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Lability of potentially toxic elements in soils affected by smelting activities

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H I G H L I G H T S

- ▶ Soils exceeded both alert and intervention limits for Pb, Cd, Cu and Zn.
- ▶ SBET extraction results show greater values than those obtained for EDTA extraction.
- ▶ The sum of exchangeable and reducible can be correlated the bioaccessible content.
- ▶ During flooding, metals became more mobile because of reducing conditions.

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Determination of total concentration of potentially toxic elements (PTEs) in soil is not a reliable tool for evaluating potential exposure risk for humans. PTE lability (EDTA, SBET and solution extraction) and chemical speciation (BCR sequential extraction) were investigated for Pb, Cd, Cu, and Zn, as well as how these could be affected by flooding in soils polluted by smelting activities.

The flooding experiment was performed in pots from which soil solution was extracted at different time intervals using Rhizone Moisture Samplers. After experiments, the soil was again subjected to the previous extractions (EDTA, SBET, and BCR) in order to reveal the changes which occurred during anoxia. From the results we can conclude that PTE lability is very high and flooding caused the increase in their mobility up to 100% (for bioaccessible Pb). The experiment demonstrated that temporary reducing conditions can increase the risk of contaminants passing to other environmental compartments and the food chain.

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1. Introduction

Soils have multiple roles in the ecosystems, so they contribute directly or/and indirectly to the quality of life (Abrahams, 2002; Ajmone-Marsan et al., 2008), therefore, it is important to gain information about their pollution status (Poggio et al., 2008). Since the industrial revolution, anthropogenic actions have caused great damages to the environment, because the social and economical development has led to a dramatic increase in the amount of pollutants discharged (Wong et al., 2006; Tandy et al., 2009). The attention of the scientific community has been focused especially on soil because it is a very dynamic system that fulfills many functions and is vital to human activities and ecosystem survival. Soil, due to its buffer capacity, may contain a variety of pollutants, representing the main route for transfer of contaminants to animals and humans (Singh, 1997).

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Among the others pollutants, potentially toxic elements (PTEs) are one of the major causes of concern, as their persistence is high (Alloway, 1995; Sharma et al., 2009; Hernández-Soriano et al., 2010), as well as their capacity of bioaccumulation (Filgueiras et al., 2002), especially because PTE from anthropogenic sources are more mobile than the native ones (Kaasalainen and Yli-Halla, 2003).

Metalliferous smelting processes are some of the most studied pollution sources because of the high concentration of PTE whose mobility is enhanced by soil acidity which may pose an environmental hazard for surrounding ecosystems (Favas et al., 2011).

Metals are neither created nor destroyed by biological and chemical processes, but may be biotransformed from one chemical species to another.

In order to evaluate the risk for humans exposed to this type of hazard, it is not sufficient to determine the total concentration of PTE in soil because it provides little information about their lability (Ahnstrom and Parker, 1999; Davidson et al., 2006). Therefore, recent attention of scientists has been focused on investigation of PTE speciation in soil. It is now widely recognized that the lability

of a PTE (total concentration, accessible and hydrated ions) (Pickering, 2002) can be evaluated by determining the chemical fractions of these elements in soil, but also through other methods aimed at identifying specific species (Kabala and Singh, 2001; Zheng and Zhang, 2011).

Once in the soil, PTE are adsorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bioavailability, mobility, and toxicity (Shiowatana et al., 2001; Wuana and Okieiem, 2011). In most chemical species, toxicity of studied PTE is high, for example, lead and cadmium were classified as substances of very high concern, being probable human carcinogens (European Parliament and Council Regulation, 2006), even if the quantities emitted in the environment decreased in recent decades.

The risk that PTE are being transferred to other environmental compartments is related to their physico-chemical properties but also to the possibility that the sinks that hold them into the soil are altered. For example, in case of an abrupt change in the red-ox condition in the soil, Mn and Fe oxides would be solubilized and the PTE that are coprecipitated or adsorbed on their surface would be released to the soil solution (Martinez and McBride, 2001; Zheng and Zhang, 2011). During red-ox processes conducted in soil columns, Green et al. (2003) observed that Zn leaching was highly correlated with that of Mn. The results of Contin et al. (2007) indicated that red-ox cycles applied to Fe-rich olive mill waste reduced the bio-availability of PTE through fixation into iron oxides, with greater mobility during the early reduction stage. Grybos et al. (2007) showed that the fate of various PTE was directly linked to that of Fe and Mn in soil nodules which act like a sink for trace elements excepting Pb which was not released, but was probably re-adsorbed on nodule surfaces. Similarly, Du Laing et al. (2009) reported that Fe and Mn oxides were the main carriers of Cd and Zn under oxic conditions. Also, Weber et al. (2009) found that PTE accumulated in floodplain soils can be released during periods of flooding through the reductive dissolution of Fe and Mn oxides, while Gasparatos (2012) observed that formation of Fe–Mn concretions and nodules is the most efficient and durable process for PTE sequestration in soils. In fact, iron behavior in changing red-ox environments has been used for choosing soil remediation technologies (Cundy et al., 2008; Wang, 2009). So, among all the parameters, soil physico-chemical characteristics, climate, pollution duration and intensity play the most important role in PTE mobility.

