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RESEARCH ARTICLE

Pedochemical fractionation of potentially toxic elements within the context of soil–plant interactions at abandoned heap-field of Caporciano (Italy)

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Abstract Technosols from the heap of the abandoned Italian Cu deposit Caporciano contain important amounts of potentially toxic elements ($Cr_{tot.}$, Co, Ni, Cu, Zn, As, Cd and Pb). Copper contents exceed the Italian law limits for industrial/commercial sites. The studied metals in *Pinus sylvestris* and *Quercus petraea* (Matt.) Liebl. show strategy of excluders (bioconcentration factor < 1.0) except Ni and Pb (calculated for branches and leaves in *Pinus sylvestris*) while the translocation factor indicates preferential metal accumulation to leaves/needles (translocation factor > 1.0) in both plant speciments.At the heap the contents of the chlorophyll in leaves in the photosynthetic tissues of *Quercus petraea* (Matt.) Liebl. (8.56 CCI—chlorophyll content index) are significantly lower as those measured at reference area (17.71 CCI). The goal of the study is to use a modified methodology for the fractional analysis of soils for the determination of the potential bioavailability of potentially toxic elements in six steps. The innovative steps of sequential analysis are adapted with respect to the release of PTEs from the clay mineral surfaces. (fraction I: 1 M ammonium acetate at pH 7; fraction II: ammonium acetate at pH 5; fraction III: H_2O_2 in ammonium acetate buffer solution; fraction IV: acidic 0.2 M ammonium oxalate (pH

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3.2); fraction V: 0.2 M ammonium oxalate and 0.1 M ascorbic acid mixture; fraction VI: 0.5 M ammonium acetate; pH 6). The best bioavailable metals are Cd, Cu, Zn and Pb. The obtained results enable international comparison with similar Cu-deposits.

Keywords Mine heaps · Bioavailability · Sequential extraction · Potentially toxic elements · Soil fractionation

Introduction

Caporciano deposit, located near Montecatini Val di Cecina is one of the most important copper mines in Italy (Chiarantini et al. 2018). It was already exploited since Etruscan times, and the mined copper was traded throughout the peninsulao. From the ports of Luni and Populonia, it was also transported to Greece via transshipment points to Cera and Dicearchia (Pozzuoli). The Romans also went on mining till 476, when the mining activity was interrupted because of invasion from Visigoths (Orlandi 2006; Riparbelli 1980). The first document on the restart of mining activity is dated from 1433. It continued during the following times and it achieved the maximum exploitation during the nineteenth century, when the mine produced the greatest amount of copper in the world. During the period from 1836 to 1866, 37,416 tons of ore (with Cu content about 30%) were exploited (Orlandi 2006). Excavations were realized as ten levels of galleries derived from ten shafts. The total length of the galleries was 35 km (Orlandi 2006). In 1902, the Montecatini company decided to limit its activities gradually, and in 1903 all activities were stopped and the mine was closed (Cavinato 1964; Dolfini et al. 2020).

The deposit is developed in a 2000 m wide and 200 m thick basalt body situated in Cretaceous shale formation (Fig. 1). Jurassic sedimentary radiolarite cover is locally preserved on the topical Southern parts of the basalt body. At the bottom of the basalt body are several serpentinite and gabbro lenses. Several serpentinite and gabbro bodies are visible in out crops in the West direction from the original oceanic basement (Terenzi 1988).

The ore mineralization is associated with ophiolites of Tuscanian Units, formed by diabase (which represents its effusive component, more or less transformed), whereas gabbros and serpentinites, can be only observed in a deeper positions. Caporciano mine may be considered a remobilization deposit and it shows features of medium temperature hydrothermal origin (Bertolani and Rivalenti 1973). From an economic viewpoint, the main exploited raw materials were massive sulphide ores (chalcopyrite, bornite, chalcocite, native copper, malachite and azurite). Fe-, Pb- and Zn- bearing minerals were also described (Dini and Boschi 2017; Klemm and Wagner 1982; Tanelli 1983).

The studied deposit (Fig. 2) is despite long-term abandonment without continuous vegetation cover (it is partly covered by vegetation, mostly by Pinus sylvestris. and ocassionally by nanic *Quercus petraea*), thus it is affected by extremely strong erosion patterns.

Potentially toxic elements (PTEs) are dangerous contaminants because of their toxicity and ability to spread into country components (soil, water, atmosphere) and, subsequently, to the food chain. There are large vineyards, orchards and gardens around the heap-field. The heap material is unreinforced and strongly influenced by extraordinary erosion. PTEs spread into the environment, thus, it is necessary to know their bioavailability of PTEs to in the surrounding biota.

