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Diffusive gradients in thin films, Rhizon soil moisture samplers, and indicator plants to predict the bioavailabilities of potentially toxic elements in contaminated technosols

Bashar Qasim^{1,2}  • Mikael Motelica-Heino¹ • Emmanuel Joussein³ • Marilyne Soubrand³ • Arnaud Gauthier⁴

Abstract The phytoavailabilities and potential remobilization of potentially toxic elements (PTEs) such as Zn, Pb, Cd, As, and Sb were assessed in contaminated technosols from former mining and smelting sites. The PTE concentrations in soil pore water (SPW) and diffusive gradients in thin films (DGT)-measured concentration (C_{DGT}) methods were used to assess the bioavailabilities of PTE and their remobilization in this study. Together with classical Chelex-100 DGT probes to measure Zn, Cd, and Pb, novel ferrihydrite-backed DGT were used for As and Sb measurements alongside with Rhizon soil moisture sampler method for SPW sampling. To assess the phytoavailabilities of PTE, a germination test with dwarf beans as a plant indicator was used for this purpose. Dwarf bean primary leaves showed high Zn concentrations in contrast to Pb and Cd which showed low phytoavailabilities. Despite As and Sb are present in high concentrations in the mine tailings, their phytoavailabilities indicate very low bioavailabilities. The amounts of Zn, Pb, Cd, As, and Sb extracted with DGT devices correlated well with the total dissolved

PTE concentrations in the SPW. The highest R values were observed for Zn, followed by Cd and Pb, indicating the ability of the soil to sustain SPW concentrations, which decreased in that order. Good correlations were also observed between each of dissolved PTE concentrations in SPW, DGT-measured PTE concentrations (C_{DGT}), and the accumulation of PTE in dwarf bean primary leaves. It could be concluded that the use of Rhizon soil moisture samplers and DGT methods may be considered to be a good methods to predict the PTE bioavailabilities in contaminated technosols.

Keywords DGT · Soil pore water · Bioavailability · Technosol · Potentially toxic elements

Abbreviations

CEC	Cation exchange capacity
DGT	Diffusive gradients in thin films
DOC	Dissolved organic carbon
EC	Electrical conductivity
LPF	La Petite Faye
MDN	Mortagne-du-Nord
PTE	Potentially toxic element
SPW	Soil pore water
TOC	Total organic carbon

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Introduction

Mining and smelting activities are the major sources of contamination through releasing of a huge amount of potentially toxic elements (PTEs) into the environment through wind and water runoff erosion (Navarro et al. 2008). In particular, the ore extraction process is accompanied by rock extraction, which contains mineral phases potentially rich in PTE such

as arsenic. Additionally, the alteration of the materials from tailings, i.e., primary phases leading to the formation of secondary phases, which are potentially more stable in supergene conditions, may control the mobilities of PTE in the environment (Wanat et al. 2014).

Many authors have discussed that the total metal contents in the solid phase are frequently used to identify their potential environmental risk; these values give little information about their toxic effects on soil organisms and plants (McLaughlin et al. 2000; Menzies et al. 2007; Plaza et al. 2010). They have suggested that the bioavailable amount of soil metals is more suitable than their total concentrations to predict their transfer from soil to plants.

The concept of bioavailability is relatively complex and reflects a dynamic process (Peijnenburg et al. 1997) involving the following two distinct notions: (i) stability of the thermodynamic equilibrium of metals at the liquid/solid interface (also known as “environmental availability”) and (ii) the physiological processes of absorption by the target organisms (also called “environmental bioavailability”). An accurate assessment of the bioavailability must consider the possibilities of both physico-chemical desorption of PTE and the biological receptors they can reach.

Water-soluble PTE can easily be mobilized and may be considered as highly bioavailable (Seguin et al. 2004). Chapman et al. (2002) concluded that soil pore water (SPW) analysis can be an effective assessment tool. Sampling of SPW has been carried out satisfactorily in numerous pot experiments in both laboratory and greenhouse conditions (Knight et al. 1998). Rhizon soil moisture samplers can be used to remove SPW while the physical structure of the soil remains intact. Additionally, the SPW removed by Rhizon soil moisture samplers probably represents the fraction of soil water that is taken up by plants, and such SPW samples have been recommended for use in ecotoxicity tests (Tiensing et al. 2001). This method has proven to be effective, relatively straightforward, and inexpensive compared to other procedures for extracting SPW (Datta and Young 2005). The PTE bioavailabilities in soil and sediments can also be assessed by several groups of extraction solutions (e.g., by 0.01 M CaCl_2 , 1 M NH_4NO_3 , or 0.005 M DTPA) (Pueyo et al. 2004).

Alternatively, another approach based on the chemical measurement of the PTE in soil by the use of a gel technique, the diffusive gradients in thin films (DGT) method, has been developed.

The DGT technique was developed for measuring the PTE concentrations in water, but it has also been used in soil and sediments to measure the pore water concentrations and metal resupply fluxes from the solid phase (Zhang and Davison 1995; Almas et al. 2006). This technique is based on the diffusion of metal(loid)s through a diffusion layer to a binding phase where they are concentrated (Zhang and Davison 1995; Hooda et al. 1999). Whereas standard DGT incorporates

Chelex-100 cation exchanger, recently, ferrihydrite-backed (FH) DGT has been reported for the measurement of anions such as inorganic arsenic, antimony, and molybdenum (Osterlund et al. 2010).

Finally, plants themselves can be used as bioindicators for the assessment of toxicity in terrestrial ecosystems (Gorsuch et al. 1991). Adriano (2001) classified plants into three types (indicators, accumulators, and excluders) depending on their PTE uptake behavior. Indicator plants can effectively be used as naturally available monitoring systems (Bargagli 1998). Dwarf beans have been extensively used for the assessment of PTE phytotoxicities based on growth experiments in the laboratory (Ruttens 2006; Meers et al. 2007b).

