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Bioaccessibility of metals in soils surrounding two dismissed mining sites in Northern Italy

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Abstract

Mining activities are one of the main contributors to metals contamination of soils, most often due to the inappropriate management of the mining residues. In Italy, hundreds of small mining sites are scattered around the mountainous areas, near small villages with fragile environments. Here, wastes and residues may have polluted the surrounding soils and become a threat to living organisms. We investigated two dismissed sites in Northern Italy with extractive wastes in unmanaged areas close to villages using bioaccessibility and size fractionation methods, focussing on particles that can potentially be eroded and/or ingested ($< 10 \mu\text{m}$ and $< 200 \mu\text{m}$). In the Campello Monti site, Co, Cu and Ni showed high values in soils near the landfills, with the highest concentrations in the $< 10 \mu\text{m}$ particles around the landfills and along the valley bottom. Lead and Ni were the most bioaccessible metals. In the Plassa site, Cd and Zn were the most important contaminants, with an average content of 118 and 34,000 mg/kg. They originated from mining wastes scattered through the slope and had a particularly high bioaccessible fractions, close to the 100% for Zn and above 80% for Cd in the fine particles. The study of the fine, more reactive and mobile particles offered a close insight into the lability of contaminants, as in both sites, a dispersion of metal contaminants through very fine particles in surrounding and downhill areas was observed, resulting in an increased risk to all living organism and for the environment.

Keywords Bioavailability · Cadmium · Potentially toxic elements · Risk assessment · Zinc

Introduction

The extraction of metals for technological applications has had a considerable impact on the environment in terms of pollution, constituting one of the most important sources of localized metal contamination of soils (Alloway 2013). Metals pose a serious health and environmental risk due to their toxicity—even at low concentrations—and persistence,

as they remain in soils and water for long periods (Alloway 2013; Flora et al. 2012).

Soil contamination around dismissed mines has been recently described throughout the world, e.g. in Tunisia (Khelifi et al. 2019), France (Courtin-Nomade et al. 2016), Spain (García-Carmona et al. 2017), Czech Republic (Weissmannová et al. 2019), Colombia (González-Martínez et al. 2019) and China (Li et al. 2014; Zhu et al. 2019). Apart from monitoring soil quality, a growing concern on the potential risk to human health has led to a large number of studies assessing the risk to inhabitants and to the ecosystems around mining sites.

In Italy, nearly 300 small and medium mining sites are scattered around the Alps (Mezzolani 2016) and very often are near small villages in remote valleys with fragile environments. Due to the less than optimal management of the exploitation process in the past, and to the frequently abrupt ending of the mining activities, residues were often abandoned onsite and may have polluted the surrounding soils and water (Courtin-Nomade et al. 2016; González-Martínez et al. 2019). While the attention is currently focused on the

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possible recovery of secondary raw materials from mining waste (Dino et al. 2018b; Mehta et al. 2020a), little is known about their influence on the surrounding environment. Choosing the best option between re-exploitation and remediation requires a better understanding of the environmental risk, not limited to the mining waste but also to the surrounding soils, where it can be assumed that natural or anthropic dispersion of metals may have occurred. Erosion of the contaminated soil on slopes and the conversion of land use of the area to different purposes such as pasture, grazing or recreational activities could increase the risk of transfer of toxic elements to other environmental compartments. Consequently, the monitoring of dismissed mining areas must be carried out to improve the environmental conditions and to prevent or mitigate the risk deriving from contaminated materials such as soils and soil-mixed mining debris or tailings (García-Carmona et al. 2017).

The possible pathways by which metals exert their toxicity on humans are inhalation, dermal contact and ingestion of contaminated particles. Ingestion, together with inhalation, is a size-dependent process with $< 10 \mu\text{m}$ particles preferentially inhaled and $< 200 \mu\text{m}$ particles accounting for almost the entirety of the ingested soil mass (Ruby and Lowney 2012; Siciliano et al. 2009; Yamamoto et al. 2006). The latter has been recognized as the most important fraction in soil exposure studies, contributing almost entirely to the total exposure, due to the larger proportion of soil ingestion compared to inhalation and to the preferential ingestion of fine particles, the most enriched in metals (Ajmone-Marsan et al. 2008; Kong et al. 2012; Ruby and Lowney 2012; Shi et al. 2011).