The aim of the presented study is to verify how significantly enter the PTEs from contaminated soil to wood organs and if this process may consequently negatively affect their development, resulting e.g. in lower chlorophyll concentrations and impaired photosynthetic activity. This study is primarily focused on the relative fractionation of PTEs content in

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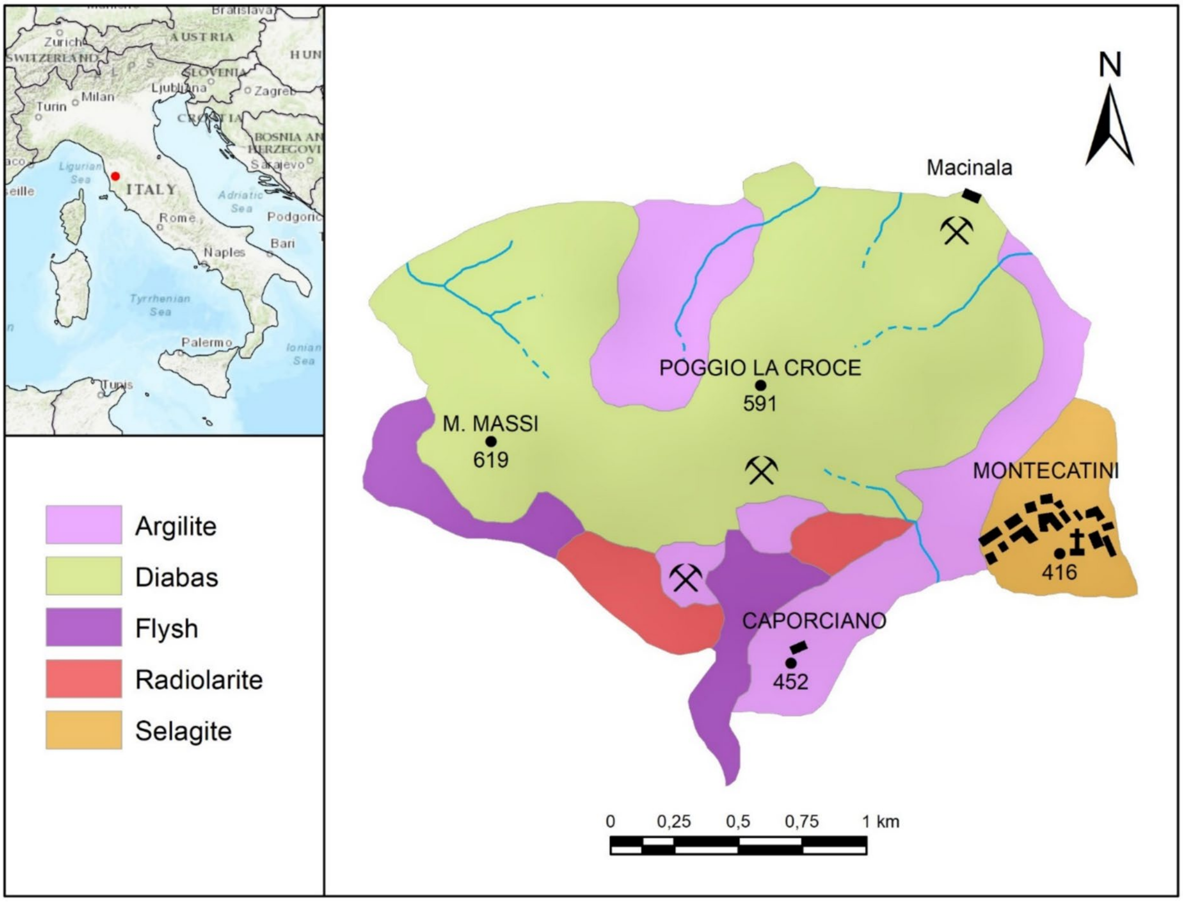

Fig. 1 Geological setting of Caporciano mining area (according to Terenzi 1988)

contaminated soil, which has consequential effects on local plants, such as lower chlorophyll concentrations and impaired photosynthetic activity.