The aim of this work was to assess the phytoavailabilities and potential remobilization of PTE such as Zn, Pb, Cd, As, and Sb in contaminated technosols (soils that have been formed or profoundly modified through long-term human activities) with laboratory experiments based on both Chelex-100 DGT and FH DGT devices, Rhizon soil moisture sampler method, and the concentrations of PTE in dwarf bean primary leaves.

Materials and methods

Soil sampling

Two contaminated areas, a former smelting area and a former mining area, were selected for this study. The first one is metallicolous grassland located at Mortagne-du-Nord (MDN) in Northern France. The area is adjacent to the former metallurgical site occupied for over 60 years by a zinc smelting unit linked to a sulfuric acid production unit and a lead smelting unit (Thiry and van Oort 1999). The second is the former mine tailings of La Petite Faye (LPF) located 60 km northeast of Limoges (France), where approximately 35,000 t of waste from a former gold mine have been stored for over 45 years. This mining waste is characterized by high total concentrations of PTE such as Pb and Sb (Néel et al. 2003; Wanat et al. 2013).

Three locations from each site named MDN1, MDN2, and MDN3, and LPF1, LPF2, and LPF3 were selected for this study according to the surface soil concentration levels of the PTE such as Zn, Pb, and Cd for MDN and As, Sb, and Pb for LPF, respectively, across a concentration gradient and spatial distribution of the vegetation cover. At the MDN site, the vegetation cover essentially consists of *Arabidopsis hallari* and *Avena sativa* L., whereas at the LPF site, *Graminea*, *Equisetum telmateia*, *Betula pendula*, *Pteridium aquilinum*, and *Rubus fruticosus* were present (Wanat et al. 2013, 2014).

The collected surface soil samples (0–20 cm) from each location were oven-dried at a constant temperature of 40 °C,

manually homogenized, sieved using a 2-mm mesh sieve, and then used for the determination of the soil physico-chemical properties.

The physicochemical properties of the soil were characterized according to standardized French (AFNOR 1999) or international (ISO 1999) procedures. The pH and electrical conductivity (EC) of each sample were determined in soil/water extract (1:2.5 w/v) (NF ISO 10390 (2005)). The total organic carbon (TOC) concentrations were determined according to ISO (1999). The soil texture analysis was based on grain size analysis, which was performed with a Malvern Mastersizer 3000 laser diffraction microgranulometer (measurement range between 0.02 and 3000 μm).

Soil total PTE analysis

The soil total PTE concentrations were determined by the method of aqua regia/hydrofluoric acid digestion (Zhang et al. 2008). Approximately 1 g of each sample was accurately weighed into a 100-ml Teflon beaker. Twenty milliliters of aqua regia (HNO_3/HCl , 1:3 v/v) and 20 ml of concentrated hydrofluoric acid were added to the beaker, heated to dryness, and then cooled to room temperature.

One milliliter of concentrated nitric acid and a further 20 ml of deionized water were added, and the beaker was heated again on a hot plate at 90–100 °C for 1 h, and then cooled to room temperature. The solution was filtered through a 0.45- μm cellulose nitrate filter and diluted to volume with deionized water in a 100-ml volumetric flask. The PTE concentrations in the solutions were determined by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Finnigan Element XR, Thermo Electron, Germany) using a Twinnabar cyclonic spray chamber and a Micromist nebulizer (Glass Expansion, Melbourne, Australia). The accuracy and precision of analyses were checked by performing calibrations with a standard reference water solution (Fisher scientific).

Germination test and plant analysis

A pot experiment was conducted with the contaminated technosols from the MDN and LPF sites. Approximately 1 kg of soil from each sub-location was potted in plastic plant pots after homogenizing and sieving the soil to pass through a 2-mm mesh sieve. Four dwarf bean seeds per pot were sown in all of the pots and cultivated for 21 days in controlled conditions (16-h light/8-h darkness regime, 25 °C/21 °C). The photoperiod was set at a 16-h light/8-h darkness regime, with an approximate photon flux of 150 $\mu\text{E m}^{-2} \text{s}^{-1}$. The soil moisture was adjusted at 65 % of the potential water holding capacity with demineralized water by weighing every second day.

The plants were harvested 21 days after sowing. The aboveground plant tissues (primary leaves) were cut and rinsed thoroughly with double deionized water. Washed leaves were dried at 80 °C for 72 h before recording the dry matter yield. Dried plant leaves were ground with a laboratory grinder and digested with a pressurized closed-vessel microwave system (Multiwave 3000, Anton Paar GmbH, Germany). Before each digestion, the microwave polyfluoroacetylene (PFA)-teflon vessels were cleaned with 10 ml of aqua regia (HNO_3/HCl , 1:3 v/v), heated for 20 min at 200 °C, and then rinsed with deionized water. After the microwave-assisted digestion procedure was optimized, the following conditions were employed: Samples were accurately weighed to 200 mg (± 0.5 mg) in the microwave vessels. The digestion program consisted of a 15-min gradual increase to 200 °C, a 15-min digestion step at 200 °C and 1200 W, and then a cooling stage. The acid mixtures used were selected according to previous reports for trace elemental analysis in soil (Das et al. 2001). After cooling to room temperature, the samples were filtered through 0.45- μm filter paper and diluted to 50 ml with ultra-pure water (18 $\text{M}\Omega\text{cm}^{-1}$). Blanks were processed via a method identical to the sample processing. HR-ICP-MS measurements were carried out to determine the PTE concentrations as described before and their mineral mass (mg plant^{-1}), calculated by multiplying the biomass of primary leaves (mg DW plant^{-1}) by their element concentration (mg DW kg^{-1}).

