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Potentially toxic element fractionation in technosoils using two sequential extraction schemes

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Abstract

This study reports the chemical fractionation of several potentially toxic elements (Zn, Pb, Cd, As, and Sb) in contaminated technosoils of two former smelting and mining areas using two sequential extraction schemes. The extraction schemes used in this study were the Tessier's scheme and a modified BCR scheme. The fractions were rearranged into four equivalent fractions defined as acid soluble, reducible, oxidizable, and residual to compare the results obtained from two sequential extraction schemes. Surface soils were samples from a waste landfill contaminated with Zn, Pb, and Cd located at Mortagne-du-Nord (MDN; North France) and from a settling basin contaminated with PTE such as As, Pb, and Sb located at La Petite Faye (LPF; Limoges, France). The study of the Zn, Pb, Cd, As, and Sb partitioning in the acid soluble, reducible, oxidizable, and residual fractions of the technosoils revealed that Zn, Cd, and Pb were mainly associated with the acid soluble and reducible fractions for MDN site, while As, Sb, and Pb were associated with residual fraction for LPF site. Fractionation results indicate that the percentages of Zn, Pb, Cd, As, and Sb extracted in Fe–Mn oxide bound fraction of Tessier's scheme were always higher than those extracted by modified BCR scheme. This may be attributed to the stronger Tessier's scheme conditions used to extract this fraction. In contrast the percentages of Zn, Pb, Cd, As, and Sb extracted in the organic fraction of the modified BCR scheme were always higher than those of the Tessier's scheme. The order of mobility of PTE was as follows: Cd > Zn > Pb in MDN site and As > Sb > Pb in LPF site. PTE were distributed in all soil fractions, with the most relevant enrichments in extractable and residual fractions. A significant amount of Cd, Pb, and Zn were rather mobile, which suggests that these elements can be readily available to plants and soil organisms.

Keywords: Potentially toxic element fractionation, Sequential extraction, Mining and smelting activities, contaminated technosoils

1 Introduction

Mining and smelting activities are considered as highly polluting sources of potentially toxic elements (PTEs) in the environment (Shu et al. 2001; Schuwirth et al. 2007). In fact both mining and smelting processes produce large amounts of wastes resulting in soil contamination (Davies 1983; Adriano 2001). These processes introduce PTE into the environment through gaseous and particulate emissions but also liquid and solid wastes (Dudka and Adriano 1997). The exposure of the population to these PTE involves a risk to human health by consuming the plants grown on the contaminated sites (Nabulo et al. 2010).

Since the determination of the total concentration of PTE in soils does not give sufficient information about the mobility and toxicity of these elements (Nowak 1995; Szulczewski et al. 1997; Rauret 1998; Petit and Rucandio 1999), additional information on the concentrations of particular physicochemical forms of the PTE is in fact required as their behavior in the environmental system depends on their chemical speciation (Merian and Clarkson 1991; Rodriguez et al. 2009). Speciation can be defined as the identification and quantification process of different species or binding forms in which an element occurs (Ure et al. 1995; Ure and Davidson 2001). PTE in soils are partitioned between the different phases present, i.e., organic matter, oxyhydroxides of iron, aluminum and manganese carbonates, sulfides, clays, etc., and are retained on these solid phases by different mechanisms, i.e., ion exchange, complexation, precipitation or co-precipitation (Weber 1991; Benedetti et al. 1995), or are retained in the lattice of soil minerals. Since the behavior of PTE in the soil–water–plant system depends on their speciation, the determination of PTE partition in soils assessed by sequential extraction schemes can give useful information. Different extraction schemes have been widely used to mimic differing environmental conditions, with strong acids being used to determine the total concentration of PTE and weaker solutions to determine compounds that are relatively soluble and bioavailable (Anju and Banerjee 2010).

The main goal of sequential extraction is to convert PTE bound in the different solid phases into soluble forms with a specific chemical extractants used at each step (Tokalioglu et al. 2000a, b). In these sequential extraction schemes, a series of progressively harsher reagents is used to dissolve increasingly refractory forms of these

elements, from the more mobile to the more refractory (MacLaren and Crawford 1973; Shuman 1985).

However, sequential extraction schemes are greatly influenced by experimental factors such as the choice of chemical reagents, specific extraction time, and weight ratio of sample to volume of the extraction solution. Thus, there are many criticisms of these schemes as several operationally defined artifacts may occur including the lack of specificity of reagents, the possibility of re-adsorption of released PTE to the remaining fractions (Belzille et al. 1989; Hass and Fine 2010) and the potential alteration of other phases during one extraction step (Li and Thornton 2001).

The best-known sequential extraction scheme (Tessier et al. 1979) consists of five steps in which PTE are considered to be distributed among different soil fractions: (1) exchangeable, (2) bound to carbonate, (3) bound to Fe–Mn oxides, (4) bound to organic matter, and (5) residual. Many sequential extraction schemes derived from the Tessier one have been applied to soils and sediments to fractionate PTE by using different chemical extractants to obtain useful information about the bioavailability and mobility of these elements (Elliott et al. 1990; Krishnamurti et al. 1995) in particular, one of the Community Bureau of Reference (BCR) (Ure et al. 1993) which is similar to that produced by Tessier et al. with the main difference in the first extraction step of the scheme.

The aims of this work was thus to: (1) investigate the chemical fractionation of PTE, respectively Zn, Pb, and Cd, in contaminated surface technosoils from a former smelting site (Mortagne-du-Nord (MDN), France) and As, Pb, and Sb from a former mining site (La Petite Faye (LPF), Limoges, France), and (2) compare the efficiency and suitability of two sequential extraction schemes (Tessier and a modified BCR) for these soils.

