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Assessment of toxic heavy metals concentrations in soils and wild and cultivated plant species in Limni abandoned copper mining site, Cyprus

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ABSTRACT

Mine tailings represent a serious source of soil pollution with public health implications. The objectives of this study were: (1) to assess the level of toxic and heavy metal mobilization from the tailing spoil-heap of Limni abandoned mine at Cyprus and the extent of soil contamination to the surrounding area by using pollution indicators; (2) to investigate the uptake and accumulation of heavy metals by cultivated crops; and (3) to estimate the potential of native wild plant species grown in the studied area to be used in phytomanagement approaches. The tailing spoil heap exhibited significantly higher S, Zn, Cu and Pb concentrations compared to the ones found in control reference samples (RS). The lateral mobilization of Mg, S, Zn, Cu and Pb resulted to the contamination of the tailing surrounding areas with these metals. Moreover, Mn and Cu concentrations in the tailing and the surrounding areas exceeded the MPLs for agricultural soils. The severe to very severe pollution of the tailing surrounding sides with S, Zn and Cu was also evident by the calculated values of enrichment factor and geoaccumulation index. The values of combined pollution index also uncovered the extremely high pollution of the tailing and the moderate pollution of the surrounding sites with all analyzed elements. The concentration of Cd in fig, peanut and lemon fruits, as well as in the grains and straw of barley exceeded MPLs, highlighting the potential Cd-mediated hazardous effects from the consumption of these produces. The examination of heavy metal content in wild native plant species showed that *Inula viscosa* L. has the potential to be used for the phytostabilization of Cd and Pb, and *Allium ampeloprasum* L. for the phytostabilization of Pb. Overall, results suggest that the Limni mine tailing and its surrounding sites are highly polluted; thus agricultural activity in the studied area should be prohibited and phytomanagement should be urgently carried out.

1. Introduction

Mining of minerals and metals is known from ancient times. Though, mining industry experienced tremendous development during the latest centuries, as it has been the key driving force behind the industrial and economic development of societies (Rashed, 2010). Beside their constructive contribution to human development, mining activities also generated huge amounts of waste (tailings), as the average amount of concentrate produced is only 1–3% of the mined ore (Adiansyah et al., 2015). Tailings are therefore constituted of non-economic fine-grained solid by-products containing small quantities of valuable minerals or metals, acid materials rich in sulphides and sulphates, heavy metals, organics, and process water, which are usually deposited untreated to form tailing dams or huge spoil-heaps covering considerable areas worldwide (Jones and Boger, 2012; Lottermoser, 2010). Active and most frequently abandoned mines' tailings are usually left without or if any, improper management, and therefore are unstable and prone to wind and water erosion, as well as to acid mine drainage (AMD) (Gomez-Ros et al., 2013; Lukacs and Ortolano, 2015; Shukurov et al., 2014). Tailings are rendered as serious environmental threats, as significant amounts of heavy metals may be transported via the emitted dust, AMD and soil erosion to the surrounding environment affecting water recourses, soils and natural ecosystems, simultaneously posing serious risk for human health (Aebischer et al., 2015; El Amari et al., 2014; Kim et al., 2012; Kwon et al., 2015; Li et al., 2014; Mileusnić et al., 2014; Shukurov et al., 2014); thus their sustainable management is of the upmost importance (Adiansyah et al., 2015; Edraki et al., 2014).

The primary concerns of human heavy metal exposure in mining areas are driven by the ingestion or inhalation of contaminated particles and the consumption of cultivated crops produced in adjacent contaminated soils (Csavina et al., 2012; Park and Choi, 2013). Heavy metals uptake and accumulation in excess rate by crop plants grown in mine contaminated sites represent the major pathway for their entrance

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into the food chain (Boussen et al., 2013; Cai et al., 2015; Chopin and Alloway, 2007; Parra et al., 2014); though the direct deposition of contaminants onto plants surfaces that later may be used as food or fodder should not be underestimated (Zhuang et al., 2009). Several studies have highlighted the potential human health risks from the consumption of heavy metal-contaminated crops in mining areas, including carcinogenic and non-carcinogenic risks (Cai et al., 2015; El Hamiani et al., 2015; Ji et al., 2013; Li et al., 2006; Zhao et al., 2012; Zhuang et al., 2009).

The prevention or mitigation of mine tailings-mediated risks to the functioning of ecosystems and human health due to heavy metal contamination include the proper management of tailings, which in turn may facilitate the stabilization of tailings and the reclamation of the contaminated sites (Conesa et al., 2006; Parra et al., 2014). Phytomanagement, in terms of phytostabilization, is a suitable, cost effective and environmentally friendly restoration technique that facilitates the decrease of environmental risks from metal(loid) enriched mine tailings (Parraga-Aguado et al., 2014; Parraga-Aguado et al., 2015). Phytostabilization provides a long term vegetal cover which may mitigate wind and water erosion and immobilize surface metal(-loid)s within the rhizosphere. However, not many plant species may be used for the phytomanagement of tailings, as these show several edaphic constrains that may interfere plant growth, including high salinity, low fertility, limited water holding capacity, heavy metal toxicity, etc. (Parraga-Aguado et al., 2015). Native plant species are preferred option in such a management technique, as they are adapted to the contamination of the tailings but also to the local climate conditions (Conesa et al., 2006; Kabas et al., 2011; Martínez-Sánchez et al., 2012).