Commonly, the total metal content and sometimes the chemical fractionation (e.g. by the BCR protocol, Rauret et al. 2000) are used to describe the status of toxic metals in a contaminated soil. However, these data provide only limited information on the metal mobility and may overestimate the exposure, thereby influencing risk assessment outcome and remediation choices (Bakircioglu et al. 2011; Mehta et al. 2019; Mehta et al. 2020b; Reis et al. 2014; Ruby et al. 1999). Not all metal species are equally mobile and absorbed by organisms, as the solubility largely depends on the chemical species and the size of the soil particles to which the elements are associated (Pascaud et al. 2014). In order to assess the risk connected with the particle size and the metal concentration, it is then necessary to estimate their bioaccessible fraction, i.e. the amount soluble in gastrointestinal fluids and, thus, potentially absorbable by living organisms (Paustenbach 2000; Ng et al. 2015; Valido et al. 2018).

Different protocols and standardized procedures have been developed for the determination of bioaccessibility in soil studies (Ruby et al. 1999; Ng et al. 2015; Pelfrène et al. 2012) that can help in defining a more accurate assessment of health risk (Pelfrène et al. 2012).

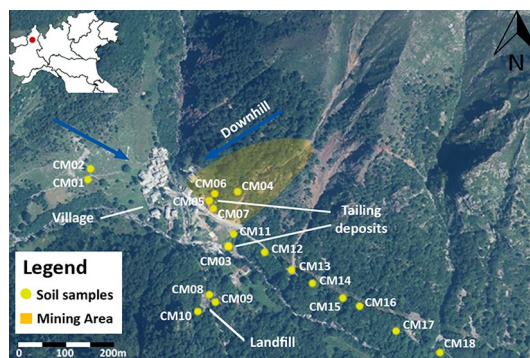


Fig. 1 Campello Monti (CM) sampling sites; the mining area is highlighted in yellow (background image from Google Maps (online), Google, DigitalGlobe, 2018)

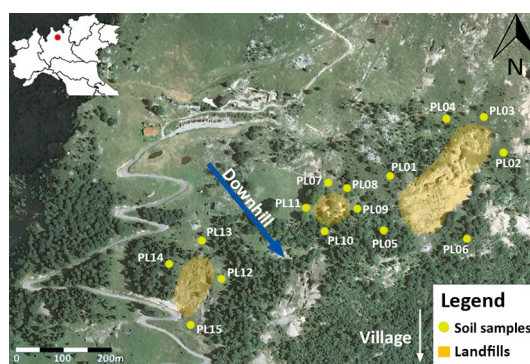


Fig. 2 Plassa (PL) sampling sites; the mining areas are highlighted in yellow. The village of Plassa is 500 m downhill (background image from Google Maps (online), Google, DigitalGlobe, 2018)

The aim of this study was to assess the environmental impact of the anthropically emitted metals on the soils surrounding two dismissed mining sites in the Alps of Northern Italy in 2017 and the potential influence on other environmental compartments. We focused on the fine fractions of the soils in view of their potential threat to living organisms. The sites had been chosen as case studies of the EU Horizon 2020 project SMARTGROUND for the presence, in both cases, of environmental risks related to unmanaged extractive wastes in areas close to villages (Dino et al. 2018a).

Materials and methods

Sites description

In this research, soils adjacent to two mine sites located in the Alps in North-Western Italy (Figs. 1 and 2) were analysed. The Campello Monti (CM) mining site ($45^{\circ} 56' 09'' \text{N}$; $8^{\circ} 14' 14'' \text{E}$) is in the Strona valley, in the Piemonte Region, near the town of Omegna (Fig. 1). This area had been

exploited for Ni mining of the Fe–Ni–Cu–Co magmatic sulphide deposits from around 1863 until 1940s, when the mining activity was terminated (Dino et al. 2018a). Here, mine tailings deposits are directly above the village and along the road that leads to the village, just above the stream.