2 Materials and methods

2.1 Soil sampling

Two sites were selected for this study. The first one is metallophyte grassland located in Mortagne-du-Nord (MDN) in Northern France. This area has been occupied for over 60 years by a Zn smelter unit linked to a sulfuric acid production unit and a Pb smelting unit for a few years. The site has been back-filled with slags and smelting crucible to a thickness of about 3 meters. More than 30 metal-bearing (Zn, Pb and Cd) mineral species have been identified such as sulfides, sulfates, carbonates, oxides and silicates (Thiry and van Oort 1999). The second site is the former mine tailing of La Petite Faye (LPF) located 60 km North-East of

Limoges (France), where mining wastes have been stored in a settling basin from 46 years ago. The main PTE present in soils are As, Pb and Sb (Néel et al. 2003; Nénert et al. 1997). Three distinct locations (zone1, zone2 and zone3) from each site were selected according to the level of PTE concentrations and spatial distribution of the vegetation cover. One kg of surface soil (0-20 cm) was sampled at each location with a stainless steel spade. In the MDN site the vegetation cover consists of essentially *Arabidopsis hallari* and *Avena sativa* L. whereas, in LPF site, *Graminea*, *Equisetum telmateia*, *Betula pendula* and *Pteridium aquilinum* were present with large horsetails of black alder and poplar (Dutreuil et al. 1997). All soil samples collected were carefully transferred to clean polyethylene bags before transport to the laboratory. Collected soil samples were oven-dried at a constant temperature of 40°C, manually homogenized and then quartered. Two equivalent fractions were obtained from each quartered sample. One fraction was used for the determination of the soil physico-chemical properties whereas the other fraction was used for chemical analysis of PTE. Samples for chemical analysis were sieved first using a 2mm mesh sieve, to remove gross plant matter and subsequently crushed to pass through a 250µm sieve (Brooks 1983).

2.2 Reagents and standards

All the reagents used to prepare the extracting solutions were products of analytical-grade quality (Merck pro-analysis, Darmstadt, Germany). All solutions and dilutions were prepared using doubly deionized water ($18.2\text{M}\Omega\text{cm}^{-1}$) (Thermo Scientific Barnstead Easy pure II systems). Standard stock solutions of $1000\text{mg}\cdot\text{l}^{-1}$ of different elements were prepared from metal wires or salts of purity higher than 99.998% (VWR international, BDH Prolabo ICP Standards, Belgium). Diluted standard working solutions were prepared from these on a daily basis. All laboratory glassware and plastic ware were rinsed three times with double deionized water after being soaked in a HNO_3 (10%, v/v) bath for 24h.

2.3 Analysis of the soil physico-chemical properties

Physico-chemical properties of the samples (<2mm fraction) were characterized by routine soil testing laboratories according to standardized French (AFNOR 1999) or international (ISO 1999) procedures (Table 3). pH and EC of each samples were determined in distilled water extracts (1:2.5 w/v) (NF ISO 10390 (2005)). Total organic carbon concentrations were determined according to ISO (1999). Cation exchange capacity (CEC) was determined by the 0.05N cobalthexamine method (Aran et al. 2008). Organic matter was determined according to (Storer 1984) procedure depends on loss of weight on ignition (LOI).

2.4 X-ray fluorescence spectrometer (XRF)

The total concentration of PTE in the contaminated soil samples was determined from X-ray fluorescence using a XMET 5100 X-ray spectrophotometer (Oxford Instruments Analytical GmbH, Germany). PTE in the soil were determined by XRF method by pressed soil pellets with an acquisition delay time of 3 min. for each sample.

2.5 Soil mineralogical characterization

Powder X-ray diffraction was used for mineralogical characterization in bulk studied soils using a diffractometer INEL XRM3000 montage transmission (geometry Debye-Scherrer), (CoK α , 40 kV, 30mA) between 5 to 90°2 θ . The analyses of minerals were carried out on thin section of the bulk sample using INEL diffractometer equipped with an INEL CPS 120 detector (Debye-Scherrer geometry).

2.5 Sequential extractions

Sequential extraction schemes of Tessier et al. (1979) and of the European Union's Standards, Measurements and Testing Program (SM&T) (Sahuquillo et al. 1999) were used in this study and are summarized in (Table1 and Table 2) respectively. Each extraction step was performed in triplicate, starting with 1g of original soil material. The aqua regia step performed on the residue from step 4 for (Tessier's scheme) or step 3 for (BCR scheme) was based on the ISO 11466 method (ISO norm 11466 (1995)).

Metal concentrations in all extracts from these sequential extraction schemes were determined by ICP-MS (Finnigan Element XR, Thermo Electron, Germany). Additionally blanks of the different extractants were analyzed in triplicate and further subtracted from the soil samples. The accuracy of the sequential chemical extraction scheme was determined by comparing the sum of the concentrations obtained at the different steps of the extraction scheme with total metal content (Cuong and Obbard 2006).

Table 1: Extraction conditions of the Tessier's scheme

Fraction	Extractants and conditions
Exchangeable	1 M MgCl ₂ (pH = 7), 20 ml, 1 h.
Bound to carbonate	1 M NaOAc (pH = 5), 20 ml, 1 h.
Reducible	0.04 M NH ₂ OH HCl, 20 ml, 95 °C, 6 h.
Oxidizable	15 ml 30 % H ₂ O ₂ and 3 ml 0.02 M HNO ₃ , 2 h, 85 °C, 3.2 M NH ₄ OAc, 5 ml, 85 °C, 3 h.
Residual	HF, HClO ₄ , HNO ₃

Table 2: Extraction conditions of the modified BCR scheme

Fraction	Extractants and conditions
Exchangeable	0.11 M CH ₃ COOH, 40 ml, 16 h
Reducible	0.1 M NH ₂ OH HCl (pH = 2), 40 ml, 16 h
Oxidizable	8.8 M H ₂ O ₂ , 10 ml, 85 C, 1 h and 8.8 M H ₂ O ₂ , 10 ml, heated to dryness, and 1 M NH ₄ OAc, (pH = 2), 50 ml, 16 h
Residual aqua regia	(ISO 11466 (ISO 1999))

3 Results and discussion

3.1 Physico-chemical properties of the studied soils

The main physico- chemical properties of the soil samples are summarized in (Table3). The pH of MDN soils was slightly acid and ranged from 6.14 to 6.92, while the pH of LPF soils was acidic to slightly acid and ranged from 3.65 to 5.75, this could be because of the acid forming process occurring during mine tailing weathering producing acid mine drainage leading to the increase in hydrogen ion activity. Organic matter ranged from 8.26 to 13.84% and from 5.27 to 6.83% for MDN and LPF respectively. Organic carbon of both MDN and LPF ranged from 3.35 to 6.45% and 0.3 to 1.67% respectively. Total PTE concentrations for MDN site ($n=3$) were as follows: Zn (3111- 7721 mg kg^{-1}), Pb (879 – 3558 mgkg^{-1}) and Cd (53 – 72 mgkg^{-1}), while, total PTE concentrations for LPF site ($n=3$) were as follows: As (2677 – 83937 mgkg^{-1}), Pb (362 – 16100 mgkg^{-1}) and Sb (100 – 871 mgkg^{-1}). The concentrations of Zn, As and Pb are greater than: (i) the possible toxicity values (10 –300, 5–20 and 30–300 mg/kg , respectively; (Kabata-Pendias 2001; Kiekens 1995; McGarth and Loveland 1992) and (ii) the normal background levels given (e.g. 1 – 50 mgkg^{-1} for Zn, 1–30 mgkg^{-1} for As and 9–50 mgkg^{-1} for Pb (Wilson et al. 2010) for soils of diverse origins and lithologies throughout the world.