Sequential extraction analysis is usually used to determine the bioavailabiltity of PTEs (metals and metaloids). Their mobility under various conditions/treatments with different leaching agents is mainly determined by their chemical forms. Soil is a very complex matrix and the bioavailability of PTEs is generally influenced above all by pH, quantity and quality of soil organic matter (hummus and fulvic acid) and by the interaction of PTEs with mineral components (Balintova et al. 2012; Huang and Sumner, 2011; Klimko 2015; Singovszka et al. 2015). Also microorganisms affect the solubility and their mobility in soil (Clapp et al. 2002; Cocozza and Miano 2002; Dercová et al. 2005; Tan 2003). A condition for input of PTEs into plants is the effective resistance to high concentrations of metals in plant tissues and cells. However, the goal of our research is to determine the potential bioavailability of PTEs from the heap material, (independently of pH and other external influences on the ability of individual plants to absorb PTEs into their organism.

Material and methods

20 soil samples, evenly taken from the heap, were dried at room temperature. Subsequently they were combined to one mixed average sample, which was homogenized and pulverized (80 mesh).

Active and paste pH$_{H2O}$/Eh$_{H2O}$ were determined according to the methodology published by Sobek et al. (1978). The active pH was determined in a soil suspension of distilled water and the paste pH$_{KCl}$/

Fig. 2 Heap at Caporciano is strongly influenced by erosion

Eh_{KCl} in a suspension of 1 M KCl (64 g KCl/1000 ml H_2O). 20 ml of distilled water or 1 M KCl solution was added to 10 g of the sample, and after two hours of stirring with an electromagnetic stirrer, the pH/Eh was determined with a WTW Multi 3420 pH meter with a SenTix ORP type redox electrode with a Ag/AgCl reference system (electrolyte 3 M KCl). The measured values were converted to a standard hydrogen electrode according to Pitter (2009).

To identify the total concentration of PTEs in soil samples, 0.1 g of homogenized sample was dissolved in aqua regia, ratio 3 (HCl): 1 (HNO_3), and subsequently digested in microwave (MARS, USA) with heating gradient up to 175 °C. The identification of potential plant-available metal pools was based on sequential extraction procedure according to Wiche et al. (2017). A homogenised split of substrate sample was dried at 60 °C for 24 h. Each sample of the equal volume 1 g was placed in a 50 ml falcon tube and extracted with five extraction solutions in sequence: Mobile/exchangeable elements by shaking with 1 M ammonium acetate (at pH 7) for 24 h (fraction I), acid soluble elements by shaking with ammonium acetate buffered to pH 5 for 5 h (fraction II), elements bound to oxidizable matter by gently heating with 10 ml H_2O_2 for 5 h in an ammonium acetate buffer solution (fraction 3). Non-crystalline components, predominantly Fe, Mn and Al-oxides were isolated by selective dissolution with acidic 0.2 M ammonium oxalate (pH 3.2) in the dark (fraction IV). Crystalline Fe and Al-sesquioxides were treated with a mixture of 0.2 M ammonium oxalate and 0.1 M ascorbic acid and gently heated for 30 min (fraction V). The forms bound on clay components were extracted by following procedure: samples were dried at a temperature at 60 °C and subsequently 100 g of samples were annealed 4 h at 800 °C. After maceration with the addition of 0.5 M ammonium acetate at pH 6 for 90 min, was the solution analysed (faction VI). After each step, the solid and supernatant was separated by centrifugation. The residual fraction was calculated for each element as the difference between the summary of analysed fractions and the total concentration.

Determining PTEs content (total + concentration in the fractions) was done by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900x, Agilent Technologies, JPN). The measurement was set by 5-step calibration (0.01, 0.5, 1, 5, 10 mg/L of certified standard AN9090MN). Five samples of *Pinus sylvestris* and six samples of *Quercus petraea* (Matt.) Liebl. were analysed for the same metals as the soils. Vegetation samples were dried at laboratory temperature. Separately 0.5 g of roots, branchess,

Table 1 Ranges of a rinse and paste pH and Eh and their average values in the soil at Caporciano heap

Heap-field	$pH_{(H2O)}$			$Eh_{(H2O)}$ (mV)			$pH_{(KCl)}$			$Eh_{(KCl)}$ (mV)		
	Range of values		$\bar{x}$	Range of values		$\bar{x}$	Range of values		$\bar{x}$	Range of values		$\bar{x}$
	5.99	7.13	6.56	−12.0	42.01	14.00	5.13	7.01	5.99	−4	111	58

leaves/needles were after split digestion in HNO_3 and then in Aqua Regia analysed using ICP-MS for ultralow detection limits in ACME Analytical Laboratories in Vancouver, Canada.