Soil samples CM03 to 11 (Fig. 1) were taken near the mining area or near mine tailings deposits and landfills, while samples CM12 to 18 were taken at increasing distance from the mining area along the valley bottom to assess the possible dispersal of metals. Soil samples CM01 and CM02 were considered as control samples, as they are located uphill from the mining area on the opposite slope, far from the metal ore but developed on the same morainic deposits. Soils in the area are prevalently Regosols according to World Reference Base classification (IUSS Working Group 2015).

The second site lies in the mining basin of Gorno, near the village of Plassa (PL) (45° 54' 35" N; 9° 47' 47" E), in the Lombardia Region, about 25 km northeast of the city of Bergamo (Fig. 2). PL mines extend over a large area on the slope of Mount Arera, where Zn was extracted since Roman times (Assereto et al. 1977). The exploited mineral ore, mainly composed of sphalerite (ZnS) and its oxidation products, i.e. Zn-rich carbonate and silicate galena (Dino et al. 2018a), was usually sorted by hand by local workers in the yard outside the mine adits, resulting in a rather inhomogeneous waste and widespread waste disposal, with mining debris scattered through the slope on the adjacent areas. Mining areas are located on the slope above the village, and soils are not fully covered by vegetation, thus prone to erosion.

Soil sampling was conducted in the surroundings of three exposed mine landfills as illustrated in Fig. 2; according to the soil map of the Lombardia Region, the prevalent soil type in Plassa is Cambisols. In PL, the area interested by the mining activity is too wide to identify any potentially non-contaminated soils to be used as control. Hence, we decided to use the literature values as choosing soils too far from the sampling area would imply that soil development conditions would be too different from the sampled soils to allow any proper comparison.

Analytical methods

All soil samples were taken at 0–15 cm depth. At each sampling site, in order to obtain representative samples, four sub-samples were collected at 1 m distance from each other and mixed into one sample. Soils were dried at 40 °C and sieved with a 2-mm sieve prior to laboratory analyses.

Particles of two size fractions, < 10 µm and 10–200 µm, were separated from the bulk soil, representing the particles accidentally entering the human body through inhalation and ingestion, respectively (Ruby and Lowney 2012;

Siciliano et al. 2009; Yamamoto et al. 2006). Soil fractions were separated by repeated sedimentation and decanting, following the protocol of Ajmone-Marsan et al. (2008). In addition to the < 10 µm and the 10–200 µm fractions, the bulk soil (< 2 mm) was also analysed.

All samples were analysed for pH (1:2.5 soil/KCl 1 M), total carbon (TC), total nitrogen (TN) (NA2100 elemental analyser, CE Instruments, USA) and carbonates (volumetric method). The particle-size distribution was measured via the sieve-pipette method. All the parameters were measured following the procedures officially adopted by the Italian Ministry of Agriculture (MIPAF 1999).

To determine the pseudo-total metal content in soil, *aqua regia* (HCl/HNO₃ 3:1 v/v) extraction was performed using the microwave method (Ethos D, Milestone srl, Italy). The pseudo-total contents of Fe, Mn, Cd, Cr, Cu, Co, Ni, Pb and Zn were determined in all samples by flame atomic absorption spectrometry, FAAS (Analyst 400, PerkinElmer Inc., USA). All analyses were performed in duplicate. Accuracy was verified using a Certified Reference Material for *aqua regia* soluble contents (CRM 141R, Community Bureau of Reference, Geel, Belgium). Recoveries were between 95 and 105% for all elements. All reagents were of ultrapure or analytical grade.

Chemical fractionation of selected metals was performed using the modified BCR sequential extraction procedure described by Rauret et al. (2000). The extracted fractions were operationally named as *exchangeable* (water and acid-soluble metals), *reducible* (bound to Fe–Mn oxides), *oxidisable* (bound to organic matter and sulphides) and *residual* (digested with *aqua regia*). All suspensions were analysed using FAAS.

