-Pendias and Mukherjee, 2011). The significant mobility of As seems to be also associated to the more enhanced complexation of As in soils to mobile form (soluble) of As compounds (i.e. MMA, $pK_a = 4.1$) compared to organic complexes with Pb, Zn and Cu whose mobility was frequently restricted (Ettler et al., 2005; Huang and Matzner, 2007). These findings revealed that the chemical mobility of As was a further forest health risk factor (Tables 1 and 3), and probably this chemical behavior affected the forest stand structure in low and heavily polluted forest ecosystems. It is important to point out that there was a significant bioaccumulation trend of As, Pb, Zn and Cu in the study site, so despite the low mobility for Pb, Zn and Cu, as well as significant mobility for As; the findings presented here suggest that once PHEs were available in soil (i.e. sluggish or enhanced mobility) they can be progressively bioaccumulated by the forest structure resulting in the continuous increment of the BAC factors (Vamerali et al., 2010). The factors that determine the accumulation of heavy metals in soils, particularly, their solubility and bioaccessibility, include soil pH, organic substances, hydroxides, clay minerals, and interactions with other elements (i.e. Table S1). The harmful effect of heavy metals manifests itself when they occur in the environment at particular concentrations. As stated, Zn and Cu play a significant role as enzyme cofactors for plants (i.e. pinus specimens) (Możdżeń et al., 2017; Allahabadi et al., 2017). The findings presented in Table 3 and Figs. 3 and 4 clearly suggest the significant bioavailability of these PHE in the forest stands (i.e. bioaccumulation), in spite of their sluggish mobility and low pollution levels in soil.

According to pH values and Table S1, the soils of the study site were moderately oxidative with an average pH of 5.38. The ORP measurements supported the idea that primary or secondary phases (Fig. 1) can undergo continuous (i.e. sluggish) weathering processes; thus, leading to the progressive increase of the total PHE concentrations since leaching of released PHE (i.e. As) can occur faster than weathering process for inorganic (i.e. $HAsO_4^{2-}$) and organic-complexed forms (i.e. Monomethylarsonic acid, MMA) (Huang and Matzner, 2007). Additionally, soil parameters can be linked to the type of soil in the region (INEGI, 2004), the content of dissolved organic matter and textural properties (Table S1). Thus, they can enable or restrict additional mechanisms to retain or release PHE in soil constituents by favoring adsorption/desorption processes, promote further complexation of PHE with organic acids, and/or the progressive weathering of the primary/secondary phases containing PHE during pluvial stages and/or with the seasonal increment of the biological activity in forest soils (Doichinova et al., 2014; Dovletyarova et al., 2018). Fig. 5 depicts typical measurements of zeta potential for forest soil samples in aqueous solutions as a function of pH, exhibiting that the average zero point charge (PZC) is ~4.4. This indicates that the adsorption of inorganic cations, as well as complexes of these PHE with organic compounds was plausible below this value if net charge of organic complexes were virtually negative (Huang and Matzner, 2007). In the present pH condition (i.e. ~5.38) there was feasible low cationic adsorption capacity for soil constituents occurring only for inorganic and noncomplexed metal species. The complexation of heavy metals with organic matter (i.e. acids organic, EDTA) is fast, and therefore, a limited chemical mobility was expected in forest ecosystems (Ettler et al., 2005; Kabata-Pendias and Mukherjee, 2011), in agreement with Table 3. According to Aiken et al. (2011), heavy metals can be highly complexed by dissolved organic matter forming nanoparticles or colloids containing PHE with presumably negative net charge. Additionally, anionic species of As (i.e. HAsO₄²⁻) can enhance their mobilities in the study site (i.e. pore-water soil structure). According to Table S1 and Fig. 5, some potential adsorption of the PHE can be sluggish and progressively achieved since a decrease of pH can be driven by further acidification of soil (i.e. primary sulfides weathering, Fig. 1) (Bolan et al., 2003), thus



Fig. 5. Behavior of potential Z determinations for the soil samples collected in the study site. This figure indicates the potential of zero charge (PZC).

enhancing PHE adsorption. These findings suggest that Z potential, pH, and chemical speciation for As should be routinely evaluated (as same as metal pool indicators, i.e.earthworms) in order to obtain a complete picture of the physicochemical conditions that favors As and heavy metals mobilities in forest ecosystems.

3.5. Geostatistical approach

Tables S2 to S5 show the results obtained from the geostatistical analysis to assess the effect of elevation, distance to the sources of pollution and type of soil upon the distribution of PHE in soil and tree components. There was no available data on the exact wind patterns at the study site, which limited the inclusion of this parameter in the geostatistical analysis. However, it was considered that the main effect of this parameter is the dispersion of fine and ultrafine waste particles from the tailing dumps (Fig. 1f and g) to surface soil, thus, that a higher elevation could be correlated with a higher concentration of PHE in the study site. No significant correlation was found between elevation and the distribution of PHE in soil and the tree components suggesting that the PHE dissemination was sluggish or had negligible prevalence in the study site (Tables S2 to S5). In the case of the relationship between distribution of PHE and the distance from the tailing dumps, it was found that concentration of Pb and Zn increases if the distance is smaller, in agreement with previous findings (Fig. 2). However, this correlation was not very strong. For instance, Tembo et al. (2006) examined the spatial distribution of four heavy metals (Cd, Cu, Pb and Zn) in soils exposed to mining. Results identified that the distribution of metals decrease with distance from the mine and were consistent with the wind flow patterns that explained the precipitation of metals. Only a significant relationship between the concentrations of Cu in surface soil and that in the stem wood or pine needles samples was found, indicating that the distance positively affects the dissemination of Cu in the forest stand structure (Tables S2 to S5), as indicated by Figs. 2d, 3d and 4d. Regarding the capacity of the different pine species to bioaccumulate PHE in the pine stem wood, the P. duranguensis was more prone to