3.2 Soil mineralogical composition

As derived from the XRD analysis, there is no significant differences in mineralogical composition between the different soil samples are found for the LPF site. Surface soils in the studied former mining area are mainly constituted by silicate species such as quartz, muscovite, clinoclore, feldspar together with clay minerals such as illite, kaolinite and chlorite. The MDN surface soils are mainly constituted by quartz, muscovite, albite, dolomite, orthoclase and calisite.

3.3 Fractionation of the PTE

Results of the PTE fractionation in the studied soils for the different zones for the two sequential extraction schemes are shown in (Fig.1and Fig.2). The contents of these elements extracted in each steps of sequential extractions scheme are summarized in (Tables 4 and 5). In the Tessier' scheme the equivalent fraction used were T1 (Exchangeable fraction), T2 (Bound to carbonate), T3 (reducible (Fe-Mn oxide bound) fraction), T4 (oxidisable (organic/sulphide) fraction) and T5 (residual fraction). Whereas, in modified BCR scheme, the equivalent fraction used were B1 (acid soluble (carbonate bound) equivalent to (T1+T2)),

B2 (reducible (Fe-Mn oxide bound) fraction equivalent to T3), B3 (oxidizable (organic/sulphide) fraction), equivalent to T4) and B4 (residual fraction, equivalent to T5).

Table 3: Physicochemical characteristics of the soils and PTE total concentrations of the selected zones from Mortagne-du-Nord (MDN) and La Petite Faye (LPF)

Zone	pH	EC ($\mu\text{s cm}^{-1}$)	OM%	TOC%	CEC (cmol kg^{-1})	Zn	Pb	Cd
						(mg kg ⁻¹)		
MDN1	6.92	112	8.26	3.35	7.2	7721	3558	72
MDN2	6.35	112	10.28	4.39	8.5	3111	876	63
MDN3	6.14	113	13.84	6.45	6.7	3124	879	53
						As	Pb	Sb
LPF1	3.65	258	6.46	0.3	18.3	83937	16100	871
LPF2	4.93	200	5.27	0.47	39.7	37458	8536	498
LPF3	5.75	150	6.83	1.67	29.1	2677	362	100

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

3.3.1 MDN site

Zinc

Tessier's extraction scheme showed that Zn recovery was between 95.7% and 98.4% for all studied samples which can be regarded as acceptable in comparison with other studies (Hongyu Liu 2005; Rodriguez 2009). Zn was mainly associated with carbonate fraction and accounted for 38.2%, 31.1% and 30.3 % of total Zn for zones 1, 2 and 3 respectively (Fig.1a). The concentration of Zn in reducible fraction ranged from 25.8 to 28.3% of total Zn for all three zones. On average, the concentration of Zn in exchangeable fraction accounted for 17–21.7% and in residual fraction 14.3–17.2% for all studied zones. Data in (Fig.1a) indicate that general distribution of Zn into the various fractions for all studied zones followed the order: T2>T3>T1>T5>T4. This observation is in agreement with that of Pardo et al. 1990.

BCR extraction scheme showed that Zinc recovery was ranged between 96.1% and 99.7% for all studied samples. Zn distribution pattern in each fraction followed the order: B1>B2>B4>B3 (Fig.2a). About 53.4%, 42.2% and 48.8% of total Zn occurs in soluble fraction (B1) for zone 1, 2 and zone 3 respectively. 21.2 – 26.1% is distributed in reducible fraction, 18 –20 % is incorporated into silicate lattice, while fraction of Zn bound to oxidisable fraction represents less than 11% of total Zn for all studied samples. The first extraction step (B1) is important for this metal. A possible explanation for this is the presence of calcareous minerals, which act as a strong adsorbent for Zn in mine tailings (Anju 2010; Nannoni et al. 2011).

Collectively, both extraction schemes gave similar results for Zn. In fact the relative Zn associations, as provided by both extraction schemes are similar for all four equivalent fractions (i.e. acid soluble > reducible > residual > organic/sulphide bound) for all studied zones. Zn fractionation is dominated by acid soluble fraction. However it was observed that the amount of Zn extracted in acid soluble fraction by BCR scheme was higher than Tessier's scheme, as more Zn was extracted in (B2) by BCR scheme than by Tessier's scheme (T3).

Lead

Lead recovery in Tessier's extraction scheme ranged between 92% and 110% for all studied samples. The relative distribution of Pb among different fractions in zone 1 followed the order: T2≈T3>T4>T5>T1 (Fig.1b). It can be seen that Pb was mainly associated with carbonate and reducible fractions accounting for 31.4% and 30.8% respectively of total Pb content. Pb in zone 1 is shown to be strongly associated with carbonate fraction. This is coherent with thermodynamic prediction (Brookins 1988) that cerussite (PbCO₃) would be the dominant lead mineral at the Eh–pH conditions of mine tailing. Additionally CaCO₃ may act as a strong

adsorbent for Pb and could complex Pb as (PbCO₃) (Li and Thornton 2001). The next Pb fractions were oxidisable and residual which represents < 18% and <15% respectively.

The fractionation pattern of Pb in both zone 2 and zone 3 was: T3>T2>T4>T5>T1 (Fig.1b). This was comparable for the two zones, demonstrating that Fe-Mn oxide bound fraction (42.9%) for zone 2 and (32.8%) for zone 3 is the predominant fraction. Fe-Mn oxides are in fact important scavengers of metals in soils particularly at a high pH range (pH > 7.0) (Tipping et al. 1986). The remaining Pb content was distributed among carbonate, oxidisable and residual fractions represents < 29%, < 13% and <10 for zone 2 and < 21%, <26% and <13% for zone 3 respectively.