Metal bioaccessibility was assessed using the Simple Bioaccessibility Extraction Test (SBET) (Oomen et al. 2002) as described in U.S. EPA Method 1340 (2017). It has been validated for Pb and As, while for the other elements, it is only a candidate to be used. The SBET method simulates very harsh gastric conditions and is used as the worst-case scenario of bioaccessibility, if we compare it with methods using other simulated fluids, e.g. saliva or intestinal fluids (Ng et al. 2015).

Elemental concentrations were determined in the SBET extracts as described (FAAS). The results were considered acceptable when the variation coefficient between duplicates was lower than 10%.

To rapidly depict the contamination degree of a soil, a large number of single and complex pollution indices could be used (Weissmannová and Pavlovský 2017), calculated using the elemental contents in contaminated and background soils. We used the geoaccumulation index (I_{geo}) (Muller 1969; Zhang et al. 2007), calculated using the following equation:

$$I_{\text{geo}} = \log_2 \left(\frac{C_n}{1.5B_n} \right)$$

where C_n is the concentration of each metal in the sample and B_n is the background value. The concentrations of the elements in upper continental crust (Wedepohl 1995) were used as baselines for both sites, while for CM, also the average concentration of the metals in control soils (CM01 and CM02) was used, and results are reported in Supplementary Material.

The index consists of seven classes of contamination: $I_{\text{geo}} \leq 0$ Uncontaminated; $0 < I_{\text{geo}} < 1$ Uncontaminated to moderately contaminated; $1 < I_{\text{geo}} < 2$ Moderately contaminated; $2 < I_{\text{geo}} < 3$ Moderately to heavily contaminated; $3 < I_{\text{geo}} < 4$ Heavily contaminated; $4 < I_{\text{geo}} < 5$ Heavily to extremely contaminated; and $I_{\text{geo}} \geq 5$ Extremely contaminated.

Data were processed using IBM SPSS 25 (IBM Corp., Armonk, USA) and Origin Pro 8 (OriginLab Corp., Northampton, USA) statistical packages.

Results and discussion

Physico-chemical soil properties in Campello Monti

The majority of soils in CM (Table 1) had a loamy sand or sandy loam texture. The sand fraction was the most abundant, with a percentage always higher than 68%, up to a maximum of 88.1%; such a coarse texture would favour the leaching of soil components, including metals.

In CM, the soils were acid (Table 1), ranging between ultra-acid and moderately acid (Soil Science Division Staff 2017). This could be ascribed to the leaching of the basic cations by the high precipitation (around 2000 mm per year), as there was no difference between the control soils (CM01–02) and the rest of the samples. A low pH could also be associated with soil acidification due to sulphide oxidation, especially near the mining landfills, where the lowest values were observed. Carbonates were absent in CM soils, so all the measured C can be considered as organic. In general, when C/N ratio is comprised between 9 and 11, the organic matter content is stable. Most soils had a higher C/N ratio, in line with the mountain environment that induces a slower

Table 1 General soil properties and pseudo-total content of metals in CM soils (\pm standard deviations). Values above legislative limits are in bold