The aim of this study was to assess the level of potential toxic heavy metal mobilization from the tailing spoil-heap of Limni Mine at Cyprus and the extent of soil contamination to the surrounding area by using pollution indicators, as well as to investigate the uptake and accumulation of heavy metals by cultivated crops. In addition, the uptake of heavy metals by native wild plant species grown in the studied area and their potential to be used in phytomanagement was evaluated.

2. Material and methods

2.1. Site description

Limni mine (35°02′12″N, 32°29′05″E) was one of the most important copper and sulphide mines in Cyprus, and is located northwest of the island, about 4km inland of the coast and 4.5km east of the Polis Chrysochus town (Fig. 1). Climate in the study area is characterized as typical Mediterranean with average winter and summer temperatures of 13.5 and 26°C, respectively, and an annual average precipitation of 437mm (occurring mostly during the winter period). Winds are blowing generally from west or north-west and south-west. Limni mine was worked back to the early Bronze Age and continued in Phoenician and Roman times, initially by opencast methods, followed by underground mining. Mining activities at Limni were ceased in about 400CE with the break-up of the Roman Empire, and were resumed as an opencast operation in early 20th century by an Australian mining company. The mine was worked intensively from 1947 till its closure in 1979. The orebody of the mine is emplaced in the Pillow Lava series, with the principal copper ore being chalcopyrite; chalcocite and bornite are also present (grade in the pit varies between 0.5 and 2.5%). Sulphide copper was liberated (~90%) following a procedure of milling, sand flotation and slime circuit, while tailing was undergone a pyrite flotation section for the extraction of pyrite concentrate (Trennery and Pocock, 1972). Tailings were deposited in an adjacent area to form a 20–25m high spoil-heap (Fig. 1).

2.2. Soil and plant sampling

Soil, wild native plant species and cultivated crop plants were sampled from the studied area. Topsoil samples (0–25cm) were collected from both the top surface of the tailing (T), as well as from surrounding areas (with lower altitude from the tailing) in various distances [AT: adjacent to tailing (50–200m), RFT: relatively far from tailing (300–1000m)], in order to evaluate the lateral dispersion of heavy metals. Soil control reference samples (RS) were also collected from areas having the same geochemical background in the west of the tailing deposits (windward from the tailing) and assumed to have background reference concentration of analyzed elements. Each site of sampling covered an area of about 200m^2 and each soil sample (6–8kg; triplicates samples were collected) was a composite of 5–6 randomly collected subsamples (1–1.5kg each) which were mixed, stored in a polyethylene bag and immediately transported to the laboratory. Native wild plant species were chosen based on the species abundance in the tailing itself and surrounding areas where soil sampling was practiced, and their above- (stems and leaves) and underground parts (roots and pulps) were sampled in triplicates from each studied site in order to evaluate their potential use as heavy metal hyperaccumulators in phytomanagement approaches. Plant species collected were *Inula viscosa* L. (small shrubby plant with yellow flowers and fluffy seeds), *Echium angustifolium* L. (small succulent plant), *Anchusa officinalis* L. (herby plant with purple flowers) and plants of the lily family (*Allium ampeloprasum* L.). Crop plant samples were collected from surrounding agricultural sites, varying in distance from the tailing heap slope (from adjacent fields to almost 1000m away). More precisely, leaves, roots and produce from green healthy and yellowish (toxicity-suffered) peanut plants, as well as the aboveground parts of barley plants (straw and grains) from adjacent to the tailing slope heap fields were sampled. In addition, figs and lemons were sampled from fields being in relatively far distance (~1000m) from the tailing. All plant and fruit samples were placed in polyethylene bags not completely closed to allow gas exchange and immediately transported to the laboratory for analysis.

2.3. Sample preparation and analysis

All soil samples were air dried laid in a glasshouse for a week, sieved through a 2mm mesh sieve, homogenized, and stored in plastic bags at room temperature till heavy metal analysis. Plant samples (native wild plants' roots and aboveground parts, and crop plants' roots, leaves and produce) were thoroughly washed with running tap water and rinsed several times with ultrapure Milli-Q H_2O in order to remove any adhering soil particles, blotted dried with tissue paper, and dried in a preheated oven at 80°C for 72h. Dried tissues were then grinded to fine powder in an agate mill (<100μm) and stored in closed plastic sample cups at room temperature till analysis.