Bioconcentration factor (BCF) in *Pinus sylvestris* and *Quercus petraea* (Matt.) Liebl. (content of PTE in branch or in needles/leaves vs. concentration in soil) was calculated according to Zhang et al. (2011). BCF values < 1.0 are characteristic for excluders (Sheoran et al. 2010). They accumulate PTEs from soil into roots and immobilize them. The BCF values $= 1.0$ are characteristic for indicators. According to Memon and Schroder (2009) the plants which accumulate PTEs in in their shoots (leaves and other aerial parts, e.g. in branches), are classified as accumulators (BCF > 1) and hyperaccumulators (BCF > 100).

Translocation factor (TF) was calculated as a concentration of PTE in branches and needles/leaves vs. their content in roots (Zhang et al. 2011). It indicates the ability of the plant species to translocate PTEs to shoot organs (Yoon et al. 2006; Singh et al. 2010).

Measurements of chlorophyll content in leaf tissue of *Quercus petraea* (Matt.) Liebl. at the heap-field and at the reference area in CCI values (chlorophyll content index) were carried out with a CCM-200 plus chlorophyll meter (Opti-Sciences, Inc.) on September 11th,2024 between 11:00 am – 11:30 am on 6 plants (6 measurements on one plant), on photosynthetically mature leaves according to the method described by Pavlović et al. (2014). Chlorophyll content was evaluated by two-factor ANOVA (LSD α 0.05, α 0.01) using Statgraphics version 5.0 software. The determination of chlorophyll was carried out only in *Quercus petraea* (Matt.) Liebl., because the mentioned device in conifers (*Pinus sylvestris*) due to the dimensions of the analyzed area is not possible.

Results

At Caporciano heap the soil reaction is characterized by values of pH_{H2O} ($\bar{x}$ 6.56) close to neutral values and of pH_{KCl} ($\bar{x}$ 5.99) which slightly lower (Table 1). The redox potential Eh indicates moderately acid and oxidic conditions (Eh_{H2O} −12.0 – 42.01, $\bar{x}$ 14.00; Eh_{KCl} −4.0 – 111, $\bar{x}$ 58; Table 1).

Table 2 Chlorophyll content of *Quercus petraea* (Matt.) Liebl

Factor		Chlorophyll content (CCI)
Surroundings	Heap	8.56 ± 2.60 a
	Reference area	17.71 ± 2.69 b
LSD α $_{0.05}$		3.50
LSD α $_{0.01}$		5.50

At the heap, substantially contaminated by PTEs, as well as because of its sandy character by poor nutrient content and consequently by lack of moisture, in leaves of *Quercus petraea* is the chlorophyll content lower (8.56 CCI) as in the same plants at reference area (17.71 CCI).

Results of the measurement of the chlorophyll content in the leaves of *Quercus petraea* (Matt.) Liebl. is presented in Table 2.

The contents of PTEs decrease in the soil from Caporciano heap in range: Cu > Zn > $Cr_{tot.}$ > Ni > Pb > Co > As > Cd (Table 3).

The content of PTEs in roots, branches and leaves/needles of *Quercus petraea* (Matt.) Liebl. and *Pinus sylvestris* is presented in Table 4. The PTE contents decrease in *Pinus sylvestris* generally in rate: Cu > Pb > Cd > Cr_{tot} > .Ni > Co > Zn > As and in *Quercus petraea* (Matt.) Liebl. in rate: Cu > Zn > Ni > $Cr_{tot.}$ > Cd > Pb > As.

All the BCF values in *Quercus petraea* (Matt.) Liebl., both calculated for branch and leaves are below 1.0, so it indicates that *Quercus petraea* (Matt.) Liebl. is a excluder of studied PTEs. *Pinus sylvestris* is in similar way excluder for all the studied PTEs, with exception of Cd and Pb for branches (BCF vary from 1.13 to 2.46) and for Pb in leaves (BCF vary in rate 3.11 to 4.54).

Most TF values calculated for couple root/branch in *Pinus sylvestris* (TF > 1.0) confirms that PTEs enter to the branch tissues. The highest TF values

Table 3 Average contents of potentially toxic elements in soil from Caporciano heap

Sample	Cr_{tot}	Co	Ni	Cu	Zn	As	Cd	Pb
mg.kg^{-1}								
$\bar{x}$	158.55	28.70	117.9	8025.97	757.62	4.87	3.58	31.48

Table 4 Analyses of plant tissues from Caporciano dump (mg.kg^{-1})