Sample	pH (KCl)	TC (%)	TN (%)	C/N	Clay (%)	Silt (%)	Sand (%)	Co (mg/kg)	Cr	Cu	Ni	Pb	Zn
CM01	4.0	4.2	0.4	10	9.6	22.2	68.2	31 ± 3	103 ± 13	38 ± 5	33 ± 26	147 ± 56	167 ± 9
CM02	4.2	4.4	0.4	11	8.4	16.0	75.6	28 ± 3	91 ± 22	36 ± 1	32 ± 25	84 ± 17	153 ± 27
CM03	4.6	3.7	0.3	12	9.8	21.4	68.8	61 ± 8	728 ± 110	595 ± 66	344 ± 287	52 ± 12	100 ± 38
CM04	5.2	3.1	0.2	16	3.8	23.1	73.1	16 ± 6	812 ± 181	168 ± 13	79 ± 59	117 ± 56	70 ± 17
CM05	4.9	3.2	0.3	11	7.2	13.1	79.7	64 ± 15	335 ± 48	214 ± 17	420 ± 338	17 ± 10	42 ± 13
CM06	5.8	6.1	0.5	12	7.1	13.1	79.8	30 ± 7	424 ± 4	971 ± 8	91 ± 75	61 ± 10	96 ± 23
CM07	2.3	0.24	0.02	12	5.0	8.5	86.5	26 ± 6	550 ± 26	846 ± 15	980 ± 107	32 ± 1	76 ± 7
CM08	3.6	36.7	2.2	17	7.8	4.1	88.1	64 ± 4	93 ± 2	35 ± 2	1075 ± 11	27 ± 6	118 ± 13
CM09	4.5	11.0	0.9	12	7.5	10.5	82.0	389 ± 15	197 ± 31	59 ± 1	2094 ± 70	22 ± 1	214 ± 36
CM10	4.9	0.32	0.02	16	6.1	8.5	85.4	12 ± 1	526 ± 59	535 ± 2	126 ± 6	156 ± 16	84 ± 4
CM11	5.2	1.0	0.1	10	6.2	7.0	86.8	29 ± 2	661 ± 94	198 ± 12	635 ± 101	77 ± 12	99 ± 7
CM12	4.0	8.8	0.7	13	10.1	7.1	82.8	38 ± 2	301 ± 143	74 ± 8	1224 ± 91	49 ± 7	48 ± 11
CM13	4.3	8.3	0.5	17	6.8	6.9	86.3	55 ± 22	1600 ± 105	242 ± 34	376 ± 279	17 ± 9	61 ± 36
CM14	4.8	11.3	0.7	16	9.3	6.5	84.2	40 ± 7	792 ± 161	231 ± 30	127 ± 104	70 ± 15	96 ± 45
CM15	4.1	12.6	0.6	21	10.4	9.7	79.9	67 ± 18	236 ± 56	55 ± 4	575 ± 471	75 ± 20	93 ± 36
CM16	4.0	20.8	1.3	16	8.4	4.8	86.8	45 ± 28	1053 ± 46	246 ± 25	115 ± 77	52 ± 15	80 ± 16
CM17	3.6	15.4	0.8	19	9.4	6.2	84.4	27 ± 5	1543 ± 34	36 ± 6	100 ± 82	77 ± 13	95 ± 18
CM18	4.0	11.2	0.7	16	8.3	15.7	76.0	47 ± 38	196 ± 52	76 ± 5	77 ± 70	103 ± 49	82 ± 17
Limit A ^a								20	150	120	120	100	150
Limit B ^a								250	800	600	500	1000	1500

Data for Cd are not reported as all samples were under the detection limit (0.1 mg/kg)

^aLegislative limits currently adopted in Italy for metal concentration in the soil, limit A is intended for green and residential areas, while B for commercial and industrial areas

recycling of organic matter leading to the accumulation of C, especially in the surface layer of the soil. Values were particularly erratic around the mine tailings deposits and the landfill (CM03–11) due to the particular soil matrix.

Among analysed metals, Fe and Mn showed fairly constant values, with Mn concentrations higher only in the control soil samples and Fe in some of the valley samples (data reported in Supplementary Material, Table SM1).

Extensive contamination was observed in CM, as in 11 soils, Ni exceeded the Italian legislation limits of 120 mg/kg of soil (Table 1) for residential and green areas (MATTM 2006). The higher concentrations were found in the two soil samples near the mining area (CM03 and CM05) and in the samples near the landfills (CM07 to 09). Ten samples were above the residential limit for Cu (120 mg/kg), and most of the soils were above the legislation levels for Cr and Co. A lower level of contamination was observed for Pb and Zn with four and three soils above the lower limit, respectively.