For the determination of heavy metal content in soil samples, 0.5g of grounded sieved soil samples were mineralized into solution using the MARS XpressMicrowave Digestion System (CEM Corp., Matthews, USA) with a mixture of concentrated (69–71%) HNO_3 and concentrated (37%) HCl (9:3mL), in a partial digestion procedure equivalent to the USEPA Method 3051 A (U.S. Environmental Protection Agency, 1998). Samples were then allowed to cool, filtered (Whatman 42 Filter Paper) into polypropylene centrifuge tubes and diluted to 50mL with ultrapure Milli-Q H_2O. A blank digest was run in the same way in all digestion events. Dried ground plant (wild native and crop plants) samples (0.4g) were dissolved in a mixture of concentrated (69–71%) HNO_3 and H_2O (4:4mL) in a microwave PTFE vessels. Samples decomposition was accelerated by microwave digestion in the MARS Xpress Microwave Digestion System, in a programme consisting of an 8min ramp to175°C, a 15min step at 175°C and then a ventilated cooling period (Carbonell et al., 2011). Solution samples were transferred to polypropylene centrifuge tubes and diluted with ultrapure Milli-Q H_2O to 25mL. A blank digest was run also, as previously described. A centrifugation was followed in order to obtain clear supernatant (7000×g, 2min). Trace (Al, Mn, Zn, Cu, Ni, Cd, Pb) and macro (Fe, Ca, Mg, Na, S) elements is soils samples were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and in plant samples by inductively coupled plasma-mass spectrometry (ICP-MS). The accuracy of applied

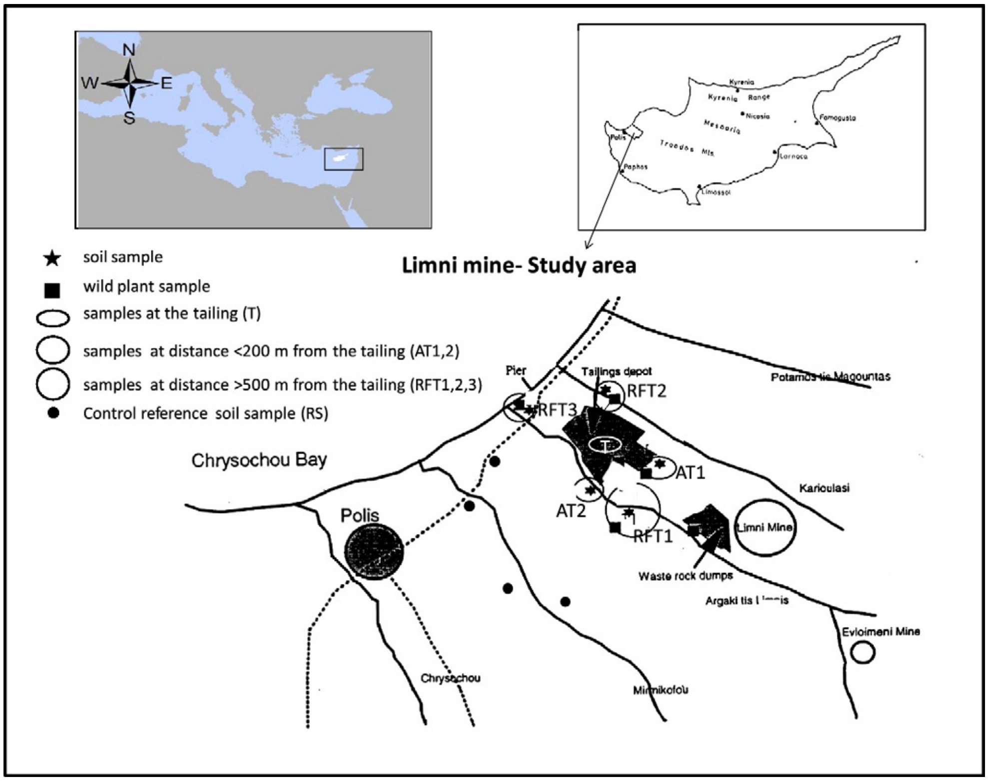

Fig. 1. Location map of the studied area depicting the Limni mine, the tailing depot and the soil and wild native plants' sampling sites. The map of Cyprus indicating the sampling area was adopted by Trennery and Pocock (1972).

methods was verified by the use of known standard materials (recovery for soil and plant samples ranged from 92 to 109%), while the precision was checked by analyzing duplicates samples (maximum relative percent difference did not exceed 5%).

2.4. Quantification of soil pollution

The degree of contamination in the studied area was assessed by using the enrichment factor (EF) (Lăcătuşu, 1998), the geoaccumulation index (GI) (Muller, 1969) and the combined pollution index (GPI) (Abrahim and Parker, 2008). All of these soil contamination indicators were calculated with respect to local median background concentration and the equations used are analytically described by Martinez-Martinez et al. (2013).