Sample	Part of plant	Cr_{tot}	Co	Ni	Cu	Zn	As	Cd	Pb
Pinus sylvestris									
MTC-1	a	1.6	0.38	1.3	138	0.2	<0.1	2.87	50
	b	1.9	0.89	2.1	163	0.9	<0.1	8.82	93
	c	2.1	0.72	1.2	23	0.2	<0.1	2.75	122
MTC-2	a	2.2	0.44	1.0	435	0.7	<0.1	2.29	80
	b	2.6	0.62	2.2	122	0.7	<0.1	3.36	86
	c	3.1	0.57	1.1	81	0.6	<0.1	0.88	119
MTC-3	a	1.9	0.27	2.3	265	0.6	<0.1	2.35	52
	b	2.2	0.37	4.2	183	0.6	<0.1	6.53	77
	c	3.2	0.34	1.7	44	0.6	<0.1	2.54	143
MTC-4	a	1.4	0.30	1.0	120	0.3	<0.1	2.20	43
	b	1.6	0.72	2.3	155	0.8	<0.1	7.12	73
	c	1.9	0.67	1.0	33	0.1	<0.1	2.25	101
MTC-5	a	1.8	0.38	0.9	388	0.6	<0.1	3.13	70
	b	2.3	0.56	3.2	122	1.2	<0.1	4.06	66
	c	2.9	0.49	0.8	90	0.5	<0.1	1.08	98
Quercus sp.									
MTC-6	a	4.4	0.98	3.5	217	51	<0.1	1.23	0.4
	b	3.2	1.44	3.4	22	61	<0.1	0.19	0.9
	c	5.4	6.26	3.7	19	45	<0.1	0.12	0.3
MTC-7	a	2.1	1.39	5.3	511	48	<0.1	0.49	1.5
	b	3.6	2.50	3.9	174	148	<0.1	0.46	2.1
	c	2.8	2.67	5.6	78	43	<0.1	0.17	1.5
MTC-8	a	2.8	1.11	4.2	446	92	<0.1	0.86	2.1
	b	4.2	2.46	3.7	37	77	<0.1	0.22	1.1
	c	3.0	2.85	4.6	17	75	<0.1	0.08	0.8
MTC-9	a	4.0	1.28	3.3	33	23	<0.1	0.43	1.0
	b	3.6	2.62	1.9	9	36	<0.1	0.59	0.6
	c	2.8	2.77	3.6	6	63	<0.1	0.23	0.3
MTC-10	a	4.2	1.02	3.5	95	32	<0.1	0.62	1.0
	b	3.0	1.57	3.4	11	55	<0.1	0.43	0.8
	c	5.0	6.37	3.7	8	39	<0.1	0.08	1.1
MTC-11	a	2.4	0:99	4.1	347	26	<0.1	0.23	0.5
	b	4.3	2.22	3.8	60	66	<0.1	0.36	1.5
	c	3.1	2.95	4.8	80	73	<0.1	0.06	1.5

Explanations: a – roots, b – steems/branches, c – leaves/needles

were determined for Zn (4.50), Ni (3.56), Cd (3.24). The introduction of PTEs to needles is lower. It vary in most cases from 0.23 to 1.00. The highest values were calculated for Pb (from 2.35 to 2.75). Most of the TF values for $Cr_{tot.}$, Co and Zn in *Quercus petraea* (Matt.) indicate accumulation of the metals (except Cu) from the roots to the branches and to the leaves.

Table 5 The content of PTEs released into the solution within individual fractions sequential analysis

Fraction	Cr_{tot}	Co	Ni	Cu	Zn	As	Cd	Pb
$mg.kg^{-1}$								
I	0.06	0.27	1.17	894.35	50.19	0.04	0.71	1.04
II	0.43	0.34	2.13	1088.77	112.12	0.08	0.34	2.45
III	2.23	6.77	17.70	3149.02	292.17	0.08	1.80	2.47
IV	8.21	0.62	2.13	352.77	52.62	4.21	0.12	11.92
V	6.01	0.53	4.06	3.39	15.21	0.59	0.04	1.33
VI	53.11	0.00	0.26	9.24	5.55	2.30	0.19	2.77
Insoluble residue	88.89	20.21	90.48	2528.43	229.76	2.42	0.38	9.50

The results of the ICP/MS of the PTEs in the individual phases of the sequential extraction are shown in Table 5 (PTEs content released into the solution) and Table 6 (percentage share of PTEs in fractions of sequential analysis).