BCR extraction scheme showed a percentage recovery for Pb ranging between 97% and 113% for all studied samples. Pb association in zone1 followed the order: B1>B2>B3>B4 (Fig.2b), indicating that highest percentages of Pb were associated with acid soluble (32.6%), Fe-Mn oxide bound (28.9%), organic/sulphide (27.2%) and residual fraction (11%). In contrast Pb distribution among different fractions in zone2 and zone3 followed the order: B2>B3>B1>B4, indicating the relative importance of Fe-Mn oxide bound (33.7% and 30.6%) and organic/sulphide fraction (31.1% and 30.1%) for both zone 2 and 3 respectively. This finding is in agreement with that of Ramos et al. 1994; Romaguera et al. 2008; Zemberyova et al. 2006.

Fractionation results obtained for Pb from the two extraction schemes were also similar for all studied zones. The relative distribution of Pb in all four fractions was also similar. The most abundant fractions were acid soluble and Fe-Mn oxide bound. Again, a higher amount of Pb was extracted with reducible fraction by Tessier's extraction scheme compared to BCR scheme. In contrast for organic/sulphide bound fractions it was the opposite.

Cadmium

Cd recovery in Tessier's extraction scheme was ranged between 84% and 105% for all studied samples. The fractionation of Cd in each fraction followed the order: T1>T5>T3>T2>T4 (Fig.1c) for zone1 and 2, while it followed the order: T1>T2>T3>T4>T5 for zone 3, matching the usual distribution of this element in contaminated soils (Narwal et al. 1999; Sanchez et al. 1999; Kaasalainen and Yli-Halla 2003). Soil Cd was mainly associated with exchangeable fraction representing about 46.1%, 46.1 % and 37.64 % of total Cd for zones 1, 2 and 3 respectively. This fraction includes Cd held by electrostatic adsorption and specifically adsorbed. This fraction may be also called easily soluble and/or exchangeable. This form of Cd is considered more mobile and phytoavailable (Dudka and Chlopecka 1990). It can be seen that for the non- exchangeable fraction, the highest percentage of Cd 22.3% and 23.9% in zone1 and 2 was associated with residual fraction followed by Fe-Mn oxide bound,

carbonate bound and organic/sulphide fractions whereas, in zone3, the fractionation pattern revealed that Cd was most abundant in carbonate bound fraction and at least in organic/sulphide bound fraction.

Cd recovery in BCR extraction scheme was ranged between 93% and 110% for all studied samples. Cd fractionation for both zones1 and 2 decreased in the order: B1>B4>B2>B3 (Fig.2c). It can be further seen that for the majority of samples analyzed, Cd is distributed between acid soluble 53.5% and 45.8%, residual 16.8% and 31.6%, Fe-Mn oxide bound 15% and 17% and organic/sulphide 14% and 5.4% fraction for zones1 and 2 respectively. Cd distribution in zone3 was followed the order: B1>B2>B3>B4 (Fig.2c), indicating the relative importance of the acid soluble fraction followed by the Fe-Mn oxide bound, organic/sulphide and residual fractions.

The relative Cd associations, as revealed by both extraction schemes, are similar in all four equivalent fractions for all studied samples indicating the suitability and comparability of both methods for Cd. The fractionation is dominated by acid soluble fraction. It was also observed that more Cd was extracted in reducible (Fe–Mn oxide bound) fraction by Tessier's extraction scheme than by BCR scheme in B2. Again, more Cd was extracted in organic fraction (B3) by BCR scheme than by Tessier's scheme. However, for both methods Cd is extracted maximally in the most mobile phases.