EF was used to determine the amount of anthropogenically-introduced heavy metal into the soil. EF of each metal analyzed (EF_x) was calculated as the ratio of metal concentration in the sample and the median of the local background concentration. GI is the $\log_2$ of the ratio of concentration of metal in the sample divided by the median of the background concentrations (multiplied by 1.5), allowing the estimation of pollution level. The factor 1.5 was used in order to correct the fluctuations of a given metal in the environment as well as the very small anthropogenic influences (Loska et al., 1997). The GPI is the sum of EF for analyzed contaminants divided by the number of EFs included in the calculation. Table 1 shows the classification of contamination based on these indicators.

2.5. Metal accumulation efficiency in wild native plant species

In order to evaluate the metal accumulation efficiency in local wild plant species, the bioaccumulation factor (BCF) and the translocation factor (TF) were calculated. BCF is defined as the ratio of metal concentration in the roots of wild native plants to that in the soil, while TF is the ratio of metal concentration in the shoots to the roots (Wahsha et al., 2012). Both factors are used to define whether a particular plant is a metal hyperaccumulator, and therefore whether it may be used in phytomanagement. A hyperaccumulator plant should have BCF or TF values greater than one, as well as total concentration of Cu, Co, Cr, or Pb greater than1000mgkg^{-1} or of Fe, Mn, or Zn >10,000mgkg^{-1} in the aerial parts (Kabata-Pendias, 2011). Plants with both BCF and TF greater than one have the potential to be used in phytoextraction, whereas plants with BCF greater than one and TF less than one have the potential to be used for phytostabilization (Kabata-Pendias, 2011).

2.6. Statistical analysis

Statistical analysis of soil heavy metal concentration measurements was carried out using the software package SPSS v21.0 (SPSS Inc.,

Table 1
Degree of soil contamination by metals according to the estimated indices.

Indicator	Author	Value	Degree of pollution
EF	Lăcătuşu (1998)	1.1–2	Slight
		2.1–4	Moderate
		4.1–8	Severe
		8.1–16	Very severe
		>16	Excessive
GI	Muller (1969)	0<	Unpolluted
		0–1	Unpolluted to moderately polluted
		1–2	Moderately polluted
		2–3	Moderately polluted to highly polluted
		3–4	Highly polluted
		4–5	Highly polluted to very highly polluted
		>5	Very highly polluted
CPI	Abrahim and Parker (2008)	<1.5	Nil to very low
		1.5–2	Low
		2–4	Moderate
		4–8	High
		8–16	Very high
		16–32	Extremely high
		>32	Ultra high

Chicago, USA) and the comparison of averages of heavy metal concentrations in the tailing and the surrounding areas, was based on the analysis of variance (One-Way ANOVA) according to Duncan's multiple range test at significance level 5% ($P<0.05$).

3. Results and discussion

3.1. Soil heavy metal content and degree of pollution in the studied area

All analyzed elements were found in significantly higher concentrations ($P<0.05$) in the tailing as compared to control RS (Table 2). The concentrations of S, Zn, Cu and Pb in the tailing were 123-, 48-, 14- and 6-fold higher than the ones found in the control RS, uncovering their high concentration in the ore, as well as the high pollution of the tailing with these metals. Moreover, adjacent to the tailing (AT) sampled sites displayed higher Mg, S, Zn, Cu and Pb concentrations compared to control RS ($P<0.05$); albeit lower to the ones found in the tailing, with the exception of Cu (in both AT1 and AT2) and Pb (AT2), whose concentrations' were not significantly different from that found in the tailing ($P>0.05$). Sampled sites that were relatively far from the tailing (RFT) displayed higher soil Mg (RFT1, RFT3), Na, S, Zn (RFT1, RFT3), Cu and Pb (RFT1) concentrations compared to control RS ($P<0.05$). Importantly, the concentrations of analyzed elements were lower in the tailing surrounding sites compared to the tailing, with the exception of Na, Cu and Ni ($P>0.05$). No significant differences in heavy metal concentrations were revealed between AT and RFT sampled sites ($P<0.05$), except the intriguingly high Zn and Cu concentrations found in the RFT3 site (Table 2). It is worth noting that both the Mn and Cu concentrations in the tailing and the surrounding area exceeded the maximum permissible limits (MPLs) for agricultural soil in some European countries (Kabata-Pendias and Pendias, 2001), as well as the EU guideline values for agricultural soils with pH>7.0 (CEC, 1986). Though, the high Mn concentration found in the sampled areas besides the tailing can be attributed to the composition of the parent rock, rather than to tailing-mediated pollution, as evidenced from the quantified Mn concentrations in the control RS. In addition, Zn concentration exceeded the MPLs in AT1, AT2 and RFT3 sites, whereas Ni in AT2 and RFT1 sites. The concentration of Pb and Cd were below the MPLs, with the exception of Cd in the tailing. The low, within MPLs, concentrations of Zn, Cu, Ni, Cd and Pb in the control RS, further corroborate to the choice of sampled areas (windward from the tailing) in providing studied areas' background reference concentrations of analyzed elements.