Soil pore water sampling

SPW was collected by using Rhizon soil moisture samplers (Rhizosphere Research Products, Wageningen, Netherlands). Measurements were made in three replicates. Two Rhizon soil moisture samplers were placed in each pot for 24 h, and approximately 20 ml of soil pore water was extracted. The collected soil pore water was separated into several sub-samples for analysis. The soluble metal(loid)s ($\text{Metal}_{\text{sol}}$) were acidified with concentrated HNO_3 and stored at 4 °C prior to the concentrations of the PTE being determined by HR-ICP-MS as described before. Other aliquots of SPW were used for determining the dissolved organic carbon (DOC) using a Teckmar–Dohrman Phoenix 8000 TOC analyzer, and the concentrations of the major cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) and anions (NO_3^- , SO_4^{2-} , and Cl^-) were analyzed by ion chromatography (Dionex ICS-2000, Sunnyvale, CA, using a CS16A column for measuring the cations and an AS17 column for measuring the anions). Before using the samplers, they were cleaned with 5 % HNO_3 and then washed twice with deionized water.

DGT deployment

DGT measurements were made for both the MDN and LPF soil samples. All experiments were carried out in three

replicates. The following two types of DGT devices were used in this study: the standard Chelex-100 DGT (Zhang et al. 2001) was used for Zn, Cd, and Pb, while the ferrihydrite-backed (FH) DGT was used for As and Sb measurements. DGT units (DGT soil samplers (LSNA), Lancaster, UK) consisting of a plastic base (25-mm-diameter piston) loaded with a protective membrane filter (0.45- μm cellulose nitrate membrane filter, 0.14 mm thick), a diffusive gel disc (0.82 mm thick), and a resin (Chelex-100 resin (for Zn, Pb, and Cd) and FH resin (for As and Sb)) were used to measure the concentrations of the PTE (C_{DGT}) in the soil samples. While there is now strong evidence for the capability of DGT to assess metal concentrations in soil (Davison et al. 2000), more recent works with FH-based binding gel have been published for assessing the inorganic species of As (Mojsilovic et al. 2011; Moreno-Jimenez et al. 2013) and Sb (Osterlund et al. 2010) in soil samples.

Before DGT deployment, soil slurries were prepared by the addition of distilled water to adjust 80 % water hold capacity (WHC) and left for 24 h to achieve equilibration. The DGT units were inserted gently 1.5 cm deep into the soil slurries. The container and DGT device were covered with parafilm to limit evaporation. After maintaining the device at room temperature ($\pm 20^\circ\text{C}$) for 24 h, DGT devices were washed with distilled water to remove the soil particles that adhered to the DGT device. Subsequently, DGT devices were opened to remove the filter and the diffusive membrane. The Chelex-100 resin gels were eluted by 1 ml of 1 M HNO_3 , while the FH resin gels were eluted by 1 ml of 1 M HCl . The eluent was diluted ten times and analyzed by HR-ICP-MS as described before. The mass of the metals that accumulated in the resin gel (M , μg) was obtained by the following equation:

$$M = Ce(V_{\text{HNO}_3} + V_{\text{gel}})/fe$$

where Ce is the concentration in the eluent ($\mu\text{g ml}^{-1}$) measured analytically, V_{HNO_3} is the volume of HNO_3 (1 ml), V_{gel} is the volume of gel (0.15 ml), and fe is the elution factor for the metals.

The time-averaged concentration at the interface soil diffusive layer (C_{DGT} , $\mu\text{g l}^{-1}$) can be calculated from the following equation:

$$C_{\text{DGT}} = \frac{M \Delta g}{D \cdot t A}$$

where Δg is the diffusion layer thickness (0.094 cm), D is the diffusion coefficient of metal in the diffusion layer ($\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), t is the deployment time (s), and A is the area of the gel membrane exposed to the soil (3.14 cm^2).

Comparison of C_{DGT} with the independently measured SPW concentration C_{sol} (both determined at the same soil moisture content 80 % WHC) provides a ratio (R) that gives

an indication of the extent of depletion of SPW concentrations at the DGT interface (Ernstberger et al. 2002):

$$R = \frac{C_{\text{DGT}}}{C_{\text{sol}}}$$

The SPW concentrations adjacent to the DGT device become depleted as the metal(loid)s are removed locally by the DGT that acts as a sink. The local depletion in the SPW concentrations therefore induces remobilization of solutes from the soil solid phase. Resupply of metal(loid)s from particles to SPW counteracts the depletion which is most pronounced when there is no resupply from the solid phase. The resupply flux of metals from the solid phase to the pore water depends on the ability of the labile metal pool of the solid phase to be released into the SPW. The accumulated mass of metal(loid)s in the DGT resin is, thus, partly governed by the resupply flux of metals from the soils to the DGT device (Nia et al. 2011).

Reagents and standards

All of the reagents used in this study were products of analytical-grade quality (Merck pro-analysis, Darmstadt, Germany). All of the solutions and dilutions were prepared using ultra-pure water ($18 \text{ M}\Omega\text{cm}^{-1}$) (Thermo Scientific Barnstead Easy Pure II systems). Standard stock solutions of 1000 mg l^{-1} of different elements were prepared from metal wires or salts with purities higher than 99.998 % (VWR international, BDH Prolabo ICP Standards, Belgium). Diluted standard working solutions were prepared from these standard stock solutions on a daily basis. All of the laboratory glassware and plastic ware were rinsed three times with deionized water after being soaked in a HNO_3 (10 %, v/v) bath for 24 h.

Statistical analysis

All tests were performed in three replicates, and the results are presented as the mean \pm standard deviation. The data were statistically analyzed using Statistica 10 package software. Statistical analysis including Pearson's correlation coefficients were used to determine the relationships between the concentrations of the PTE measured by the DGT technique (C_{DGT}), in soil pore water (C_{spw}), and in dwarf bean primary leaves (C_{plant}) as well as the total soil PTE concentrations (C_{tot}).