In general, the soils along the valley bottom (CM12 to 18) showed values similar to the soils around the mining area. Probably, the redistribution of materials caused by soil erosion or by the dispersion of waste during mining activities has had the effect of transporting the metal downhill, giving rise to an erratic distribution, with high values of Cr, Cu and Ni in samples far from the mining area, possibly revealing a hidden risk also at a considerable distance from the known polluted areas.

Data of I_{geo} for the most important contaminants in CM soils are reported in Fig. 3 (calculated against UCC values). Complete data and I_{geo} calculated against control samples are reported in Supplementary Material (Table SM2).

Nickel showed the highest values of I_{geo} among all metals, with 15 samples out of 18 moderately to extremely contaminated (values between 2 and 5); Cu and Cr also appeared as a contaminant in sites near the mining area, as in 13 samples, their I_{geo} was between 2 and 6. The only samples not contaminated from these elements appear to be the control soils (CM01 and 02), sampled on the slope facing the mining area; thus, the enrichment of the metals appears to be directly correlated with the mining activity.

Conversely, the relatively high levels of Co, Zn and Pb also in soils used as background suggest a lithogenic origin for their concentrations and conceal a possible contamination from these metals.

Sequential fractionation

The geochemistry of selected metals was investigated applying the BCR sequential extraction scheme to the bulk soils. In CM samples, Co, Cr and Ni were determined, as they were the metals exceeding the legislative limits in almost all samples. Results are reported in Figure SM1.

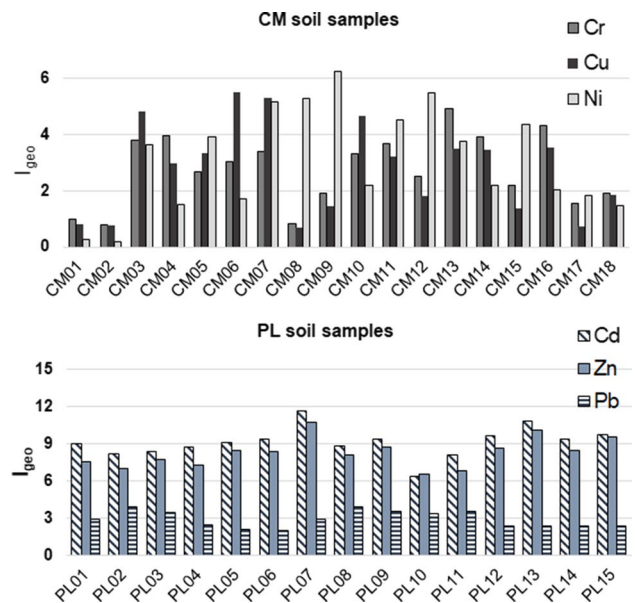


Fig. 3 Geoaccumulation indices (I_{geo}) for the most abundant metals in CM and PL soil samples. Indices had been calculated using the concentrations in the upper continental crust as reference

On average, all metals were predominantly in the *residual* fraction of the soils, consistently with their supposed lithogenic origin. Cobalt showed a scattered fractionation, with a relatively high mobility of the metal, the *exchangeable* and the *reducible* fractions being more important than the *oxidisable* one (linked to organic matter and sulphides). There was no clear difference between the control samples (CM01 and 02) and others apart for sample CM09, the one with the highest concentration of Co, Ni and Zn, having the 63% of Co in the *exchangeable* fraction, thus presenting evident leaching risks to the environment. This sample was located below the landfill and therefore could have been enriched by the eroded mining debris or from the water leachate from the tailings.

Chromium appeared to be more stable than other metals, with almost all the metal in the *oxidisable* or *residual* fractions, while Ni had also a substantial proportion in the *reducible* and the *exchangeable* fractions in the samples near the landfill (CM08–10) the nearest to the mining area, and in the first sample in the valley bottom (CM11). This indicates a high potential for Ni to be removed through leaching and run-off of the fine particles. These results, together with the erratic distribution of the contamination observed along the valley, indicate a risk for the environment due to the leaching and erosion of contaminated particles.