The calculation of EF uncovered the excessive enrichment of the tailing spoil-heap with S, Zn and Cu, as well as its moderate enrichment with all other examined metals (Table 3). The tailing surrounding sides also suffered severe to very severe Cu, S and Zn pollution, as shown by the EF values calculated. The calculation of GI provided further support to the EF estimated pollution level, as it uncovers the very high pollution of tailing with S (GI>5), as well as the high to very high pollution with Zn (4<GI<5), the high pollution with Cu and Pb (3<GI<4), and the moderate to high (2<GI<3) pollution with Cd (Table 3). In addition, the tailing was found to be unpolluted to moderately polluted (0<GI<1) with all other analyzed elements (Fe, Al, Mn, Ca, Mg, Na, Ni). The tailing surrounding sites (AT, RFT) were not polluted with Fe, Al, Mn, Ca, Mg, Ni and Cd according to the GI calculated values, whereas AT sampled sites were moderately polluted with S, Zn and Pb (1<GI<2) and moderately to highly polluted with Cu (2<GI<3). Sites that were relatively far from the tailing (RFT) were found to be unpolluted to moderately polluted with Na and Zn (0<GI<1) and moderately to high polluted with S and Cu, respectively (Table 3). Results obtained from the combined pollution index (GPI) showed that the soil in the tailing was extremely highly polluted (GPI=19.97), while both the AT and RFT sites were moderately polluted, as they displayed GPI values of 2.92 and 2.88, respectively (Table 3). Mileusnić et al. (2014) reported similar pollution indicator values and contamination levels for Pb and Cu in arable soils near to the copper and lead Kombat mine, in Namibia.

Table 2
Total concentration of analyzed elements in soil samples collected from the tailing, as well as from surrounding sites in various distances from the Limni mine tailing spoil-heap.

Sampled site	Distance from the tailing (m)	Analyzed elements												n
		Fe (%)	Al (%)	Mn ($mgkg^{-1}$)	Ca (%)	Mg (%)	Na (%)	S (%)	Zn ($mgkg^{-1}$)	Cu ($mgkg^{-1}$)	Ni ($mgkg^{-1}$)	Cd ($mgkg^{-1}$)	Pb ($mgkg^{-1}$)	
ATI	0–200	3.73 ± 0.23^{b}	2.49 ± 0.31^{b}	877 ± 211^{c}	5.44 ± 0.79^{b}	$1.77\pm0.28^{b,c}$	0.05 ± 0.06^{d}	0.26 ± 0.03^{d}	630 ± 88^{c}	1021 ± 212^{b}	46.74 ± 15.23^{b}	0.27 ± 0.09^{c}	14.08 ± 4.14^{b}	4
AT2	0–200	$3.87\pm0.45^{a,b}$	2.94 ± 0.25^{b}	1280 ± 278^{b}	4.70 ± 0.57^{b}	$2.120.26^{b}$	0.34 ± 0.04^{a}	0.53 ± 0.07^{b}	342 ± 56^{d}	1191 ± 164^{b}	118.16 ± 23.23^{a}	2.11 ± 1.21^{b}	$20.35\pm6.18^{a,b}$	3
RFT1	550	3.30 ± 0.50^{b}	3.04 ± 0.23^{b}	$1347\pm309^{a,b}$	4.64 ± 0.53^{b}	2.00 ± 0.31^{b}	0.37 ± 0.04^{a}	0.40 ± 0.04^{c}	226 ± 43^{d}	367 ± 78^{c}	108.33 ± 19.56^{a}	0.87 ± 0.36^{b}	14.91 ± 5.06^{b}	3
RFT2	350	1.75 ± 0.25^{c}	1.64 ± 0.65^{b}	529 ± 123^{c}	6.76 ± 0.77^{b}	1.09 ± 0.26^{c}	0.22 ± 0.03^{b}	0.15 ± 0.03^{e}	50 ± 43^{e}	580 ± 121^{c}	35.05 ± 11.46^{b}	0.11 ± 0.08^{c}	4.23 ± 2.56^{c}	3
RFT3	750	3.43 ± 0.40^{b}	2.97 ± 0.23^{b}	933 ± 135^{b}	1.94 ± 0.36^{c}	1.87 ± 0.20^{b}	0.25 ± 0.04^{b}	0.72 ± 0.05^{b}	1081 ± 211^{b}	9653 ± 1479^{a}	95.00 ± 24.68^{a}	2.12 ± 0.79^{b}	0.25 ± 0.19^{d}	3
T		4.84 ± 0.35^{a}	3.96 ± 0.55^{a}	1823 ± 273^{a}	10.57 ± 0.81^{a}	2.99 ± 0.83^{a}	0.23 ± 0.06^{b}	8.46 ± 3.75^{a}	4132 ± 1523^{a}	1534 ± 537^{b}	121.70 ± 12.52^{a}	6.41 ± 1.01^{a}	28.61 ± 7.34^{a}	4
RS	>2000	2.88 ± 0.70^{b}	2.60 ± 0.46^{b}	919 ± 132^{b}	5.68 ± 1.48^{b}	1.33 ± 0.24^{c}	0.13 ± 0.04^{c}	0.07 ± 0.02^{f}	86 ± 16^{e}	109 ± 33^{d}	51.31 ± 8.82^{b}	1.70 ± 0.91^{b}	4.82 ± 3.72^{c}	4
Kabata-Pendias and Pendias (2001)[a]									300	100	100	5	100	
86/278/EEC Directive (CEC, 1986)[b]				500					300	140	75	3	300	