Results and discussion

Soil properties

The main physicochemical properties of the soil samples are summarized in Table 1. Soil samples from MDN and LPF differed in their main physical and chemical properties. The

Table 1 Physico-chemical characteristics of the selected soil samples from Mortagne-du-Nord (MDN) and La Petite Faye (LPF) ($n = 3$; \pm standard deviation)

Parameters	MDN1	MDN2	MDN3	LPF1	LPF2	LPF3
pH-H ₂ O	6.9 \pm 0.1	6.3 \pm 0.3	6.1 \pm 0.1	3.6 \pm 0.1	4.9 \pm 0.4	5.7 \pm 0.1
EC (μ S cm ⁻¹)	112 \pm 3	112 \pm 7	113 \pm 1	258 \pm 4	200 \pm 3	150 \pm 3
CEC (cmol(+) kg ⁻¹)	7.2 \pm 0.7	8.5 \pm 0.2	6.7 \pm 1.2	18.3 \pm 0.7	29.1 \pm 0.2	39.7 \pm 0.3
TOC %	3.3 \pm 0.9	4.3 \pm 0.1	6.4 \pm 0.1	0.3 \pm 0.8	0.4 \pm 0.4	1.6 \pm 0.8

EC electrical conductivity, CEC cation exchange capacity, TOC total organic carbon

pH values of the MDN samples were acidic to slightly acidic and ranged from 6.1 to 6.9, while the pH values of the LPF samples were acidic and ranged from 3.6 to 5.7. The total organic carbon (TOC) ranged from 3.3 to 6.45 % and 0.30 to 1.67 % for the MDN and LPF samples, respectively. The cation exchange capacity varied from 6.7 to 8.5 cmol⁽⁺⁾/kg and 18.3 to 39.7 cmol⁽⁺⁾/kg for the MDN and LPF samples, respectively.

Physicochemical analysis of the SPW

Results of the SPW physicochemical parameters are displayed in Table 2. A noticeable difference in the pH of the SPW was observed for the MDN and LPF soil samples. The pH values of SPW for MDN samples were slightly acidic (6.08–6.90), while the pH values of the LPF samples were acidic (3.66–5.73). In fact, there is no significant difference between the pH values before and after bean cultivation; this may be attributed to the low exudates effect, which did not alter the pH value.

The DOC concentration differs between the soil samples. The highest DOC concentration for the MDN samples was for MDN3. The same pattern was also observed for the LPF samples.

The concentrations of the major cations and anions in the SPW varied according to the locations for both the MDN and LPF samples. Ca²⁺ appeared to be the main cation, and it showed the highest concentration among the other cations. The highest Ca²⁺, NH₄⁺, Mg²⁺, K⁺, and Na⁺ concentrations were observed for the LPF3 sample, whereas their concentrations were comparable among the MDN samples. The SPW of

the LPF samples was characterized by higher anion (Cl⁻, NO₃⁻, and SO₄⁻²) concentrations than the MDN samples.

Soil pore water and DGT measured PTE concentrations

The Zn, Pb, Cd, As, and Sb total soil concentrations, total dissolved concentrations in SPW, DGT measured concentrations, concentrations in plant leaves, and *R* values for both the MDN and LPF samples are summarized in Tables 3 and 4, respectively. Columns represent the average of three replicates (\pm standard deviation).

The total dissolved concentrations of Zn in the SPW for the MDN samples were different. The largest solubilization of Zn was observed for MDN1 (with the highest total Zn content), which presents a higher Zn concentration in soil pore water compared to both MDN2 and MDN3. Otherwise, the minimum solubility of Zn was reached for MDN2 (with the lowest total Zn soil concentration), which also holds the lowest Zn soil pore water concentration.

The highest DGT measured Zn concentrations were observed for MDN1 and MDN3, whereas the lowest was observed for MDN2, which is in agreement with the observations for the SPW concentrations.

The *R* value ($R = \frac{C_{DGT}}{C_{sol}}$) is a measure of the extent of replenishment of the metal in SPW at the DGT interface. The lower value for *C*_{DGT} than for *C*_{spw} (Fig. 1) could also be because only a fraction of the metal species was labile (Vandenhove et al. 2007).

The *R* values for Zn in all studied samples varied between 0.5 and 0.72, which suggest significant resupply from the

Table 2 Soil pore water physicochemical parameters for the MDN and LPF samples

Zone	pH	DOC (mg l ⁻¹)	Na ⁺	Cations (mg l ⁻¹)				Anions (mg l ⁻¹)		
				NH ₄ ⁺	Mg ²⁺	K ⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻²
MDN1	6.90	18.4	5	2	1.9	11.9	17.8	6.4	55.6	15.9
MDN2	6.33	20.2	5.2	4	1.4	11.4	16.4	2.5	72.2	14
MDN3	6.08	24.6	4.9	3.5	4.5	9	20.8	2.1	103.4	22.6
LPF1	3.66	36	31.3	5.6	5.7	13.3	33.5	26.4	141.6	155.6
LPF2	4.91	51.9	11.5	1.5	4.1	11.8	20.7	13	89.3	28.3
LPF3	5.73	143.5	29	6.2	12.7	71.4	86.1	45.2	393.4	109

DOC dissolved organic carbon.