The best solubility in 1 M ammonium acetate (at pH 7) and those bioavailability of PTEs in first phase of sequence analysis was described for Cd and less for Cu > Zn and Pb (Fig. 3). High Cu > Zn and also less Cd > Pb concentrations were found in the leachate of ammonium acetate at pH 5 in the second phase of the sequence analysis. The oxidizable part of PTEs and PTEs bound to the organic part released in the third phase of sequence analysis decrease in range: Cd > Cu > Zn > Co > Ni > Pb. The concentrations of PTEs bound to amorphous porous Fe- Al- and Mn oxides decrease in acid 0.2 M ammonium oxalate leachate in range: As > Pb > $Cr_{tot.}$ > Zn. The part of the PTEs contents bound to cristall structure of Fe in Mn and Al oxides show a more significant released share only in case of As and less also in case of $Cr_{tot.}$ and Ni. Within sixth phase are released to the ammonium acetate solution mainly Pb > As > Cr_{tot}. The substantially great part of the Ni > Co > Cu > Zn > Cd > $Cr_{tot.}$ remain in the insoluble residue.

Table 6 Percentage share of PTEs in individual fractions of sequential analysis

Fraction	Cr_{tot}	Co	Ni	Cu	Zn	As	Cd	Pb
I	0.03	0.92	0.99	11.14	6.62	0.79	19.80	3.31
II	0.27	1.19	1.80	13.57	14.80	1.59	9.43	7.79
III	1.40	23.56	15.01	39.24	38.56	1.70	50.25	7.84
IV	5.16	2.15	1.81	4.40	6.94	86.31	3.25	37.86
V	3.78	1.83	3.44	0.04	2.01	12.14	1.24	4.22
VI	33.42	0.00	0.22	0.12	0.73	47.12	5.44	8.81
Insoluble residue	55.93	70.34	76.72	31.50	30.33	0.00	10.59	30.18

Discussion

The soil reaction (pH) is considered of the most important soil proprieties because it affects microbial activity, nutrient availability, PTEs bioavailability, and plant growth (Andráš et al. 2014; Klimko 2015). The sandy nature of the heap-material does not allow moisture to be trapped. More or less general lack of hummus and resulting understandable lack of nutrients and the redox potential (Eh_{H2O} $\bar{x}$ 14.00) indicating oxidic conditions and the pH_{H2O} ($\bar{x}$ 6.56) close to neutral values.

Comparison of PTEs content in heap material with the limits given by Italian *Legislative Decree No. 152/2006 approving the Code on the Environment* show that Cd, Co, $Cr_{tot.}$, Ni slightly and Cu and Zn substantially exceed the more strict limits for public green, private and residencial sites A, while limits for industrial/commercial sites B (Table 7) exceed only Cu.

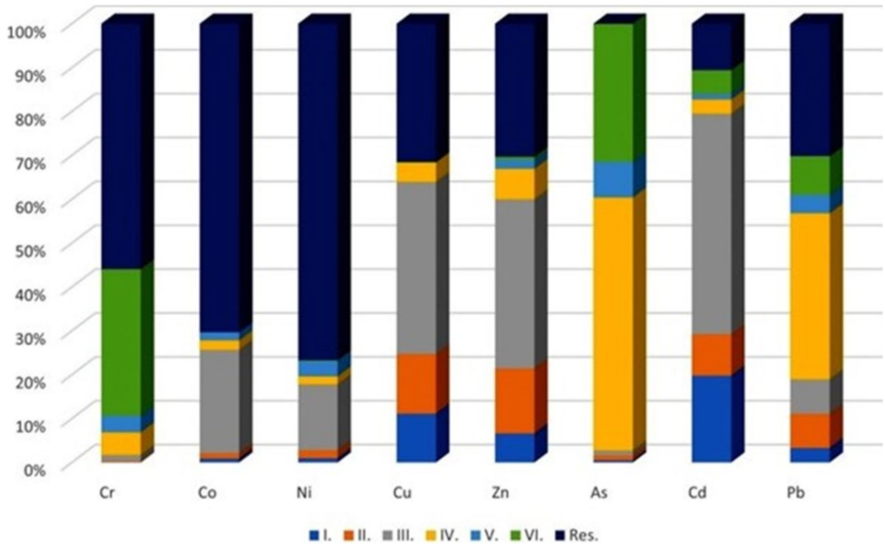

Fig. 3 Percentage of PTEs in fractions I – VI of the sequence extraction analysis; fraction I–1 M ammonium acetate, fraction II–ammonium acetate (pH 5); fraction III–H_2O_2; fraction IV–0.2 M ammonium oxalate (pH 3.2); fraction V–0.2 M ammonium oxalate and 0.1 M ascorbic acid; fraction VI–0.5 M ammonium acetate (pH 6)