AT, Adjacent to the tailing; RFT, Relatively far from the tailing; T, Tailing; C, Control Reference background concentration; Mean values with different letters in a single analyzed element are significantly different according to Duncan's multiple range test ($P<0.05$).

[a] Maximum permissible agricultural soil concentration in some European countries.

[b] European Union guidelines values for agricultural soils with a pH>7.

Table 3
Enrichment factors (EF), geoaccumulation indices (GI) and combined pollution indices (GPI) of the tailing and of surrounding sites in various distances from the Limni mine tailing spoil-heap.

Pollution indice	Sampled site	Distance from the tailing (m)	Analyzed elements												
			Fe	Al	Mn	Ca	Mg	Na	S	Zn	Cu	Ni	Cd	Pb	GPI
EF	T		2.41±0.57	1.91±0.46	2.30±0.50	2.63±0.57	2.58±0.73	1.89±0.46	172.77±71.28	25.26±6.08	17.37±7.80	2.64±0.75	2.89±0.57	4.99±1.16	19.97
	AT	0-200m	1.32±0.03	1.04±0.09	1.17±0.22	0.89±0.07	1.47±0.13	1.56±1.16	5.82±1.97	5.65±1.67	10.14±0.78	1.61±0.69	0.74±0.54	3.57±0.65	2.92
	RFT	350–750	0.98±0.19	0.98±0.18	1.02±0.26	0.78±0.25	1.25±0.21	2.23±0.38	6.17±2.43	5.26±3.72	12.41±1.07	1.54±0.44	0.61±0.034	1.34±0.91	2.88
GI	T		0.59±0.39	0.25±0.42	0.54±0.34	0.73±0.35	0.62±0.52	0.24±0.34	6.56±0.66	4.93±0.89	3.22±0.068	0.68±0.46	2.26±0.64	3.27±1.70	
	AT	0-200m	−0.18±0.03	−0.53±0.12	−0.38±0.27	−0.75±0.11	−0.04±0.13	−0.53±1.39	1.87±0.51	1.85±0.44	2.75±0.11	−0.05±0.67	−1.75±1.48	1.23±0.27	
	RFT	350–750	−0.67±0.31	−0.67±0.29	−0.66±0.39	−1.11±0.53	−0.31±0.28	0.53±0.23	1.76±0.66	0.84±1.28	2.96±1.47	−0.11±0.51	−2.11±1.26	−1.53±1.74	

EF, Enrichment factor; GI, Geoaccumulation index; GPI, Combined pollution index; T, Tailing; AT, Adjacent to the tailing; RFT, Relatively far from the tailing.

Table 4
Heavy metal, and Fe, Mg and Na concentrations (mg kg^{-1} dry weight) in above- and underground parts and the produce of cultivated plant species sampled in various distances from the Limni mine tailing spoil-heap.

Plant	Part sampled	Distance from the tailing (m)	Analyzed elements								n
			Al	Cu	Fe	Mg	Mn	Na	Zn	Cd	
Fig (*Figus carica* L.)	Fruit	1000–1200	488.25±290.30	4.52±0.78	25.25±2.29	1.15±0.11	5.02±1.22	59.43±9.91	8.65±1.08	2.28±0.78	4
Peanut (*Arachis hypogaea* L.) - green healthy plants	Leaves	50–300	578.12±112.33	33.81±4.64	824.22±120.83	8.01±3.44	99.66±18.11	197.12±78.87	78.39±22.51	63.33±27.23	3
	Roots		4063.63±429.31	28.54±8.26	5026.76±677.46	6.30±2.56	179.46±34.24	1460.22±357.74	27.60±11.12	83.11±19.44	
	Fruit		419.33±210.69	15.10±1.19	552.00±243.25	2.46±0.07	30.93±7.58	270.33±158.57	50.23±4.29	24.56±5.75	
Peanut (*Arachis hypogaea* L.) - yellowish plants	Leaves	50–300	2616.24±243.64	30.30±5.21	3307.02±478.63	5.50±4.38	117.23±29.27	471.05±112.23	43.74±15.38	74.88±13.90	3
	Roots		5108.89±793.33	14.9±4.92	6093.31±903.56	4.11±3.21	187.22±22.26	1878.55±291.38	32.90±9.92	76.91±21.59	
	Fruit		1439.21±301.12	32.6±5.56	1909.54±278.44	4.03±2.31	54.12±18.54	513.33±211.34	46.61±9.78	44.36±14.58	
Barley (*Hordeum vulgare* L.)	Staw and grain	50–300	50.22±9.68	5.11±3.51	94.08±12.71	1.31±0.96	13.46±4.79	944.55±169.58	21.76±9.44	8.68±3.59	
Lemon (*Citrus limon* L.)	Fruit	1200–1500	23.05±8.56	4.10±2.45	20.65±6.88	1.12±0.83	3.38±1.57	253.89±56.43	6.15±2.74	0.81±0.27	3
Maximum Permissible Limit (MPL)[a]				73.3					99.4	0.2	
Critical tissue concentration for phytotoxicity[b]							500		350		