Table 3 Soil total metal concentration (C_{tot}), total dissolved concentration of metal in the soil pore water (C_{spw}), DGT measured concentration (C_{DGT}), concentration of metal in bean leaves (C_{plant} , DW), metal mineral mass (M_{m}), and R value for the MDN samples

Element	Unit	MDN1	MDN2	MDN3
Zn _{tot}	mg kg ⁻¹	7726 ± 12	3114 ± 11	3127 ± 10
Zn _{spw}	μg l ⁻¹	4940 ± 37	3770 ± 23	4781 ± 49
Zn _{DGT}	μg l ⁻¹	3486 ± 27	2419 ± 32	3456 ± 16
Zn _{plant}	mg kg ⁻¹	372.5 ± 2.8	240 ± 1.5	252.7 ± 4.7
Zn _{Mm}	mg plant ⁻¹	59.5 ± 1.2	25.2 ± 0.9	30.2 ± 1.7
R		0.70	0.64	0.72
Pb _{tot}	mg kg ⁻¹	3551 ± 12	881 ± 9	874 ± 8
Pb _{spw}	μg l ⁻¹	173 ± 18	122 ± 4	151 ± 6
Pb _{DGT}	μg l ⁻¹	101 ± 7	53 ± 6	82 ± 7
Pb _{plant}	mg kg ⁻¹	29.2 ± 2	16 ± 1	23.3 ± 0.5
Pb _{Mm}	mg plant ⁻¹	4.6 ± 0.4	1.6 ± 0.1	2.7 ± 0.8
R		0.58	0.43	0.54
Cd _{tot}	mg kg ⁻¹	72 ± 13	64 ± 8	51 ± 8
Cd _{spw}	μg l ⁻¹	178 ± 13	141 ± 8	139 ± 7
Cd _{DGT}	μg l ⁻¹	126.2 ± 6	69.7 ± 9	92.7 ± 3
Cd _{plant}	mg kg ⁻¹	6.30 ± 0.4	3.12 ± 0.1	4 ± 1
Cd _{Mm}	mg plant ⁻¹	1 ± 0.04	0.32 ± 0.01	0.48 ± 0.09
R		0.7	0.49	0.66

$$R = \frac{C_{\text{DGT}}}{C_{\text{spw}}}$$

DW dry weight

solid phase. Degryse et al. (2003) observed R values from 0.02 to 1.5 for Zn-contaminated soils. This ratio decreased with a decreasing distribution coefficient (K_d) of Zn in the soil, which is in agreement with the predictions of the DGT-induced fluxes in soils (DIFS) model. In MDN3, which had high R values, the soil pore water Zn concentrations were readily replenished after being employed with DGT. DGT was also used to measure the distribution and rates of exchange of Zn, Cd, and Ni between the solid phase and solution in five different soils with various textures, pH values, and TOC values (Ernstberger et al. 2005). In a previous study, the DGT induced fluxes in soils (DIFS) model (Ernstberger et al. 2002) was used to derive distribution coefficients for labile metals (K_{dl}) and the rate at which the soil system can supply a metal from the solid phase to solution. The major factor influencing the K_{dl} values for Zn and Cd was the pH, but their association with humic substances in the solid phase also appeared to be important.

A similar picture was observed for the concentrations of Pb in the SPW and DGT measurements for both the MDN and LPF soil samples. Again, the highest Pb concentrations were observed for MDN1 and LPF1 followed by MDN3 and LPF2, while the lowest Pb concentrations were observed for MDN2 and LPF3, respectively. The R values for Pb ranged between

Table 4 Soil total metal concentration (C_{tot}), total dissolved concentration of metal in the soil pore water (C_{spw}), DGT measured concentration (C_{DGT}), concentration of metal in bean leaves (C_{plant} , DW), metal mineral mass (M_{m}), and R value for the LPF samples

Element	Unit	LPF1	LPF2	LPF3
As _{tot}	mg kg ⁻¹	83941 ± 11	37462 ± 10	2672 ± 4
As _{spw}	μg l ⁻¹	1611 ± 47	3827 ± 56	5040 ± 40
As _{DGT}	μg l ⁻¹	718 ± 23	1918 ± 26	2427 ± 23
As _{plant}	mg kg ⁻¹	ng	55.7 ± 4	72.7 ± 2.8
As _{Mm}	mg plant ⁻¹	ng	3.34 ± 0.81	5.08 ± 1.1
R		0.44	0.5	0.48
Pb _{tot}	mg kg ⁻¹	16109 ± 14	8541 ± 9	367 ± 9
Pb _{spw}	μg l ⁻¹	462 ± 9	39 ± 2	21 ± 1
Pb _{DGT}	μg l ⁻¹	49 ± 2	14 ± 1	2.7 ± 0.2
Pb _{plant}	mg kg ⁻¹	ng	9.6 ± 1	6.7 ± 3
Pb _{Mm}	mg plant ⁻¹	ng	0.57 ± 0.04	0.53 ± 0.13
R		0.11	0.36	0.12
Sb _{tot}	mg kg ⁻¹	863 ± 12	493 ± 9	107 ± 13
Sb _{spw}	μg l ⁻¹	65 ± 3	37 ± 4	136 ± 12
Sb _{DGT}	μg l ⁻¹	17 ± 2.7	8.2 ± 1	28 ± 2
Sb _{plant}	mg kg ⁻¹	ng	1.48 ± 0.2	1.52 ± 0.8
Sb _{Mm}	mg plant ⁻¹	ng	0.08 ± 0.01	0.12 ± 0.03
R		0.26	0.22	0.20