Table 7 Limit values for soils concerning public green, private and residential sites (A), and industrial/commercial sites (B), provided by the Italian Legislative Decree 152/2006

Element	A	B
	$mg \cdot kg^{-1}$	
As	20	50
Cd	2	15
Co	20	250
Cr_{tot}	150	800
Cu	120	600
Ni	120	500
Pb	100	1000
Zn	150	1500

The highest PTE contents in *Pinus sylvestris* were confirmed for Cu, Pb, Cd and Cr_{tot}.and in *Quercus petraea* (Matt.) Liebl. for Cu, Zn, Ni and Cr_{tot}. The BCF values in *Quercus petraea* (Matt.) Liebl. and *Pinus sylvestris* prove that both plants are excluders with exception of Cd and Pb for *Pinus sylvestris*. The TF values indicates, that mainly in *Pinus sylvestris* most of the metals (mainly Zn, Ni, Cd and Pb) accumulate in shoots (branches and leaves). On the other hand, the studied plants are not suitable for phytoextraction, because the whole PTEs content in plants are not high and the TF values are not so high that the plats could be considered as accumulators.

Measurement of the chlorophyll content in the leaves of *Quercus petraea* (Matt.) Liebl. demonstrated that the heap environment, rich in PTEs and pure in nutrients and moisture, acts on the vegetation as an abiotic stressor, which significantly damages the photosynthetic apparatus and the production of plant chlorophyll. The toxic impact of the PTEs causes syntetis the damage to chloroplasts (as a result of interference of PTEs ions with photosynthetic enzymes and chloroplast) and of photosynthesis (Aggarwal et al. 2011; Kuklová et al. 2019; Lin and Jin 2018; Wisniewski and Dickinson 2003).

The best soluble and exchangeable which PTEs extraction within the first three phases of sequential extraction analysis was described for metals that are the weakest bound in the soil are the weakest bound in the soil. The group of metals mobilized in the first step of sequential analysis in ammonium acetate at pH 7 includes free ions and complexes of metals with soluble organic ligands (Davidson 2012), which better released to the solution under low values of pH (Filgueiras et al. 2002). As the pH at the studied polygon is only slightly acid, only low concentrations of Cd and Cu > Zn were described in the solution (Table 1).

In the second step under more acid conditions at pH 5 and in the third step the PTEs were bound to oxidizable matter leached by 10 ml H_2O_2 in an ammonium acetate buffer. They release to solution in range: Cd > Cu > Zn > Co > Ni > Pb. The Cu and Zn seems to be more mobile at lower pH in the second step, as it is presented also in Van der Mervel et al. (1994) and Fleming et al. (2013). According to Cotton and Wilkinson (1972) or Stumm and Morgan (1970) Cu and Zn forms usually soluble ammonium complexes. These results correspond also correspond with the data published, e. g., by Melčáková et al. (2013), Slukovskaya et al. (2020), or in more acid conditions by Thomas et al. (1994). During these steps were released to solution the substantial bioexchangable parts of above mentioned elements (Tables 5 and 6, Fig. 3).

In the fourth step treatment with acidic 0.2 M ammonium oxalate at pH 3.2 in the dark, start the release to the liquid phase of As > Pb > $Cr_{tot.}$ > Zn bound to amorphous Fe- Al- and Mn oxides. In the case of As, the mean concentration of As in forms of Fe, Al and Mn sesqui oxides is just slightly lower than the total concentration, thus, it could be presumed that most of this element is concentrated in fraction IV.. Figure 3 reflects the i PTEs solubilization in the first four fractions, so consequently,the ratio of the bioavailable vs. insoluble part of the metals. Exchange of PTEs between solution and Fe- and Mn oxides surface with respect to their physical sorption capacity was studied by Andráš et al. (2009).

Ascorbic acid in combination with ammonium oxalate is used for the sequential analysis only rarely. Only negligible part of the As and substantially less part of $Cr_{tot.}$ and Ni was mobilized from the crystalline Fe and Al-sesquioxides in this fifth step of the treatment.

Among PTEs forms bound on clay components mobilized in 0.5 M ammonium acetate (pH 6; fraction VI) $Cr_{tot.}$ is the most effectively released to the solution. The second most mobile metal element seems to be As, while release of Pb and Cd is limited. The original approach to the issue is given mainly by specific determination of metal forms bound on clay components, which were extracted in ammonium acetate under neutral conditions at pH 6. The D_{pH} show that the soil colloids are characteristic by negative surface charge. In this condition has substantial part the negative charge of the clay minerals surface.