[a] WHO/FAO (2007).
[b] Macnicol and Beckett (1985).

Table 5
Heavy metal concentrations (mgkg^{-1} dry weight) in above- and underground parts of wild native plant species sampled from the Limni mine tailing spoil-heap and from surrounding sites in various distances from the tailing.

Local native plant specie	Site sampled	Plant part	Analyzed elements							n
			Al	Cu	Mn	Zn	Ni	Cd	Pb	
Inula viscosa L.	T	1	2397±283	211±15	141±16	139±22	4.7±0.8	0.4±0.1	0.1±0.1	4
		2	1041±97	94±21	56±12	62±8	28±17	0.7±0.4	1.4±0.2	
	AT	1	878±108	60±8	82±16	124±35	5.7±1.2	0.2±0.1	0.5±0.1	4
		2	555±171	50±13	445±17	46±16	15.4±6.4	0.3±0.1	1.1±0.4	
	RFT	1	1041±324	534±16	93±12	118±29	12.1±2.3	0.7±0.2	0.1±0.1	8
		2	1716±508	121±32	78±12	77±20	31.1±6.3	1.5±0.3	2.3±0.9	
Echium angustifolium L.	T	1	4351±249	628±32	180±13	151±10	37.6±10.5	1.4±0.6	0.7±0.1	3
		2	588±44	148±22	74±17	46±6	18.7±6.2	1.1±0.5	0.8±0.1	
Anchusa officinalis L.	RFT	1	446±189	13±4	121±67	33±6	3.5±0.6	0.3±0.2	0.1±0.1	3
		2	268±89	19±5	18±4	43±11	11.3±2.7	0.1±0.1	0.4±0.1	
Allium ampeloprasum L.	T	1	1234±128	55±9	91±27	51±9	9.3±2.7	0.1±0.0	0.1±0.0	3
		2	2628±628	599±143	212±35	249±56	69.5±24.1	1.1±0.3	6.1±0.2	
	RFT	1	1514±570	40±12	71±23	40±12	12.4±3.7	0.1±0.0	0.1±0.0	3
		2	1862±495	105±24	86±10	61±7	35.5±23.5	0.2±0.1	1.5±1.4	

T: tailing; AT: adjacent to tailing; RFT: relatively far from the tailing; 1: above ground (aerial) plant parts; 2: underground plant parts (roots, bulbs).

Overall, results obtained from the pollution indicators examined revealed the high pollution of the sampled sites, and especially the tailing, with S, Zn and Cu, and urge the need for undertaking management practices for alleviating such pollution.

3.2. Heavy metal content and safety of the agricultural produce harvested from sites surrounding the tailing

The heavy metal, and Fe, Mg and Na contents in above- and underground parts and the produce of cultivated plant species sampled from various distances from the Limni mine tailing spoil-heap are presented in Table 4. Interestingly, Cu and Zn concentrations in fig, peanut and lemon fruits, as well as in the grains and straw of barley were below the MPLs for produce safety set by the Joint FAO/WHO food standard programme codex alimentarius commission (WHO/FAO, 2007). Adversely, Cd was found in significantly higher levels than the MPLs in all sampled agricultural produces, highlighting the potential Cd-mediated hazardous effects from the consumption of these produces. Moreover, Mn and Zn concentrations in all samples were below the critical tissue concentration for phytotoxicity, proposed by Macnicol and Beckett (1985). Yellowish peanut plants probably suffered Al, Fe and Na toxicity, as the content of these metals in both the leaves and fruits of these plants were significantly higher compared to the respective concentrations found in the green healthy plants (Table 4). The low, within MPLs, contents of analyzed elements in the agricultural produce (beside Cd) may be attributed to the alkaline (pH values 7.86±0.08) with high $CaCO_3$ (ranging from 17 to 40%) and clay content (ranging from 14 to 28%) soil of the studied sites (data not shown), which in turn facilitates the adsorption of heavy metals to soil particles (especially clay) and the precipitation of metal hydroxides and carbonates, or the formation of insoluble organic complexes (Smith et al., 1996).