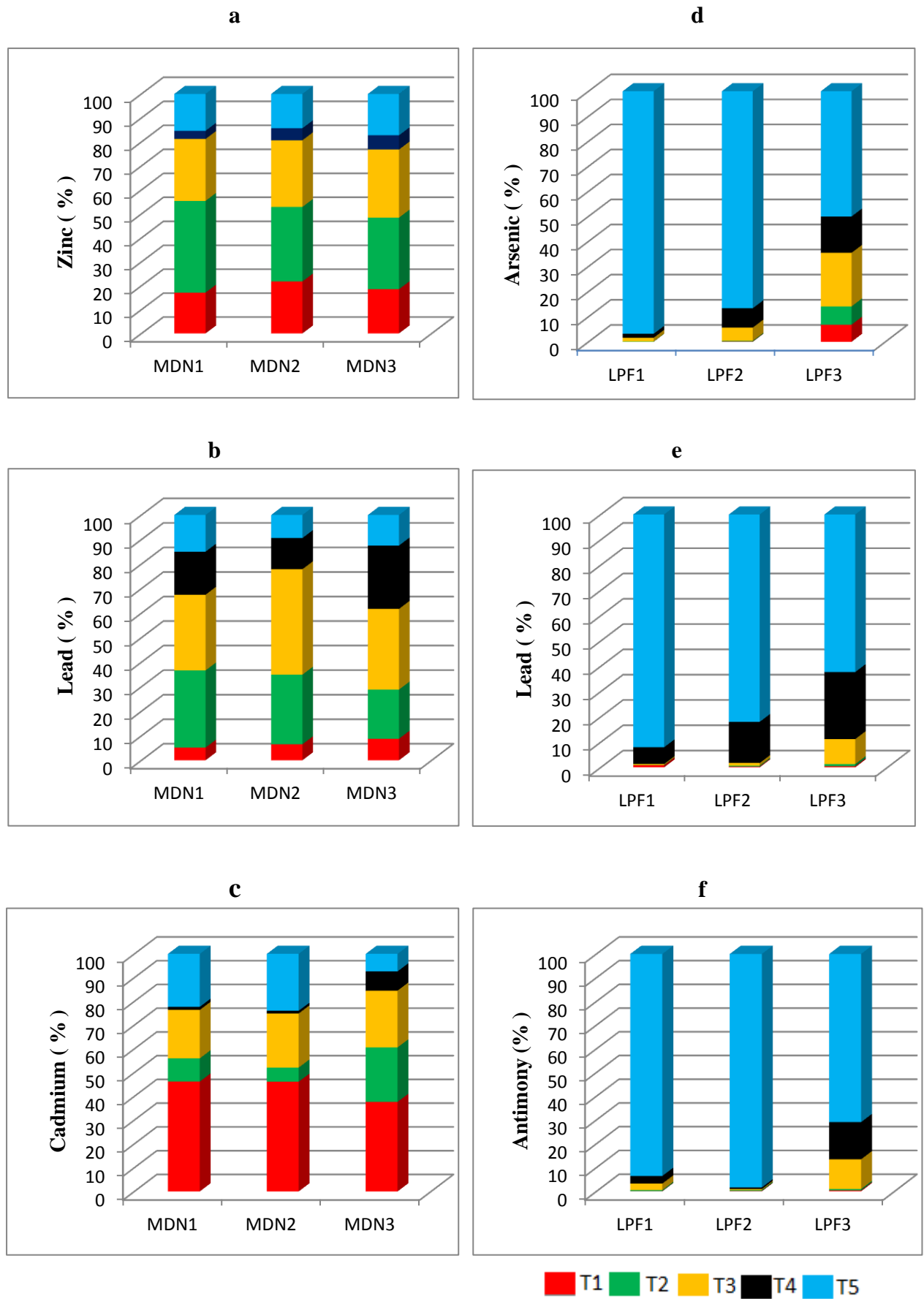


Fig.1: Chemical distribution of Zn (a), Pb (b and e), Cd (c), As (d), Sb (f) in the different soil fractions in MDN and LPF (Tessier's scheme): T1 (exchangeable), T2 (carbonates), T3 (reducible), T4 (oxidizable), T5 (residual).

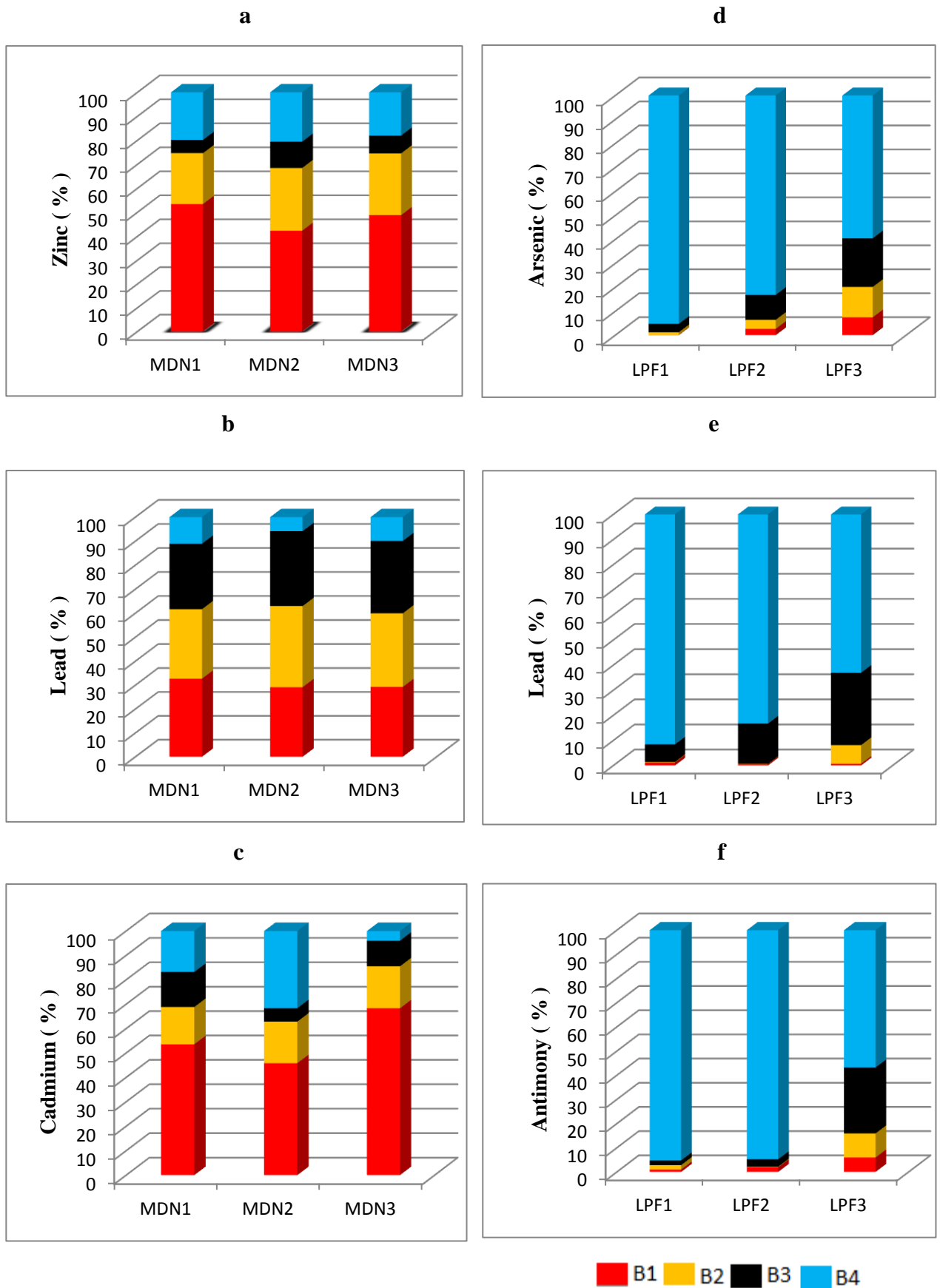


Fig.2: Chemical distribution of Zn (a), Pb (b and e), Cd (c), As (d), Sb (f) in the different soil fractions in MDN and LPF (modified BCR scheme): B1 (acid soluble), B2 (reducible), B3 (oxidizable), B4 (residual).

Table 4: Potentially toxic element fractionation in the different solid phases as obtained from the Tessier's scheme^a.