According to Artioli (2008) the adsorption and desorption activation energy is low. The cation exchange sorption capacity of the determined clay minerals smectite and mainly vermiculite is not very high (Klimko 2015; Uddin 2017). Sorption capacity of vermiculite is pH controlled and decrease with decreasing pH in order: Mn > Ni > Zn > Cd > Cu > Pb (Malandrino et al. 2006) and Cd > Cu ≥ Ni > $Cr_{tot.}$ (Helios-Rybicka and Wójcik 2012). Mainly Pb and $Cr_{tot.}$ seems to be bound only weakly by cation exchange sorption on the clay minerals of smectite and vermiculite group surface (Malandrino et al. 2006; Volzone 1998). The most effective release of PTEs from clay minerals under field of relatively suitable pH value ($\bar{x}$ 6.56) at the Caporciano heap was determined for Pb > As > $Cr_{tot.}$. This finding correspond with results published by Helios-Rybicka and Wójcik (2012). The very limited release of Cd > Zn to the solution in similar conditions from vermiculite was described also by Malandrino et al. (2006). Our results correspond also with those published by Andráš et al. (2009).

According to Rauret et al. (1991) the high values of most PTEs (except As and Pb) in residual fractions may be the immobile metals bound in anoxic conditions both in crystalline and amorphous oxides (Filgueiras et al. 2002) or in insoluble silicates (Young 2012).

The main environmental problem of the heap at Caporciano is the strong erosion, which is accompanied by spreading of the PTEs (by winter, water and mechanical processes) to the surrounding area. From this reason will be necessary to reduce this process as much as possible. The metal contents are not very high and part of the PTEs is fixed by sorption on the clay minerals surface. On the other hand, the heap is covered with extraordinary poor vegetation cover. This vegetation is presented mostly by pine trees, which root system ich very shallow, so their ability to stop the erosion is very limited. The first step of the remediation should consist of deciduous trees species planting. The spreading of the PTEs to the country is partly limited by the swamp beneath the heap, where the PTEs are sorbed on the surface of the clay minerals. The atom absorption analysis of Cu in the swamp sediment is up to 60.930 $mg.l^{-1}$ (not published data). The swamp should be changed to two-stage system, consisting both from anaerobic and aerobic wetland.

Conclusions

Soil reaction (pH) is close to neutral values. Values of the oxidation–reduction potential indicates slightly acid and oxidic conditions..

Metal contents of Cu, Zn, Cd, Co, $Cr_{tot.}$ and Ni exceeds only the strict limits for public green, private and residencial sites, given by Italian Legislative Decree No. 152/2006 approving the Code on the Environment. The limits for industrial/commercial sites exceed only Cu. The highest PTEs contents in *Pinus sylvestris* were described for Cu, Pb, whereas in *Quercus petraea* (Matt.) Liebl.: Cu, Zn and Ni. The BCF values calculated both for *Quercus petraea* (Matt.) Liebl. and *Pinus sylvestris* prove that they are excluders, with exception of Cd and Pb in Pinus sylvestris.

The BCF and TF factors indicates, that the woods are not suitable for phytoextraction, but their roots stabilize the soil and they reduce the degree of erosion. The PTEs released to the solution in the first four fractions can be considered bioavailable. In the first three steps of sequential analysis procedure, it represents mainly Cd, Cu and Zn and in four step As and Pb. Metals $Cr_{tot.}$, Co and Ni seems to be the less bioavailable.

The best release of the PTEs to solution for Pb, As and Cr_{tot}. They are bioavailable only in ammonium acetate solution. This preferential desorption reflects their weak sorption ability on the vermiculite and smectite surface.

Relatively substantial part of the $Cr_{tot.}$, Co and Ni seems to be bound in the crystalline or amorphous phase (probably in non soluble oxides or silicates).

Comparison of chlorophyll content in *Quercus petraea* (Matt.) Liebl. at the heap-field vs. reference area confirms the negative impact of heap-field environment rich in PTEs and with a low content of nutrients and moisture on the development of vegetation. It results the significantly lower chlorophyll content in the *Quercus petraea* (Matt.) Liebl. at the heap-field. The content of the PTEs in the heap is not very high and their bioavailability is limited, so the substantial influence on the development of woods has the low content of nutrients in the soil and lack of moisture. Among the main remedial procedures should be erosion limitation by afforestation of the heap surface. The swamp at the bottom of the heap can reduce the spread of PTEs into the wider environment.

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