The aim of this study was to determine PTE lability (for Pb, Cd, Cu and Zn) and to evaluate how it is influenced by changes in red-ox conditions in highly polluted soils. The necessity of the study was underlined by the little knowledge about the fate of the PTE in these soils while the possibility for them to undergo submersion, being near a river, is not unlikely. The paper aimed to show the utility of all the used tools and to show that each one is useful in its way. No one can substitute others, and all of them help in drawing a general image of the pollution status.

2. Materials and methods

2.1. The studied area

Zlatna is a relatively small city in Romania (25 000 ha), located at an altitude of 415 m in the “Metaliferi” (metal-bearing) Mountains which are rich in mineral resources. Sulphide ores, mainly contained in Alpine magnetite associated with sedimentary Cretaceous rocks were extracted for centuries from this area (Pope et al., 2005).

The non-ferrous metal ore smelter from Zlatna has caused great damages to the environment because of the dispersion of large PTE quantities in the surroundings (2715 tones of particulate matter – Pb: 44%, Zn: 26%, Cu: 21% – per year) which led to its closure in 2004 (Rusu et al., 2006). The environmental investigations performed by National Environmental Protection Agency (ANPM, 2007) stated that the accumulation of PTE in soil caused soil acidification and structure degradation, bringing about a reduction of the levels of nutrients (especially phosphorus) followed by a decrease of vegetation cover, which in turn causes soil erosion and eventually landslides.

In this area, the soil is sandy loam and the climate is continental. Soils are mostly used for agriculture and pasture, being covered by vegetables and grass, they generate a high risk of transfer of contaminants to the food chain. The main pathways for the PTE to reach the receptor are via inhalation or ingestion of soil, plants and water, each pathway being more harmful for an element than for the other. The extension of the contamination makes it difficult to prioritize the areas which must be remediated and strongly requires studies to assess the potential transfer of contaminants from soils to receptors.

In Fig. 1, an overview of the study area is shown. It can be observed that the city (Zlatna) and the smelter are close to each other. Because they are located in a valley, the geographical position hampers the dispersion of contaminants. Also, until 2010, the slag heap located near the preparation plant was uncovered, which led to a smelter post-closing pollution. Consequently, in the area, the PTE in soil are up to four times higher than intervention limits set by National Legislation (Popescu et al., 2011).

2.2. Soils

In order to evaluate PTE lability, a set of two types of soil was sampled: a pasture (at 0–10 and 10–20 cm depth) and a garden (0–20 cm). The pasture soil was collected at two depths because two main soil layers were evident, while the garden soil was sampled at one depth because of the uniformity caused by agricultural practices (ploughing). Each sample of 5 kg was composed of five subsamples disposed in the corners and in the middle of a square with the area of 400 m². Sampling sites were chosen along the main wind direction, at a distance of about 200 m from the border of the pollution source (smelter), downwind both slag heap and smelter area. The sampling sites were also selected considering their position which is below the average altitude level of surroundings, increasing the probability of standing water as a consequence of heavy rains. The reason for choosing only two areas for this study was that preliminary investigations for Pb, Cu and Zn concentration in soil showed a classic point source pollution pattern (Rusu et al., 2006).

Samples were collected with plastic tools, stored in HDPE bags, immediately taken to the laboratory where they were air dried (40 °C), gently crushed in ceramic mortar and sieved to 2 mm (ISO 11464, 2006). The samples were characterized for pH (ISO 10390, 1994), texture (Burt, 2004) cation exchange capacity (ISO 13536, 1995), organic carbon and total nitrogen (ISO 10694, 1995). Aqua regia, available (EDTA-extractable), oral bioaccessible (SBET method) and soluble Cd, Cu, Pb, and Zn contents were determined for all the samples. Chemical forms of PTE were determined through BCR-modified sequential extraction procedure (Rauret et al., 2000).

2.3. Pseudo-total content of PTE

Aqua regia extractable contents were obtained by microwave-assisted digestion of 0.5 g of dry soil in 10 mL of extractant (HCl:HNO₃ in ratio 3:1) (ISO Standard 11466). The solution was



Fig. 1. Sketch map of Zlatna area.

analyzed by flame atomic absorption spectrometry with a Perkin–Elmer AAnalyst 400 using monoelement tubes. Analytical determinations were carried out in triplicate and the standard solutions used were provided by CertiPUR by MERK.