Zone	Exchangeable (T1)	Carbonate (T2)	Reducible (T3)	Oxidizable (T4)	Residual (T5)	% Recovery
<i>MDN1</i>						
Zn	17.12	38.28	25.8	3.42	15.36	95.77
Pb	5.19	31.43	30.86	17.54	14.97	96.8
Cd	46.19	9.78	20.41	1.3	22.3	84.55
<i>MDN2</i>						
Zn	21.77	31.11	27.78	5.01	14.31	97.73
Pb	6.52	28.37	42.97	12.7	9.41	110.25
Cd	46.13	5.95	22.79	1.13	23.96	86.83
<i>MDN3</i>						
Zn	18.53	29.91	28.36	5.92	17.25	98.41
Pb	8.8	20.01	32.89	25.82	12.46	92.4
Cd	37.64	23.91	22.95	8.1	7.36	105.43
<i>LPF1</i>						
As	0.01	0.09	1.49	1.57	96.82	99.51
Sb	0.09	0.42	2.72	3.21	93.53	91.93
Pb	0.83	0.09	0.39	6.62	92.05	98.33
<i>LPF2</i>						
As	0.11	0.28	5.26	7.69	86.63	99.27
Sb	0.16	0.37	0.41	0.7	98.33	90.14
Pb	0.32	0.35	1.05	16.25	82	92
<i>LPF3</i>						
As	6.81	7.27	21.32	14.51	50.07	97.07
Sb	0.36	0.58	12.48	15.62	70.94	88.47
Pb	0.45	0.83	9.89	26.5	62.31	87.46

^a All values are in percentages.

Table 5: Potentially toxic element fractionation in the different solid phases as obtained from the modified BCR scheme^b.

Zone	Acid soluble (B1)	Reducible (B2)	Oxidizable (B3)	Residual (B4)	% Recovery
<i>MDN1</i>					
Zn	53.44	21.2	5.51	19.48	95.77
Pb	32.69	28.94	27.27	11.08	105.1
Cd	53.56	15.28	14.34	16.8	93.44
<i>MDN2</i>					
Zn	42.29	26.15	10.93	20.61	97.73
Pb	29.14	33.79	31.17	5.88	113.39
Cd	45.84	17.03	5.48	31.63	96
<i>MDN3</i>					
Zn	48.80	25.75	7.39	18.04	99.71
Pb	29.22	30.69	30.12	9.95	97.14
Cd	68.31	17.21	10.49	3.97	110.1
<i>LPF1</i>					
As	0.11	1.11	3.49	95.27	99.7
Sb	0.98	1.84	1.91	95.26	93.72
Pb	1.19	0.22	6.97	91.61	94.92
<i>LPF2</i>					
As	2.62	3.8	10.39	83.17	99.05
Sb	1.9	0.27	3.04	94.77	96.36
Pb	0.51	0.13	16.04	83.3	98.01
<i>LPF3</i>					
As	7.43	12.72	20.29	59.54	93.89
Sb	5.96	9.97	27.24	56.8	90.75
Pb	0.65	7.45	28.79	63.08	91.49

^b All values are in percentages.

3.3.2 LPF site

Arsenic

Tessier's extraction scheme exhibits As recovery ranged between 97% and 99% for all studied samples. Data obtained during the sequential extraction steps carried out on soil samples of LPF site indicate that As was distributed in the order: T5>>T4>T3>T2>T1 (Fig.1d) for all three zones. Results showed that in zone1 more than 90% of As was distributed in residual fraction, while, in zone2 and 3 it represents more than 80% and 50% respectively of total As content. The majority of As remained from residual fraction was distributed among other different fractions. The sum of As extracted in fractions T1, T2, T3 and fraction T4 was almost negligible for zone1 and 2 samples, whereas, in zone 3, Fe-Mn oxide and organic/sulphide fractions represent 21.3% and 14.5% respectively.

As recovery by BCR extraction scheme ranged between 93% and 99% for all studied samples. More than 90% of total As was bound to residual fraction in zone1, while both zone 2 and 3 represents 80% and 60% respectively of total As content. The other fractions showed a lower As content, especially for B1 and B2 which showed less than 1% of total As content. In contrast zone 3 presents 7.4 and 12.7 % for B1 and B2 respectively. As was concentrated in residual fractions (Fig.2d), which in term of mobility may be considered immobile. The important quantities of As in residual fraction were in agreement with results of other studies investigating the distribution of this element in contaminated soils (Fernandez et al. 2004; Novoa-Munoz et al. 2007; Pueyo et al. 2008). The distribution of As into soil fractions B4>B3>B2>B1 did not change significantly as a function of contamination level; nevertheless, the anthropogenic input mainly affected residual and reducible fractions.

It can be seen that fractionation results obtained from the two methods were similar (Table 2), the most abundant fraction being the residual fraction. Despite of the highest As contents leached from residual fraction, it can be seen that percentage of As extracted by Tessier's scheme for reducible fraction is little higher than that of BCR scheme, while As extracted in oxidisable fraction of BCR scheme was higher than that extracted in Tessier's T4 (oxidisable) fraction.

Antimony

In Tessier's extraction scheme, Sb recovery ranged between 88% and 91% for all studied samples. Sb was largely distributed in residual fraction accounting for 93.5%, 98% and 70.9% for zones1, 2 and zone 3 respectively. Results showed that highest percentage of Sb was associated with residual fraction which represents metal bound to crystalline phase, followed by oxidisable fraction which represents metal bound to organic/sulphide fraction with a

percentage of (0.7 - 15.6 %) for each three zones. Sb amount relate to other fractions was very low and represents less than 3% for all zones. In all three zones, the distribution of Sb into various fractions was as follows: $T5 \gg T4 > T3 > T2 \approx T1$ (Fig.1f).

BCR extraction results showed a suitable Sb recovery ranged between 90% and 96% for all studied samples. More than 90% of total Sb was found to be bound with refractory minerals in residual fraction in zone 1 and 2, while zone 3, represented only 57% of total Sb content. Sb distribution followed the order: $B4 \gg B3 > B2 > B1$ (Fig.2f). This finding is in agreement with that of Alvarez-Ayuso et al. 2012; Nannoni et al. 2011, which they found that more than 90% of Sb was partitioned in residual fraction in former mining sites. In non- residual fraction, the highest percentage of Sb (27.2%) in zone 3 was associated with organic /sulphide fraction (B3), while in zones 1 and zone 2 it represents less than 2% and 1% respectively. Reducible fraction represents less than 10% in zone 3 and less than 2% in zones 1 and zone 2.

It can be seen that a uniform fractionation pattern (residual > organic > oxidisable > reducible > exchangeable) was observed for Sb by both extraction schemes. The most abundant fraction was residual bound; amount of Sb extracted in reducible fraction by Tessier's method was in general higher than that by BCR scheme. However, more Sb was extracted in B3 fraction than in T4 (oxidisable) fraction.