$$R = \frac{C_{\text{DGT}}}{C_{\text{spw}}}$$

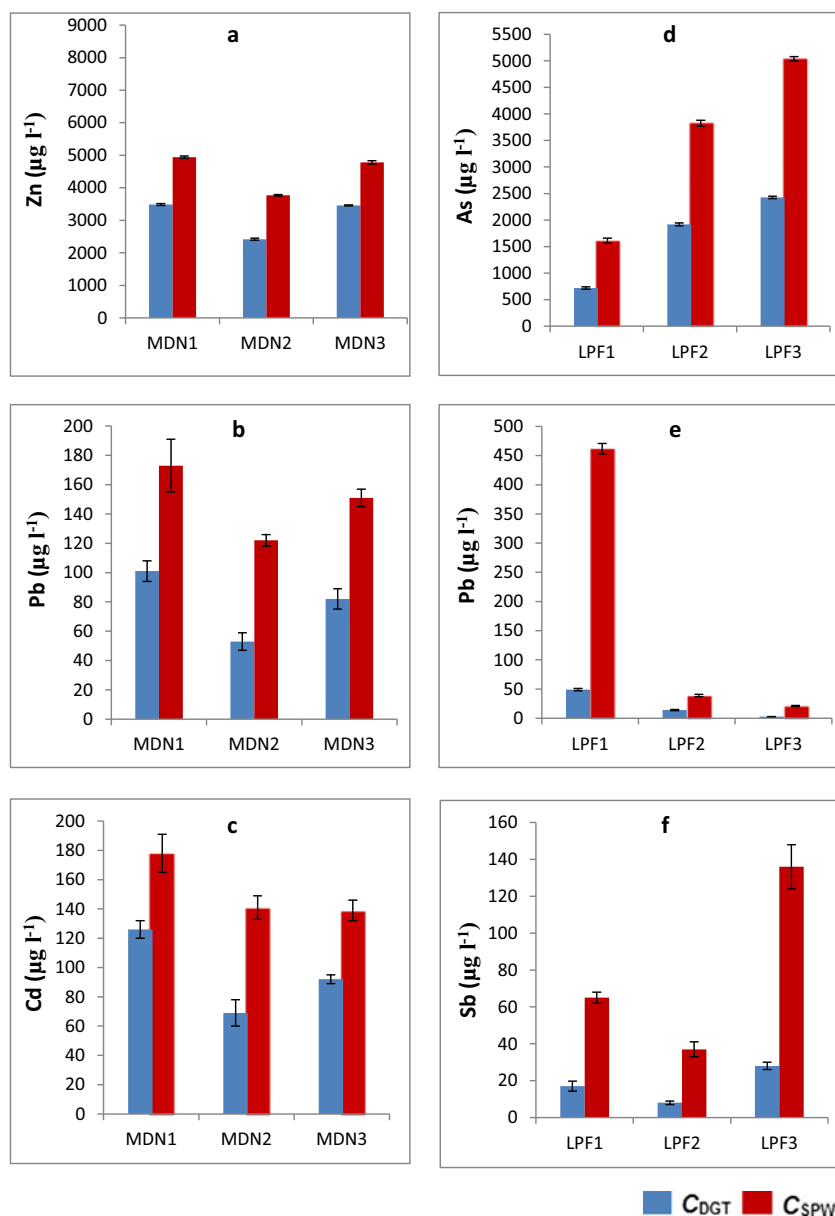
DW dry weight, ng no growth

0.43 and 0.58 and between 0.11 and 0.35 for both MDN and LPF samples, respectively, suggesting a moderate resupply from the solid phase. Pb usually shows restricted mobility in soil, which is reflected here by the low concentrations of this metal in the SPW. Nolan et al. (2003) found low Pb concentrations in centrifuged extracted pore waters from acid-contaminated soils. Clemente et al. (2008) also found a low Pb concentration in the SPW of a multi-element contaminated soil.

In the case of Cd, the soil sample with the largest Cd concentration (MDN1) also showed the highest SPW concentration, and the soil sample with smallest Cd content (MDN3) showed the lowest SPW concentration. A similar pattern was observed for the Cd concentrations measured by DGT for the studied samples with the exception of MDN2, which presents the lowest Cd concentration in comparison to both MDN1 and MDN3. The R values for Cd ranged between 0.49 and 0.7.

The highest values of R were observed for Zn, followed by Cd and Pb, indicating the ability of the soil to sustain SPW concentrations, which decreased in that order. The highest extracted amounts of As were observed for LPF3, which had with the lowest As concentrations, followed by LPF2, while, in the contrary, the lowest extracted amounts were observed for the most highly contaminated soil sample (LPF1). Similarly to As, the highest amounts of extracted Sb were also

Fig. 1 PTE-DGT measured concentrations (C_{DGT}), and PTE concentrations in the soil solution (C_{SPW}) for both MDN (a, b, and c) and LPF samples (d, e, and f)



observed for LPF3 followed by LPF2, and the lowest concentration was for LPF1, which had the highest Sb concentration.

C_{DGT} for both As and Sb correlated well with their concentrations in SPW and showed that As and Sb were considerably less soluble in comparison to their total soil contents. That finding might be explained by the fact that previous results of sequential extraction showed that the majority of both As and Sb was bound to residual phase, and very small proportions were water soluble especially for both LPF1 and LPF2 (Wanat et al. 2013, 2014).

PTE phytoavailabilities

The phytoavailability is the capacity of a plant for the adsorption of soil or sediment components, and it is dependent on

many factors, such as the plant species, total metal concentrations, adsorption, and desorption from mineral surfaces (Adriano 1986; Li and Thornton 1993). The pot experiment of dwarf beans grown in the studied samples for 21 days showed an accumulation of varying amounts of PTE in the primary leaves of the dwarf beans. On average, the total biomass of the leaves after 21 days varied between 0.06 and 0.16 g/plant dry weight.

Dwarf bean primary leaves showed a high Zn concentration, indicating that this metal was phytoavailable and incorporated into plant leaves. On the contrary, Pb and Cd showed low phytoavailabilities, suggesting that small amounts of these metals, although present in mining and tailings in high concentrations, were absorbed by plant leaves. It may also be suggested that the remobilizing abilities of Pb and Cd from

roots to shoots were much lower than those of Zn. As and Sb are present in high concentrations in LPF mine tailings, but their phytoavailabilities indicate very low bioavailabilities. These data are in agreement with those of Casado et al. (2007) and Levresse et al. (2012) for the arsenic and antimony uptake by plants in an abandoned mining area in NW Spain and Mexico, which also concluded that these metals have low bioavailabilities in mine waste. These low phytoavailabilities can be explained by the association of As and Sb with stable phases, such as sulfide minerals, iron oxides, or the residual phase (Gal et al. 2007; Denys et al. 2008).