2.4. Bioavailability of PTE

The EDTA extractable contents were obtained according to the method used by Lakanen and Erviö (1971) from subsamples of 5 g of soil extracted with ethylenediaminetetraacetic acid (pH = 4.65 with CH_3COOH) for 2 h at room temperature with continuous shaking. The mixture was centrifuged, and the supernatant was filtered through Sartorius biotech 388 filter paper. The PTE concentrations were also analyzed by flame atomic absorption spectrometry with a Perkin–Elmer AAnalyst 400 using monoelement tubes and the analytical determinations were carried out in triplicate.

2.5. Bioaccessibility of PTE

Bioaccessible forms were determined by SBET method (Simple Bioaccessibility Extraction Test) according to Ruby et al. (1996). The digestion was performed as follows: 50 mL of Glycine (0.4 M; pH = 1.5 with conc. HCl) were added to 0.5 g of dry soil. The mixture was rotated end-over-end at 30 rpm for 1 h, then transferred into a disposable syringe and filtered through a 0.45 μm regenerated

cellulose syringe filter. All the determinations were carried out in triplicate and the extractant was analyzed by flame atomic absorption spectrometry with a Perkin–Elmer AAnalyst 400.

2.6. Sequential extraction of PTE

The four steps BCR Procedure developed by Rauret et al. (2000) for soils with a high content of iron was used for the study. In the first step the exchangeable and water and acid soluble metals were extracted with acetic acid, in the second step the reducible metals were extracted with hydroxylamine sulphate, in the third step the oxidisable metals were extracted with hydrogen peroxide, and in the last step the metals bound to sulphides were extracted with ammonium acetate. After BCR extraction, the residual fraction was microwave digested with Aqua regia in order to calculate the recovery rate of this technique. For this procedure, a Refrigerated Centrifuge 4227R ALC, an Universal Table Shaker 709 and a Thermostated Waterbath from High Technology of Scandinavia were used. For all the extractions, PTE concentrations in solution were analyzed by flame atomic absorption spectrometry (Perkin–Elmer AAnalyst 400) using monoelement tubes because this technique has extremely high sensitivity and the detection limits are 10 ng mL^{-1} for Pb, 1 ng mL^{-1} for Cd, and 2 ng mL^{-1} for Cu and Zn. Analytical determinations were carried out in triplicate and all reagents were of analytical grade provided by Fulka, Sigma–Aldrich and Baker. The standard solutions used were provided by

CertiPUR by MERK. The 142R Certified Reference Material (CRM) was used and included in every batch of analyzes for quality control and the results were accepted for 10% standard deviation of the CRM.

2.7. Experiments under moist and flooded conditions

In order to evaluate the likelihood that PTE pass from soil to soil solution under reducing conditions, an experiment was conducted in oxygen free glass vials. The soil:water ratio was 1:10 (1 g of soil and 10 mL of distilled water) and anoxic conditions were obtained by purging nitrogen in the vial before its closure. The supernatant was extracted at 1, 3, 7, 14 and 21 d with a plastic syringe, filtered through a 0.45 μm regenerated cellulose syringe filter and analyzed for Pb, Cd, Zn and Cu in the same manner as the previous analyzes.

Pot experiments were also set up with soil at field capacity moisture and flooded for evaluating the changes in PTE lability which can occur in normal and under reduction conditions. The solution from pots was extracted with inert Rhizon Moisture Samplers (RhS) (Rhizosphere Research Products, The Netherlands). RhS were selected because they are suitable for long-term leaching laboratory experiments (Sigfusson et al., 2006). Each pot contained 500 g of soil sieved at 2 mm and in the middle of each pot was horizontally introduced a RhS for the extraction of the soil solution. The experiment was performed at field capacity moisture level and under flooding conditions. All pots were set up in triplicate. For simulating flooded conditions, the water was kept at 1 cm above the soil level. Soil solution was extracted through RhS with a 20 mL plastic syringe after allowing the system to equilibrate for 1 d, at 1, 3, 7, 14 and 21 d. The same RhS was left in place during the whole experiment in order to not disturb the system.

EDTA and SBET extractions were performed on soil at $t = 0$ (beginning of the experiment) as well as after each sampling time ($t = 1, 3, 7, 14$ and 21 d). These soil analyzes were performed after decanting the supernatant and drying the vials at 40 °C. The supernatant was filtered through a cellulose syringe in order to determine the PTE concentration by the same method used for the previous analyzes.

3. Results and discussions

In Table 1S, the general characterization of pasture soil (0–10 cm – P1 and 10–20 cm – P2), and vegetables garden soil (0–20 cm – VG) is reported.

While there is homogeneity in texture, organic carbon appears to accumulate in the upper layer. The higher cation exchange capacity was found for the pasture soil, especially in the 0–10 cm layer. Also, there are pH differences of one unit between pasture and vegetable garden soil.

In Table 1, the pseudo-total contents of metals in the studied area confronted with Romanian National alert and intervention limits (Ord. 756/1997) are presented.

Soils at depth 0–20 cm exceeded both the alert and the intervention thresholds for Pb, while for Cd, Cu and Zn concentrations

Table 1
Pseudo-total PTE concentration.