Size fractions and bioaccessibility in Campello Monti

In addition to the bulk soil analysis, metal concentrations were measured in two particle-size fractions: in fine

particles, with a diameter smaller than 10 μm , and in particles between 10 and 200 μm . This size fractionation and the analysis of the bioaccessible proportion in each fraction are rarely evaluated, but it provides an appraisal of the risk connected to the inhalation of eroded particles or to accidental ingestion (Fig. 4). In this case, moreover, the size distribution of the metals in the samples collected along the valley bottom might give a clearer indication about the redistribution of the particles associated with the contamination.

Metals were, in general, more concentrated in the fine particles, especially in samples near the waste rock deposits (from CM03 to CM12); this is in line with other studies (Ajmone-Marsan et al. 2008; Padoan et al. 2017) that observed an inverse relationship between the amount of fine particles and the concentration of metals due to the physico-chemical nature of the particles, such as a higher surface area, and to a higher clay minerals and organic matter content. Cobalt, Cu and Ni showed the highest concentration in the finest fraction (< 10 μm) of the soils near the landfills, in particular those below them, CM08-09. The same trend was observed in the first two sites along the valley bottom, confirming that fine materials have likely been removed and transported downhill. This trend is also supported by the strong correlations between these metals in the fine fraction (Table SM3) ($r_{\text{Co-Cu}}=0.83$; $r_{\text{Cu-Ni}}=0.95$; $r_{\text{Co-Ni}}=0.91$).

Chromium was concentrated in the coarse fraction of the soil, with values in the 10–200 μm fraction and in bulk soil higher than in < 10 μm particles. Although its values are only weakly correlated ($r > 0.60$, Table SM3) with Fe in the two

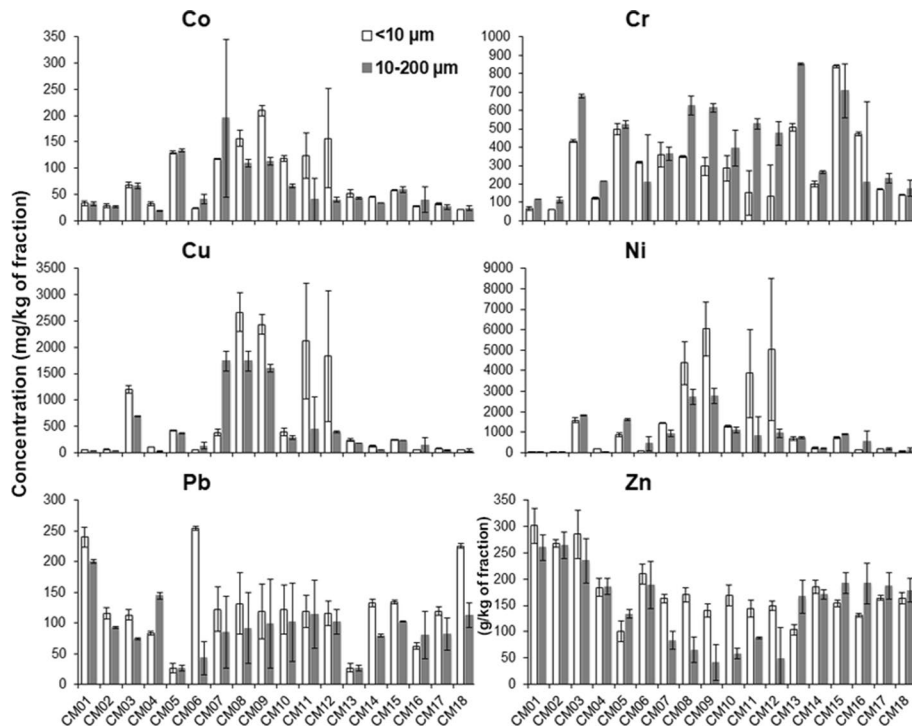
fine size fractions, this would be in line with a lithogenic origin due to the presence of chromites in the area (Dino et al. 2018a) and with the resistance of these minerals to physical alteration. Chromium high concentration in the coarse fraction could be due to the erosion of chromite debris exposed on the slope.