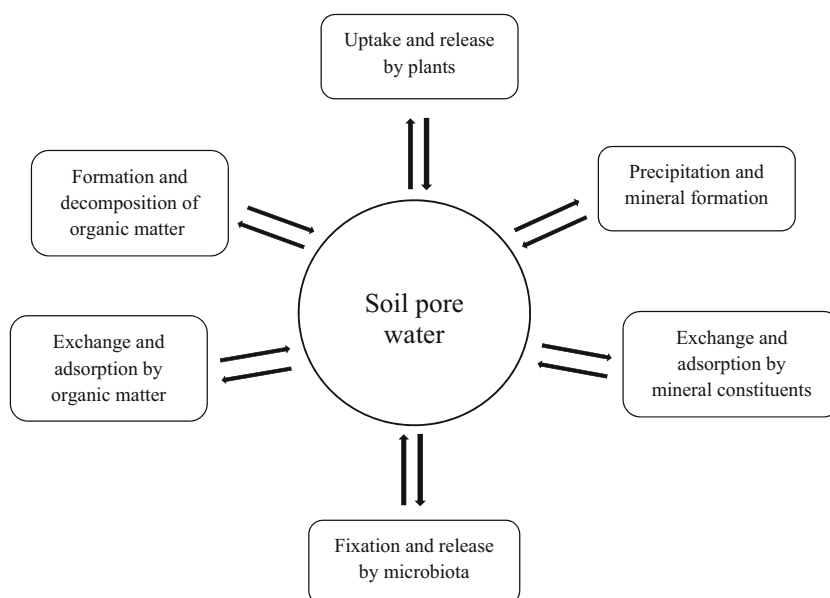
The mobility of PTE as well as their bioavailability depends on their interactions between the solid and liquid phases in soils. In fact, many mechanisms such as, for example, sorption/desorption reactions, precipitation, redox reactions, and the complexation reaction with organic or inorganic ligands can affect or control the PTE bioavailability as well as their toxicity (Fig. 2). Many factors such as pH, soil organic matter, chemical speciation, and root exudates affect these mechanisms and influence the behavior of chemical elements (Impellitteri et al. 2001; Carrillo-Gonzalez et al. 2006).

Correlation between the concentrations of PTE in SPW, as measured by DGT devices and accumulated in plant leaves

A correlation analysis was performed to investigate the relationships between each of the concentrations of PTE in soil pore water (C_{spw}), as measured by the DGT technique (C_{DGT}), in dwarf bean primary leaves (C_{plant}) and in the total soil (C_{tot}).

The results of Pearson's correlation test to establish the relationships between the above variables are presented in Table 5.

Fig. 2 Possible mechanisms involved in the soil–soil pore water–plant transfers of PTE (source: Alina Kabata-Pendias, 2010).



In our study, we observed a significant relationship between the Zn concentrations in soil pore water and each of the Zn concentrations measured by DGT as well as the Zn concentrations accumulated in the dwarf bean primary leaves. Additionally, the Zn concentrations as measured by DGT were linearly correlated with the Zn concentrations accumulated in dwarf bean primary leaves. Conversely, there was no significant correlation with the total Zn concentrations in the soil samples. However, the Zn contents in plant leaves correlated well with the total soil Zn concentrations.

A good correlation between C_{DGT} and SPW concentrations has been observed by many authors. Degryse et al. (2003) found a significant linear correlation between the Zn pore water concentrations and the DGT-measured Zn concentrations of Zn-amended soil samples. Zhang et al. (1998) found significant linear correlations between C_{DGT} and the concentrations of Zn, Cd, Ni, and Cu in the pore water of soil amended with sludge. Koster et al. (2005) also found that the DGT-extractable Zn concentration correlated well with the extractable Zn concentration for Zn-amended soil samples. Many authors have also noted the relationship between the concentrations of PTE in SPW, as measured by DGT and in plant shoots. The effective concentrations (CE) of Zn measured by the technique of DGT were compared along with the total concentrations of Zn and the concentrations of Zn in SPW to the Zn concentrations in plants (Zhang et al. 2004). Correlations between the concentration of Zn in the plants and the measured soil parameter followed the order $CE > SPW > total\ Zn$. Muhammad et al. (2012) observed that both the Zn and Cd concentrations in *Plantain* shoots were strongly correlated with their concentrations in both the soil pore water and as measured by DGT devices. Conversely, Song et al. (2004) also observed a good relationship between the Cu contents in the shoots of both *Silene vulgaris* and

Table 5 Pearson's correlation coefficients between potentially toxic element indices: total dissolved concentration of metal in the soil pore water (C_{spw}), DGT measured concentration (C_{DGT}), concentration of metal in plant leaves ($C_{plant, DW}$), metal mineral mass (M_m), and soil total metal concentration (C_{tot}) in the MDN and LPF samples

Element		C_{spw}	C_{DGT}	C_{plant}	C_{tot}	M_m
<i>MDN</i>						
Zn	C_{spw}	1				
	C_{DGT}	0.99***	1			
	C_{plant}	0.65*	0.70*	1		
	C_{tot}	Ns	Ns	0.99***	1	
	M_m	0.70*	0.73*	0.98***	0.98***	1
Pb	C_{spw}	1				
	C_{DGT}	0.62*	1			
	C_{plant}	0.93***	0.76**	1		
	C_{tot}	0.86**	0.62*	0.73**	1	
	M_m	0.61*	0.66**	0.89***	0.82**	1
Cd	C_{spw}	1				
	C_{DGT}	0.59*	1			
	C_{plant}	0.83**	0.86**	1		
	C_{tot}	0.61*	0.57*	Ns	1	
	M_m	0.54*	0.82**	0.81**	Ns	1
<i>LPF</i>						
As	C_{spw}	1				
	C_{DGT}	0.99***	1			
	C_{plant}	0.91***	0.92***	1		
	C_{tot}	-0.99***	-0.98***	-0.91***	1	
	M_m	0.83**	0.85**	0.92***	-0.80**	1
Pb	C_{spw}	1				
	C_{DGT}	0.92***	1			
	C_{plant}	0.82**	0.73*	1		
	C_{tot}	0.87**	0.92***	0.89**	1	
	M_m	Ns	Ns	Ns	Ns	1
Sb	C_{spw}	1				
	C_{DGT}	0.56*	1			
	C_{plant}	0.73*	0.69*	1		
	C_{tot}	-0.67*	-0.56*	-0.68*	1	
	M_m	Ns	Ns	Ns	Ns	1