Type of soil	Pb	Cd	Cu	Zn
	(mg kg ⁻¹) Soil			
P1	4000	9.9	1191	1564
P2	430	1.8	135	383
VG	1288	3.8	335	800
Alert limit ^a	50	3.0	100	300
Intervention limit ^a	100	5.0	200	600

^a Limit for sensitive uses according to National Legislation.

Table 2
Available content of PTE (percentage of pseudo-total content).

Type of soil	Pb (%)	Cd (%)	Cu (%)	Zn (%)
<i>EDTA</i>				
P1	49	40	78	57
P2	25	25	38	44
VG	58	37	47	57
<i>SBET</i>				
P1	79	83	50	53
P2	17	51	38	34
VG	53	81	48	50

were above both limits only at 0–10 cm. According to the National Legislation, immediate remediation actions would therefore be required.

In Table 2 results are reported for EDTA and SBET extractable content of PTE. The values are calculated as percentage of pseudo-total contents shown in Table 1. In general, PTE pseudo-total concentration in VG soil is lower than in P soil considering the average of P1 and P2, probably because of the high phytoextraction capacity of vegetables, or/and the dilution of contaminants brought about by ploughing operations.

Results show that a large proportion of all PTE is in an available form for plants and not only. The upper layer of the pasture soil shows higher values than the deeper one for all PTE, indicating that the accumulation occurred on the soil surface and that the risk of transfer along the food chain is particularly high. The large amount of plant-available Cu is in line with its affinity for organic matter, abundant in this soil. Also, this behavior can be explained by the existence of complex salts of Cu which can be very mobile. For plants, Cu is an essential element, but excessive available concentration in soil can be phytotoxic and represent a threat for humans who consume them (Hernández-Soriano et al., 2010; Guan et al., 2011). Also, the other PTE represent a threat for humans because 58% of pseudo-total content of Pb from the vegetables garden is available to plants and Cd and Zn plant-available contents in the upper layer of pasture soil are higher than the alert limit.

The SBET extraction results showed greater values than those obtained for EDTA, in concordance with data reported by Madrid et al. (2008). The highest human bioaccessibility is observed for Pb and Cd, making these two PTE of big concern if ingested. The bioaccessible soil Pb is reported in the literature to reach elevated values (89%) (Luo et al., 2011). For the deeper layer of pasture soil, Cu has a greater bioaccessibility than expected, according to the plant-available content, presumably because the organometallic complexes from the upper soil dissociate slowly, facilitating Cu leaching. Among the studied PTE, Cu and Zn have the highest lability in soil (Florido et al., 2011) and are most likely to be transformed in other species in soil (Zheng and Zhang, 2011).

In Table 3, results of BCR sequential extraction for the soils before flooding are presented, expressed as percentage of the pseudo-total PTE content which is the same with the sum of the extracted content because the last step of BCR extraction was Aqua regia microwave assisted digestion.

The very high proportion of Cd and Zn in the exchangeable fraction confirms the potential risk associated to these contaminants. Pb and Cu are in small amount contained in exchangeable forms and in large amount in reducible forms, while for Cd and Zn the proportion between exchangeable and reducible is equivalent. The enrichment of Pb in the reducible fraction can be explained by its affinity to Fe and Mn oxides (Poggio et al., 2008). Although there are some differences in PTE distribution among the fractions in the studied soils, the potential mobility of all PTE appears to be high, showing a certain risk of release to other environmental compartments. The sum of the exchangeable and reducible is very

Table 3
PTE fractionation (percentage of pseudo-total content).

Type of soil	Fractions	Pb (%)	Cd (%)	Cu (%)	Zn (%)
P1	Exchangeable	7	47	10	39
	Reducible	86	38	44	36
	Oxidisable	5	2	19	6
	Residual	2	13	27	20
P2	Exchangeable	5	39	11	30
	Reducible	80	30	48	30
	Oxidisable	5	2	6	10
	Residual	10	29	35	30
VG	Exchangeable	8	64	7	23
	Reducible	84	23	36	23
	Oxidisable	4	2	9	5
	Residual	4	11	20	17