Lead

Pb recovery in Tessier's scheme was ranged between 87% and 98% for all studied samples. It was apparent from the preliminary Tessier's sequential extraction procedure that most of Pb was mainly associated with residual fraction accounting more than 90% of total Pb content in zone 1, while it represents 82% and 62% for zones 2 and 3 respectively. Pb distribution in both oxidisable and reducible fractions was variable for all zones accounted 6.26 to 26.5% for oxidisable fraction and 0.39 to 9.89% for reducible fraction in all zones. The low amount of Pb was associated with T1 and T2 fraction representing less than 1% for all zones. Despite the variability in total concentrations, Pb in all zones showed a similar distribution into various fractions: $T5 > T4 > T3 > T2 > T1$ (Fig.1e). The high percentage of Pb in residual fraction is in broad agreement with that observed by Paulo et al. (2011) in soil contaminated by mining activity. The input of Pb in contaminated soils was redistributed among various soil fractions, with highest enrichment in residual and reducible fractions.

BCR extraction scheme exhibits Pb recovery ranged between 91% and 98% for all studied samples. The relative distribution of Pb in different soil fractions followed the order: $B4 \gg B3 > B2 > B1$ (Fig.2e). This fractionation pattern revealed that Pb was most abundant in residual fraction showing a comparable percentage with that of Tessier's scheme. The amount of Pb distributed in oxidisable fraction was ranged between 6.9 to 28.7%, while, it represents

0.22 to 7.45 % in reducible fraction for all zones. T1 and T2 also showed lowest Pb percentages < 1%. Pb partitioning indicates that this element is rather stable, since it is mainly associated with residual fraction.

It can be seen that the distribution of this metal among different equivalent fractions is similar for the two methods. Also, the extracted amounts of Pb in the two schemes are slightly comparable. Pb content in oxidisable fraction extracted by BCR scheme was slightly higher than those of Tessier's scheme. Despite the analogous pattern in all fractions, fractionation by both extraction schemes substantiate that acid soluble bound fraction is the least abundant for all zones.

3.4 Potential mobility of PTE in the technosoils

The knowledge of the mobility and bioavailability of PTE depends not only upon the total concentration but also upon the chemical form of the PTE. In fact little information is provided by the total soil concentration. For instance of more soluble metal compounds are more mobile and toxic (Kwon et al. 2001). On the other hand, the first extraction steps in any sequential extraction procedure represent the most mobile and bioavailable fractions and may provide useful information about the PTE.

The order of mobility of PTE considering their abundance in different soil fractions followed the order: exchangeable > bound to carbonate > bound to Fe-Mn oxide > bound to organic matter > residual fraction (Tessier et al. 1979). Exchangeable elements are a measurement of those elements which are released most readily into environment under acidic conditions and may be considered the most dangerous fraction to environment (Stone and Marsalek 1996). Changes in ionic composition, influencing adsorption-desorption reactions or lowering of pH could cause remobilization of these PTE from this fraction (Ure 2001; Marin et al. 1997; Sutherland 2000). PTE bound to Fe-Mn oxides that would be released under reducing conditions represent the reducible fraction. These oxides are well known "sinks" in the surface environment for these elements (Baruah et al. 1996b) and are thermodynamically unstable under anoxic conditions (Tokalioglu 2000). PTE bound to organic matter / sulphides would be released under oxidizing conditions and thus represent the oxidisable fraction. PTE associated with oxidisable phases are assumed to remain in the soil for a longer period but may be mobilized by decomposition processes (Kennedy et al. 1997). Residual fraction represents the elements that have the strongest association with crystalline structures of the minerals and are therefore the most difficult to mobilize.

The determination of PTE mobility in soils is based on the relative amount of the metal in exchangeable fraction (T1) containing the mobile forms and in carbonate bound fraction (T2)

containing easily mobilisable phases. The mobility index of PTE was calculated as the mobility factor (MF) based on the following equation by (Kabala and Singh 2001; Narwal et al. 1999; Salbu et al. 1998):

$$MF = \frac{(T_1 + T_2)}{(T_1 + T_2 + T_3 + T_4 + T_5)} \times 100$$

Consequently, the mobility factor value determines the relative mobility and biological availability of PTE in the soil. On this basis high mobility factor (MF) values have been reported or interpreted as evidence of relatively high reactivity, high lability and high biological availability of PTE in soil (Karczewska 1996; Ma and Rao 1997).

On the basis of the MF values, the average mobility of PTE in the studied soil samples is shown graphically in Fig.3 and 4 to help compare the MF values of PTE in each studied sites. On average, the potential mobility of Cd was 52.89 % for MDN studied samples. Cd can be considered the most mobile element, as about half of its total content was in exchangeable fraction. The relationship between Cd concentrations in exchangeable fraction and carbonate content suggest that a substantial portion of Cd was contained in minerals such as calcite (in which Cd may replace Ca). As an overview of the study area, the fractionation data indicate a high mobility and bioavailability of Cd. The results are in accordance with those obtained by Kapusta et al. 2011 and Vaněk et al. 2005, indicating that Cd is the most mobile of the three metals tested (Cd, Zn, Pb).

The average potential mobility factor of Zn was 42.24%. Under reducing and acidic conditions, Zn will easily be mobilized to the environment. Therefore compared with other PTE they were mostly abundant in the residue fraction. Thus Zn was more available and potentially toxic in the environment. Part of Zn was likely related to carbonates such as Zn-rich calcite and/or smithsonite ($ZnCO_3$). Other acid-soluble minerals affecting the occurrence of Zn in acid soluble fraction could be sulphates ($ZnSO_4$) and oxide-sulphates [$ZnO \cdot ZnSO_4$; $Zn(OH)_2 \cdot ZnSO_4$], whose presence was commonly detected in contaminated soils collected in mining and smelting areas (Li and Thornton 2001).