DW dry weight, Ns not significant

*** $p < 0.001$; ** $p < 0.01$; * $p < 0.05$

Elsholtzia splendens and the Cu concentrations in soil pore water, while the correlation was less with Cu_{DGT} .

Cd contents measured by DGT showed a positive correlation with those found in dwarf bean primary leaves and with the total Cd contents. In contrast to Zn, the Cd content in plant leaves was well correlated with the total soil Cd concentration. Our results are in agreement with those of Meers et al. (2007b), who found that Rhizon Cd extraction was well correlated with the Cd contents in *Phaseolus vulgaris* considering that it provided the best measure of Cd phytoavailability in the

soil. Duquene et al. (2010) found a good correlation between the DGT-measured uranium concentrations with that in SPW. Pérez and Anderson (2009) also found that Cd_{DGT} correlated well with the Cd concentration SPW. Conversely, many authors observed a significant correlation between C_{DGT} and the plant uptake of PTE (Zhang et al. 2001; Nowack et al. 2004). Almas et al. (2006) also found a correlation between C_{DGT} and the ryegrass uptake of Zn, but such a correlation was not found for Cd, whereas no linear relationship between the effective concentrations (CE) measured by DGT and the metal contents in spinach was found.

Despite the differences in the soil sample properties, a similar pattern to Zn was observed for Pb in both the MDN and LPF samples. Again, a significant positive correlation was observed between each of the Pb concentration in soil pore water, Pb concentration as measured by DGT, and Pb content in the plant primary leaves with the total Pb content for MDN and LPF samples. The Pb content in plant leaves was well correlated with the total soil Pb concentration for the MDN and LPF samples.

The Pb_{DGT} concentration also exhibited positive linear correlations with the Pb content in plant primary leaves and the total soil Pb content for the MDN and LPF samples.

The As and Sb SPW concentrations collected at the end of the period of plant growth showed positive correlations with their concentrations measured by DGT and their concentrations in plant leaves, while they exhibited a negative correlation with their total soil concentrations. Conversely, As and Sb concentrations measured by DGT showed a positive correlation with those found in dwarf bean leaves, while they showed a significant negative correlation with their total soil concentrations. As and Sb concentrations in plant leaves also showed a significant negative correlation with their total soil contents. Relationships between the Sb concentrations in plants and the total soil are based on numerous data from the literature. Tschan et al. (2009b) showed a relationship between the soluble Sb concentration in soil and the Sb concentration in plants. Previous studies of soils from abandoned mining areas have shown that As and Sb tend to be present in the soil and sediments at low solubility levels (Flynn et al. 2003; Gal et al. 2007) associated with organic matter or the residual phase (Tighe et al. 2005; Nóvoa-Muñoz et al. 2007), indicating that As and Sb are geochemically immobile (Diemar et al. 2009). Their low phytoavailabilities and uptakes into biological systems are the result of the presence of relatively insoluble species or low contents of mobile fractions, resulting in low accumulations of these metals in food chains (Hammel et al. 2000; Flynn et al. 2003).

More generally, plant roots play an important role in the transformation of PTE in soils (Koo et al. 2005) via its exudates including organic acids as well as several forms of carbohydrates which could affect the mechanisms of the transformation of chemical form of PTE, biosorption, and the

modification of the soil environment in the rhizosphere. At the rhizosphere which includes the interface between plant roots and soil system, the behavior of PTE in the soil solution should be demonstrated to better understand their soil-to-plant transfer. The concentration of PTE in the rhizosphere soil solution is often considered to reflect accurately the plant-available concentration of PTE in the soil, which is influenced by properties as the dissolved organic carbon (DOC) and pH (Sauvé et al. 1997; Vijver et al. 2003). Three mechanisms can be in fact influenced by plant roots: modification of the soil environment in the rhizosphere, transformation of chemical form of PTE, and biosorption. Plants developing on a PTE-contaminated soil will respond differently depending on their biomass, root exploration volume, and PTE accumulation capability. Additionally, root exudates could be plant-specific

Conclusions

The article provides new information on PTE speciation and mobility in contaminated soils presenting a multi-metallic contamination from a former mining and smelting site. This study aimed to assess the ability of both the diffusive gradients in thin films (DGT) and Rhizon soil moisture sampler methods to predict the bioavailabilities of PTE in two contaminated technosols contaminated with Zn, Cd, Pb, As, and Sb.

In contrast to classical single extraction methods that did provide poor correlation for As and Sb, for all of the studied PTE, we found a significant correlation between the DGT-measured concentrations and the PTE concentrations in the SPW. Good correlations were also found between both the PTE in SPW and as measured by DGT (C_{DGT}) with the PTE accumulation in dwarf bean primary leaves. The most general conclusion is that the two methods used to measure the PTE concentrations in this study of contaminated technosols result in significant correlations between the PTE pools assessed.

The chemical assessment of bioavailabilities using Rhizon soil moisture samplers and DGT methods may thus provide the information required to predict PTE bioavailabilities. Zn, Pb, and Cd were readily mobile elements and potentially phytoavailable in the technosols from the smelting site whereas Pb, Sb, and As were much less available in the mining site.

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