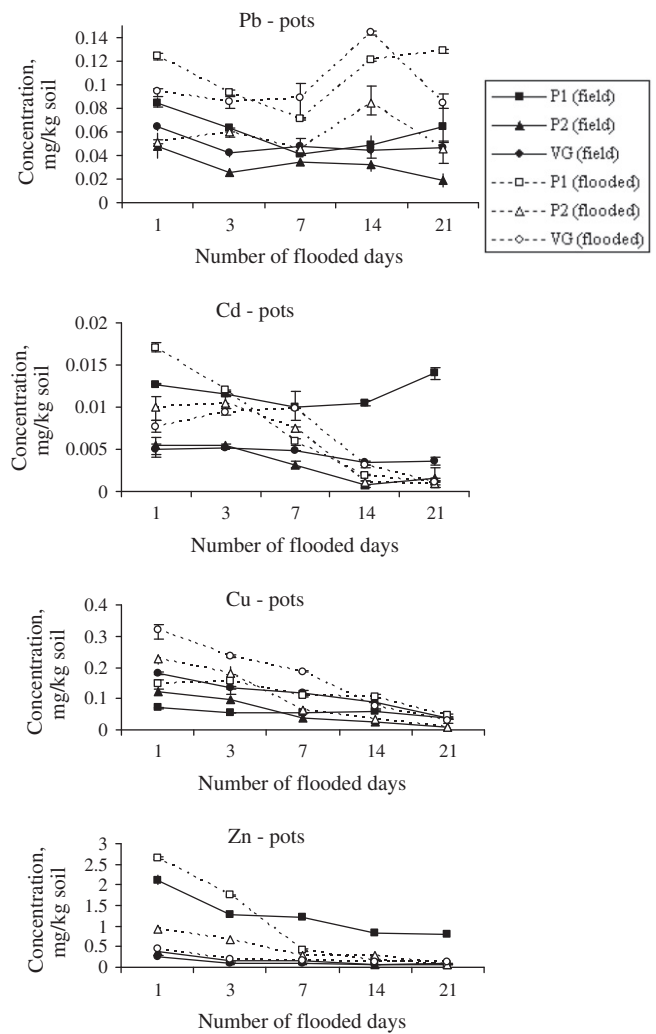
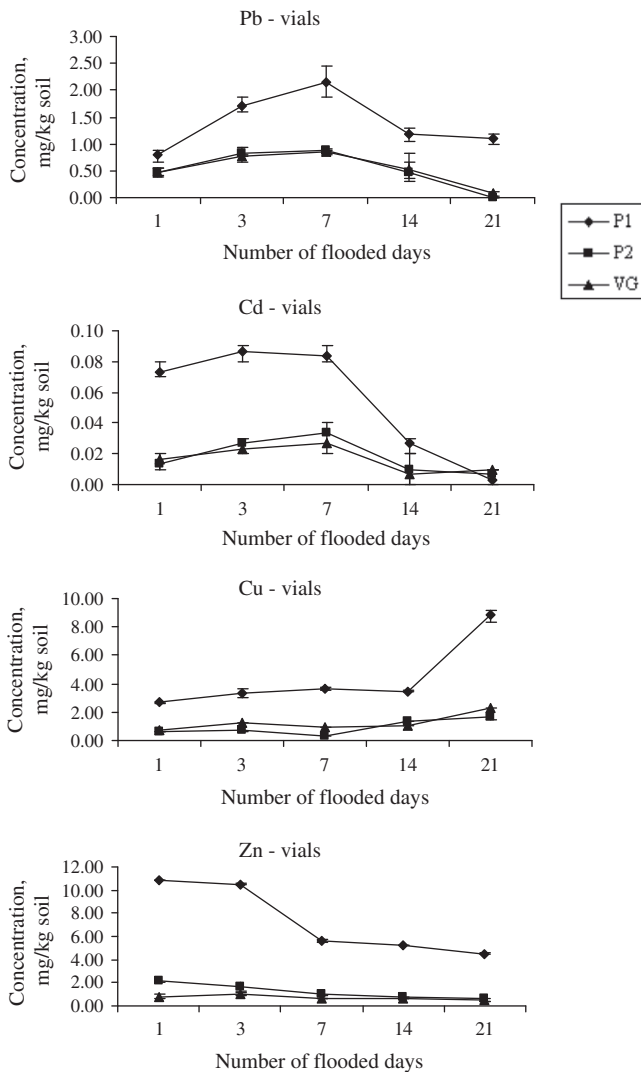


Fig. 2. PTE concentration in soil solution under flooding conditions in vials.

Fig. 3. PTE concentration in soil solution under field and flooding conditions in pots.

similar to the bioaccessible content, sometimes even higher, confirming that these two fractions are human bioaccessible, results in concordance with those obtained by Sialelli et al. (2011).

The potential lability of PTE as showed by sequential extraction (SE) results was further investigated in the flooding experiment.

Figs. 2 and 3 show the concentrations of PTE measured in soil solution after different periods of flooding, in vials and pots, respectively. All the figures contain error bars representing the

standard deviations. Where the results for triplicate were very similar, the bars are not visible.