The exposure of residents near mining areas to heavy metals through the consumption of agricultural commodities from food crops grown in such contaminated areas is of great concern. The uptake of heavy metals by food crops grown in copper mining areas have been evaluated in previous studies. Ji et al. (2013) reported similar to our findings Zn content, though significantly lower Cd and higher Cu contents, in barley grains collected near abandoned Cu mines in Goseong, Korea. Furthermore, higher Mn and Zn contents were reported in figs, hard wheat and oranges collected from Cu mining areas in south Morocco (El Hamiani et al., 2015), as compared to the contents found in this study. No human health risk assessment was carried out in this study, as the figs and lemons were sampled from few individual plants grown in the studied area, whereas peanuts and barley where grown in a total area less than a hectare and the produce was mixed with other from the wider local area. Though, caution and monitoring should be applied for the prevention of cultivating food crops near the tailing, as the soil is moderately polluted by the analyzed heavy metals (GPI~2.9), while previous reports highlighted the potential risks from such a practice (Kim et al., 2012; Li et al., 2014).

3.3. Heavy metal content in wild native plant species and their potential use in phytomanagement approaches

The aerial and underground parts of four native wild plant species (*Inula viscosa* L., *Echium angustifolium* L., *Anchusa officinalis* L., *Allium ampeloprasum* L.) found in abundance in the tailing itself and surrounding areas were sampled and their tissue heavy metal content was determined. It is worth noting that Al was found in high concentrations (well above 1000mgkg^{-1} dry weight) in both the aerial and underground parts of *Inula viscosa* L. and *Allium ampeloprasum* L. In addition, *Echium angustifolium* L. plants displayed high Al (4351mgkg^{-1} dry weight) and Cu (628mgkg^{-1} dry weight) content in their aerial parts, while *Allium ampeloprasum* L. plants displayed high Cu content (599mgkg^{-1} dry weight) in their bulbs (Table 5). Mn, Zn and Ni contents were found in the range of 40 to 400mgkg^{-1} dry weight in all examined wild plant species, whereas Cd and Pb content was below 10mgkg^{-1} dry weight. The calculation of TF and BCF values (Table 6) uncovered that none of the four studied wild species has characteristics capable to render it as a hyperaccumulator plant, while *Inula viscosa* L. has the potential to be used for the phytostabilization of Cd and Pb, and *Allium ampeloprasum* L. for the phytostabilization of Pb; both plants displayed BCF values greater than one and TF values less than one (Kabata-Pendias, 2011).

4. Conclusions

The determination of heavy metal content in adjacent or relatively far from the tailing sampled sites uncovered the lateral mobilization of

Table 6
Translocation (TF) and bioaccumulation factors (BCF) of the studied wild native plant species.

Wild native plant specie		Element studied							n
		Al	Cu	Mn	Zn	Ni	Cd	Pb	
Inula viscosa L.	TF	1.50	2.62	1.30	2.16	0.31	0.57	0.19	19
	BCF	0.05	0.12	0.20	0.36	0.37	2.91	1.68	
Echium angustifolium L.	TF	7.40	4.24	2.43	3.28	2.01	1.27	0.88	3
	BCF	0.01	0.10	0.04	0.01	0.15	0.17	0.03	
Anchusa officinalis L.	TF	1.07	0.39	3.58	0.49	0.22	1.55	0.13	3
	BCF	0.01	0.03	0.02	0.36	0.18	0.36	0.57	
Allium ampeloprasum L.	TF	0.64	0.24	0.63	0.43	0.24	0.30	0.04	3
	BCF	0.08	0.22	0.11	0.40	0.57	0.58	1.67	

heavy metals, especially Mg, S, Zn, Cu and Pb, which resulted to the contamination of the surrounding area with these metals. Mn and Cu concentrations in the tailing and the surrounding area exceeded the MPLs for agricultural soil in some European countries, as well as the EU guideline values for agricultural soils with pH>7.0. The severe to very severe pollution of the tailing surrounding sides with S, Zn and Cu was also evident by the calculation of EF and GI pollution indicators values. Moreover, the calculation of the GPI uncovered the extremely high pollution of the tailing and the moderate pollution of the surrounding sites with all analyzed elements. Interestingly, Cu and Zn concentrations in fig, peanut and lemon fruits, as well as in the grains and straw of barley were below the MPLs, whereas Cd exceeded MPLs in all sampled agricultural produces, highlighting the potential Cd-mediated hazardous effects from the consumption of these produces. The examination of heavy metal content in the above- and underground parts of four wild native plant species showed that *Inula viscosa* L. has the potential to be used for the phytostabilization of Cd and Pb, and *Allium ampeloprasum* L. for the phytostabilization of Pb. Overall, results suggest that the Limni mine tailing and its surrounding sites are highly polluted, mainly with Mg, S, Zn, Cu and Pb; thus agricultural activity in the studied area should be prohibited and phytomanagement should be urgently carried out.

Conflict of interest

The authors declare no conflict of interest.

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