Potential mobility of Pb in MDN and LPF zones were 33.44% and 0.66 % respectively. Change in the concentration was low because Pb in soil in this environment was relatively immobile. It could be noted that any change to anoxic soil conditions (e.g. caused by water-flooding) could mobilize significant amounts of adsorbed Pb through the destabilization of the Fe–Mn oxyhydroxide lattices. Many researchers referred to that Pb in acid soluble fraction of the most contaminated soils was mainly in carbonate phases such as cerussite ($PbCO_3$) and

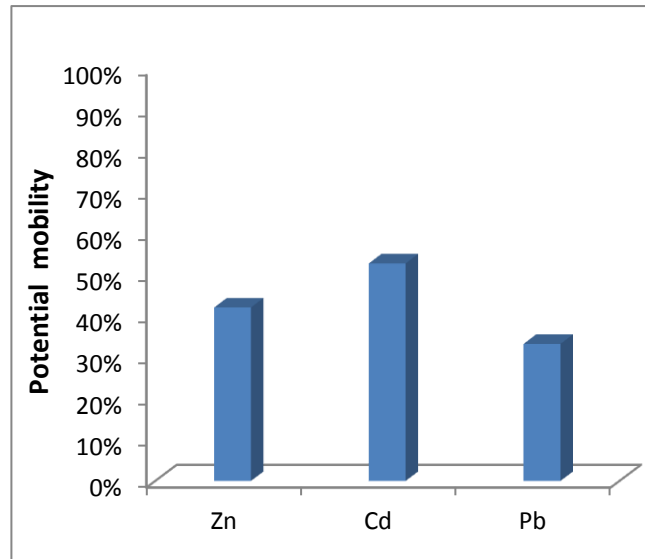


Fig.3: Potential mobility of the potentially toxic elements from the MDN site

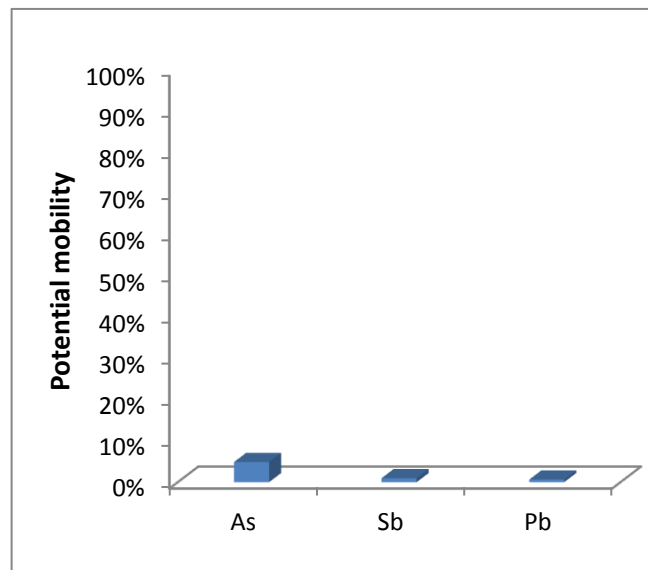


Fig.4: Potential mobility of the potentially toxic elements from the LPF site

hydrocerussite $[Pb_3(CO_3)_2(OH)_2]$ which therefore play an important role in the mobility and bioavailability of this element (Clevenger et al. 1991; Ettler et al. 2009).

The average potential mobility factor of As was 4.86 %. In our site, As can be considered a rather immobile element as most of this metalloid is bound to the residual mineral fraction. The chemistry of arsenic precipitation–dissolution and adsorption–desorption is complex and depends on the charge of the absorbing species and the soil surface characterization. The

results for arsenic fractions should reflect the geochemical behavior of arsenic in the surface environment. In our study on sequential extraction of arsenic from contaminated technosoils, we found that only a very small proportion of arsenic was extracted in the early fractions compare to the total arsenic content for both extraction schemes. However, high concentrations of arsenic found in residual fractions indicate that arsenic present in these soils is difficulty released by chemical extractants from the first steps of the schemes. The important quantities of As in residual fraction were in agreement with the results of other studies investigating the distribution of this element in contaminated soils (Filippi et al. 2004; Ghosh et al. 2004; Matera et al. 2003).

Sb potential mobility factor in the LPF zones was 0.96 %. Similar to arsenic, Sb distribution into the soil fractions indicates that this element was rather immobile in the contaminated soils as being largely present in residual fraction. In a recent study on sequential extraction of Sb from contaminated soils, Tighe and Lockwood 2007; He 2007; Denys et al. 2008 found that a large amount (up to 90%) of Sb was associated with the residual fraction. In general, a number of similar general trends in As and Sb fractionation in soil are evident. These include the low mobility of both As and Sb and the high proportion of both metalloids associated with the residual fraction depending on metalloid source. Metalloid associated with the crystalline and non-crystalline oxide and hydroxide minerals is often assumed to be immobile (Filella et al., 2009).

4 Conclusion

This study aimed to evaluate the soil fractionation of of Zn, Pb, Cd, As and Sb in selected technosoils of two PTE contaminated sites.

The percentages of Zn, Pb, Cd, As and Sb extracted in Fe–Mn oxide bound fraction of Tessier's scheme were always higher than those extracted by modified BCR scheme. In contrast the percentages of Zn, Pb, Cd, As and Sb extracted in organic fraction of modified BCR scheme were always higher than those of Tessier's scheme.

Zn, Pb and Cd from MDN technosoils were distributed in all fractions, with greatest enrichments in acid soluble fraction in the case of Cd. The results showed that PTE from LPF zones have the highest abundance in residual fraction. This indicates that the PTE were rather immobile. The largest proportions for As, Pb and Sb were extracted in residual phase, in which PTE are strongly retained in soil minerals. This shows that the environmental risk of these PTE may be limited. However, the relatively high PTE content in LPF zones may represents some indirect environmental risk due to clay dispersion, and disaggregated soil particles bearing PTE may eventually reach and accumulate in ground waters and food chain.

The order of mobility in technosoils was: Cd>Zn>Pb in MDN zones and As>Sb>Pb in LPF zones. The mobile and potentially bioavailable pools of these heavy elements were considerably higher in contaminated soils with respect to uncontaminated ones. In MDN zones, Cd, Zn and Pb can be considered the most mobile elements and potentially available to the biosphere, representing therefore a more significant environmental risk than Pb, Sb and As in LPF zones. The quantity of mobile and potentially bioavailable PTE in MDN soils could threaten the quality of crops, with the real risk that these elements enter the food chain. The partitioning patterns of PTE in soils of this region will therefore be a sound basis for studies focusing on soil organisms (such as earthworms), cultivated and wild vegetables and the safety of food stuffs. Comparison of both sequential extraction schemes indicates that the results are only empirically defined and are not totally exclusive to the specified mineral phase.

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