Vials experiment show that metal concentration in soil solution depends on the system composition. The amount and the content of the infiltration water in soil influences the chemistry of the soil solution and the processes which take part. During flooding, all metals were released into solution in large concentrations because of reducing conditions which decreased the pH

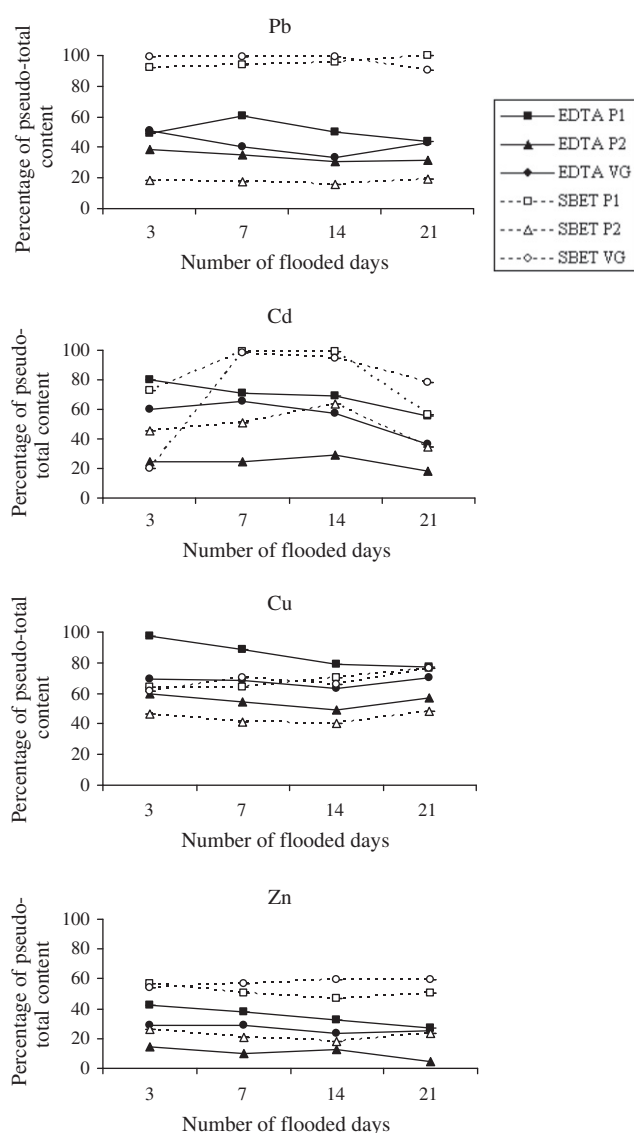


Fig. 4. EDTA and SBET extractions on soil (vials experiment) after different periods of flooding.

(Zhao et al., 2009). The amount of Pb in solution measured in the vials experiment reached a maximum after 7 d, Cd and Cu content increased until the third day, and Zn had the maximum mobility only after 1 d. This can be explained by the lower mobility of Pb than that of Cu and Zn (Florido et al., 2011). Excepting Cu, all PTE concentration in soil solution decreased after 7 d, probably due to the progressive dissolution of iron and manganese oxides which led to the disruption of soil aggregates cemented by these oxides and exposed new adsorbing surfaces (Ajmone-Marsan et al., 2006) or other compounds like chelates were formed.

In pot experiments, concentration of all metals in solution increases under reduction conditions for all soils, therefore, the risk of release to the water table is high.

Lead concentration slowly decreases in the first 7 d, probably because of its partial removal with soil solution through RhS. After 7 d, Pb concentration increases as a consequence of reductive dissolution of Fe-oxides, similarly to what was observed for the vials experiment. Cd, Cu and Zn follow a similar pattern, decreasing during the first 7 d and reaching an equilibrium afterwards. The difference between flooded and field conditions is that Cd (VG, P2) and

Cu (VG, P1, P2) tend to precipitate after 14 d in field conditions, while under anoxic conditions precipitation is hindered, probably as a consequence of the lower pH.

At the end of the flooding experiment, labile (EDTA and SBET extractable) and chemical forms (BCR extraction) of PTE were investigated in order to assess changes as a consequence of reduction.

Fig. 1S presents PTE fractions extracted before and after flooding experiment. Because of the high concentration differences between pseudo-total PTE and the amount extracted by RhS and because of the processes which take place after the flooded soil dries, no noticeable fraction changes appeared. Excepting Pb in P1, all the PTE for both types of soil reveal a small decrease in residual fraction due to flooding experiment which is in accordance with the other investigations. Also, an obvious remark is that for Cd, the most harmful PTE from the studied ones, the sum of the first two fractions, exchangeable and reducible, is much higher after being submerged.

Fig. 4 contains PTE results after flooding for EDTA and SBET extraction.

The plant available content of PTE follows a similar trend to that observed in soil solution, reaching a maximum after 7 d for Pb, 3 d for Cu, Cd and Zn.

The most harmful PTE in terms of release under reduction appears to be Pb because its bioaccessibility reaches 100% after 21 d of flooding. Cd and Zn are most bioaccessible between 7 and 14 d (99% and 59% respectively), and Cu bioaccessibility is continuously increasing until the 21st day when it reaches 76%, maybe because Cu has a high affinity for Glycine, extractant used in SBET (Poggio et al., 2008).

4. Conclusions

The pseudo-total concentration of PTE in the studied soil appeared to be much above the intervention limits, while their lability was extremely high, revealing a serious risk for resident population.