bioaccumulate simultaneous concentrations of Zn and Cu, in agreement with experimental results (Figs. 3c and 3d, Table S3). Nonetheless, the greatest capacity to bioaccumulate Zn in pine stem wood was only shown for *P. strobiformis* (Table S3). In the case of PHE bioassimilation in the pine needles of the different species sampled, *P. leiophylla* and *P. arizonica* tend to enhance Zn; however, *P. arizonica* was the most prone to bioaccumulate Pb (Table S4). The greatest bioaccumulation of Pb in *P. arizonica* was then not due to its proximity to the tailing impoundments but rather to its physiological characteristics since the most predominant species located at a shorter distance from the tailings were *P. durangensis* and *P. strobiformis*.

The presence of synergies in the bioaccumulation of some PHE in surface soil, pine stem wood and pine needles samples was further assessed. In the case of soil samples there was a positive correlation between Pb and As, however, was not very strong and only suggested a progressive trend (Tables S2 and S5), which was consistent with our experimental findings (Figs. 2-4). This suggests that higher concentrations of As will occur with higher concentrations of Pb. This same behavior was identified in the case of Zn with respect to Cu. Unlike the synergies presented between the PHE in the soil for pine stem wood, it was identified that there was a synergy between Pb and Cu (Tables S3 and S5). Therefore, higher concentrations of Pb in the pine stands should be accompanied by higher concentrations of Cu. This same behavior occurred in the case of pine needles, where higher concentrations of Pb usually indicated higher concentrations not only of Cu but also of Zn, according to its observed positive relationship (Tables S4 and S5). However, these behaviors seem to be associated mainly to physiological properties of pine species instead of environmental factors. The geostatistical approach highlights a series of non-obvious mechanisms that can help to complement the geoecological analysis of the PHE pollutant gradient in surface soil and the forest structure of the study area (i.e. North-western Mexico), which may be similar to other low or heavily polluted forest regions, particularly for the North-American forests (i.e. USA, Canada, Mexico).

The results herein presented showed a general starting point to account for specific forest behavior at low (incipient) pollution levels of PHE in pine wood and needles, to better understand their pollution gradients. These findings highlight the necessity of a deeper assessment of all stages of PHE bioaccumulation in laboratory tests (i.e. pine, oak) in forthcoming studies, to identify potential indigenous tree species for bioremediation of the polluted soils (i.e. P. arizonica, P. duranguensis, P. teocote, P. leiophylla and P. strombiformis), and for a better determination of forest health and biota responses (i.e. earthworms sensitivity). It is also necessary to carry out a systematic study where the capacity of bioaccumulation of PHE by growth rings in pine specimens is evaluated, since this study would reveal the sensitivity of the pine species to the PHE bioaccumulation and therefore, it would allow a better understanding of the evolution of the BAC in all stages of forest pollution.

4. Conclusions

The As, Pb, Zn and Cu spatial distributions were comprehensively assessed in soil and the forest stands within low-polluted forest ecosystem located at the North-western region of Mexico (i.e. Santiago Papasquiaro, Durango). SEM-EDS/WDS, XRD, MP-AES, ICP-AES, Z-potential measurements and standard protocols were synergistically applied to the analysis of surface soil and forest stands. Mineralogy of As, Pb, Zn and Cu-bearing phases are dominated by occurrence of ultrafine ($<5-10 \mu m$) grain particles of arsenopyrite, sphalerite (and complex Zn-Fe phase), complex Cu-Fe-Pb phases and Cu-O like phases, respectively, revealing the solid phases that control chemical mobility and translocation of the forest structure. The spatial distributions of As, Pb, Zn and Cu in soil did not depend on elevation, being the concentrations of Pb and Zn the highest ones. While those of As and Cu were the lowest, suggesting a potential risk to forest health at some points of the study site and by concentration vs. depth soil profiles. In all cases, the bioaccumulation factors of As, Pb, Zn and Cu were <1.0, indicating the progressive bioaccumulation of these elements, especially for Cu and Zn in pine needles. The highest bioavailable concentrations in the pine stem wood samples correspond to Zn, Pb and Cu in P. teocote and almost at the same level P. duranguensis; P. teocote also exhibited the highest concentrations for Zn, Pb and Cu. Concerning As, all the forest elements showed similar bioaccumulation capacity. Negligible and/or low mobility was assessed for Pb, Zn and Cu (<3.5%), while significant mobility was observed for As (<85%). A rapid bioaccumulation was also found for Cu, Pb, Zn and As in the forest stands regardless their sluggish and/or enhanced mobility. All findings herein presented contribute to better describe geochemical-environmental behavior of As, Pb, Zn and Cu in lowpolluted forest ecosystems, which may be similar to other forests in North America.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.07.004.

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