Both reduction experiments, in pots and vials, showed that after a period of 1–7 d of flooding, PTE become more plant available and human bioaccessible, increasing the risk for receptors. PTE measurements in soil solutions along the experiment revealed release trends which are not so obvious for BCR extractions, but are confirmed by changes in EDTA and SBET.

As soil solution represents the main pathway for PTE absorption by plants or leaching to the water table, this experiment proved to be useful to demonstrate that temporary reducing conditions such as those consequent to intense rain events can increase the risk for humans and the ecosystem in broad terms, related to soil pollution in the area.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2012.09.091>.

References

- Abrahams, P.W., 2002. Soils: their implications to human health. *Sci. Total Environ.* 291, 1–32.
- Ahnstrom, Z., Parker, R., 1999. Development and assessment of a sequential extraction procedure for the fractionation of soil Cadmium. *Soil Sci. Soc. Am. J.* 63, 1650–1658.
- Ajmone-Marsan, F., Cote, D., Simard, R.R., 2006. Phosphorus transformations under reduction in long-term manured soils. *Plant Soil* 282 (1–2), 239–250.
- Ajmone-Marsan, F., Biasioli, M., Kralj, T., Grcman, H., Davidson, C.M., Hursthouse, S., Madrid, L., Rodrigues, S., 2008. Metals in particle-size fractions of the soils of five European cities. *Environ. Pollut.* 152, 73–81.
- Alloway, B.J., 1995. *Heavy Metals in Soils*. Wiley, New York.
- ANPM – Agentia Nationala de Protectia Mediului, 2007. Raport anual privind calitatea mediului in anul 2007, pp. 99–101.
- Burt, R., 2004. *Soil Survey Laboratory Methods Manual*. Soil Survey Investigations Report no. 42, United States Department of Agriculture – Natural Resources Conservation Service.
- Contin, M., Mondini, C., Leita, L., De Nobili, M., 2007. Enhanced soil toxic metal fixation in iron (hydr)oxides by red-ox cycles. *Geoderma* 140, 164–175.
- Cundy, A.B., Hopkinson, L., Whitby, R.L.D., 2008. Use of iron-based technologies in contaminated land and groundwater remediation: a review. *Sci. Total Environ.* 400, 42–51.
- Davidson, C., Urquhart, G., Ajmone-Marsan, F., Biasioli, M., Dacostaduarte, A., Diazbarrientos, E., Grcman, H., Hossack, I., Hursthouse, A., Madrid, L., 2006. Fractionation of potentially toxic elements in urban soils from five European cities by means of a harmonized sequential extraction procedure. *Anal. Chim. Acta* 565, 63–72.
- Du Laing, G.D., Rinklebe, J., Vandecasteele, B., Meers, E., Tack, F.M.G., 2009. Trace metal behavior in estuarine and riverine floodplain soils and sediments: a review. *Sci. Total Environ.* 407, 3972–3985.
- European Parliament and Council Regulation, 2006. REACH Law 1907/2006.
- Favas, P., Pratas, J., Gomes, M., Cala, V., 2011. Selective chemical extraction of heavy metals in tailings and soils contaminated by mining activity: environmental implications. *J. Geochem. Explor.* 111, 160–171.
- Filgueiras, A.V., Lavilla, I., Bendicho, C., 2002. Chemical sequential extraction for metal partitioning in environmental solid samples. *J. Environ. Monit.* 4, 823–857.
- Florido, C., Madrid, F., Madrid, L., 2011. Effect of an organic amendment on availability and bio-accessibility of some metals in soils of urban recreational areas. *Environ. Pollut.* 159, 383–390.
- Gasparatos, D., 2012. Fe–Mn concretions and nodules to sequester heavy metals in soils. *Environ. Chem. Sustain. World, Part 2*, 443–472.
- Green, C.H., Heil, D.M., Cardon, G.E., Butters, G.L., Kelly, E.F., 2003. Solubilization of manganese and trace metals in soils affected by acid mine runoff. *J. Environ. Qual.* 32, 1323–1334.
- Grybos, M., Davranche, M., Gruau, G., Petitjean, P., 2007. Is trace metal release in wetland soils controlled by organic matter mobility or Fe oxyhydroxides reduction? *J. Colloid Interface Sci.* 314, 490–501.
- Guan, T.X., He, H.B., Zhang, X.D., Bai, Z., 2011. Cu fractions, mobility and bioavailability in soil-wheat system after Cu-enriched livestock manure applications. *Chemosphere* 82, 215–222.
- Hernández-Soriano, M., Degryse, F., Smolders, E., 2010. Mechanisms of enhanced mobilisation of trace metals by anionic surfactants in soil. *Environ. Pollut.* 159, 809–816.
- Kaasalainen, M., Yli-Halla, M., 2003. Use of sequential extraction to assess metal partitioning in soils. *Environ. Pollut.* 126, 225–233.
- Kabala, C., Singh, B.R., 2001. Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. *J. Environ. Qual.* 30, 485–492.
- Lakanen, E., Erviö, R.A., 1971. A comparison of eight extractants for the determination of plant available micronutrients in soils. *Acta Agriculturae Fennicae* 123, 223–232.
- Luo, X.S., Yub, S., Li, X.D., 2011. The mobility, bioavailability, and human bioaccessibility of trace metals in urban soils of Hong Kong. *Appl. Geochem.* 27, 995–1004.
- Madrid, F., Biasioli, M., Ajmone-Marsan, F., 2008. Availability and bioaccessibility of metals in fine particles of some urban soils. *Arch. Environ. Contam. Toxicol.* 55, 21–32.
- Martinez, C., McBride, M., 2001. Cd, Cu, Pb, and Zn coprecipitates in Fe oxide formed at different pH: aging effects on metal solubility and extractability by citrate. *Environ. Toxicol. Chem.* 20, 122–126.
- Pickering, W.F., 2002. *General strategies for speciation*. Blackwell Science, pp. 9–11.
- Poggio, L., Vrscaj, B., Hepperle, E., Schulin, R., Ajmone-Marsan, F., 2008. Landscape and urban planning introducing a method of human health risk evaluation for planning and soil quality management of heavy metal-polluted soils – an example from Grugliasco (Italy). *Landsc. Urban Plan.* 88, 64–72.
- Pope, J., Farago, M., Thornton, I., Cordos, E., 2005. Metal enrichment in Zlatna, a Romanian copper smelting town. *Water Air Soil Pollut.* 162, 1–18.
- Popescu, I., Biasioli, M., Ajmone-Marsan, F., Stănescu, R., 2011. Potentially toxic metals contamination in soils. A comparison of tools to assess their lability (EDTA, SBET, soil solution). In: *Proceedings of the Third International Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE 2011) & SECOTOX Conference*.
- Rauret, G., López-Sánchez, J.-F., Sahuquillo, A., Barahona, E., Lachica, M., Ure, M., Davidson, C.M., Gomez, A., Lück, D., Bacon, J., Yli-Halla, M., Muntau, H., Quevauviller, Ph., 2000. Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid. *J. Environ. Monit.* 2, 228–233.
- Ruby, M.V., Davis, A., Schoof, R., Eberle, S., Sellstone, C.M., 1996. Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Environ. Sci. Technol.* 30, 422–443.
- Rusu, A., Jones, G.C., Garcia-Sanchez, R., Purvis, O.W., 2006. Multi-element including rare earth content of lichens, bark, soils and waste following industrial closure. *Environ. Sci. Technol.* 40, 4599–4604.
- Sharma, K., Agrawal, M., Marshall, F., 2009. Heavy metals in vegetables collected from production and market sites of a tropical urban area of India. *Food Chem. Toxicol.* 47, 583–591.
- Shiowatana, J., McLaren, R.G., Chanmekha, N., Samphao, A., 2001. Fractionation of arsenic in soil by a continuous flow sequential extraction method. *J. Environ. Qual.* 30 (6), 1940–1949.
- Sialelli, J., Davidson, C., Hursthouse, A., Ajmone-Marsan, F., 2011. Human accessibility of Cr, Cu, Ni, Pb and Zn in urban soils from the city of Torino, Italy. *Environ. Chem. Lett.* 9, 197–202.
- Sigfusson, B., Paton, G., Gislason, S., 2006. The impact of sampling techniques on soil pore water carbon measurements of an Icelandic Histic Andosol. *Sci. Total Environ.* 369, 203–219.
- Singh, B.R., 1997. *Methods for Assessment of Soil Degradation*. CRC Press, New York, pp. 279–280.
- Tandy, S., Healey, J.R., Nason, M.A., Williamson, J.C., Jones, D.L., 2009. Remediation of metal polluted mine soil with compost: co-composting versus incorporation. *Environ. Pollut.* 157, 690–697.
- Wang, L., Luo, L., Ma, Y.B., Wei, D.P., Hua, L., 2009. In situ immobilization remediation of heavy metals-contaminated soils: a review. *Chin. J. Appl. Ecol.* 2011.
- Weber, F.A., Voegelin, A., Kretzschmar, R., 2009. Multi-metal contaminant dynamics in temporarily flooded soil under sulfate limitation. *Geochim. Cosmochim. Acta* 73, 5513–5527.
- Wong, C.S.C., Li, X., Thornton, I., 2006. Urban environmental geochemistry of trace metals. *Environ. Pollut.* 142, 1–16.
- Wuana, R., Okieiemien, F., 2011. *Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation*. International Scholarly Research Network Ecology.
- Zhao, L., Schulin, R., Nowack, B., 2009. Cu and Zn mobilization in soil columns percolated by different irrigation solutions. *Environ. Pollut.* 157 (3), 823–833.
- Zheng, S., Zhang, M., 2011. Effect of moisture regime on the redistribution of heavy metals in paddy soil. *J. Environ. Sci.* 23, 434–443.