Lead and Zn were distributed more evenly among the two fractions, where both presented concentrations slightly higher than the bulk soil also in the control samples, indicating a unique principal source in most of the sites. Lead appeared to be of natural origin and not correlated with any metal, while Zn had a characteristic trend; in the bulk soil, it was correlated with Co and Ni but in neither of the small size fractions. In particular, a higher concentration of Zn was observed only in the finest fraction of the soils near the landfills (CM07 to 12), with lower concentrations in coarser particles. As Zn was present as zinc sulphide (Dino et al. 2018a), at low concentrations in the extracted rocks, this trend could be due to the discarding of the zinc minerals from the bulk mineral material during the extraction processes.

The gastric bioaccessibility of the metals, measured with the SBET method, is reported in Fig. 5 as the average percentage of the pseudo-total content in each fraction. Complete data are available in Table SM4.

Lead had the highest average proportion of bioaccessible fraction (49 and 46%), ranging from 37 up to 60% of the < 10 μm fraction and up to 81% in the 10–200 μm size. Chromium showed the lowest values, confirming its

Fig. 4 Pseudo-total content of metals in CM in the < 10 and 10–200 μm fraction of soils samples (expressed in mg/kg of fraction; bars represent the analytical standard deviation)



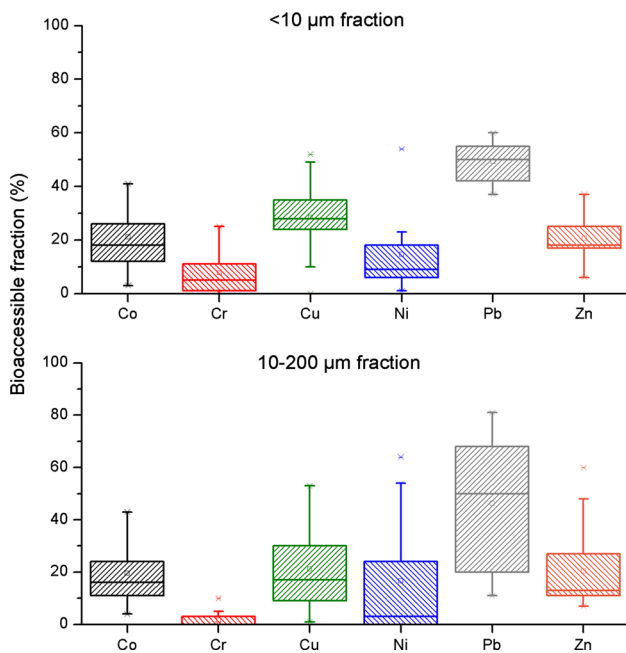


Fig. 5 Bioaccessible metals in size fractions of CM soils. Boxplot represents the proportion (%) of the pseudo-total content in each fraction; bars represent the interquartile range, while dots represent outliers

preferential retention in minerals structures, as reported above.

Copper, Co and Zn had an average bioaccessible fraction around 20–30% of the total content, with erratic values especially in the coarser fraction of the soils farther from the mine landfills (CM11–18). This was more evident for Ni, whose bioaccessibility was high or very high (up to 64%) near the landfills but dropped to zero in soils along the valley bottom. Considering the concentrations of this metal (Table 1), these values appeared very high in absolute quantities; for example, in CM08 and 09, the samples with the highest bioaccessible percentage, the quantity of bioaccessible Ni was 2276 and 3232 mg/kg of fraction in < 10 μm particles, and 1686 and 1763 mg/kg in 10–200 μm fraction. These very high values, exceeding tenfold the Italian legislative limits for the total concentration in soils, represent a serious risk to the environment and the biota in particular, as the bioaccessible fraction is an estimate of the amount of metals available to living organisms.

The two size fractions of the CM soils had a bioaccessible proportion higher than the bulk soil, as observed in previous studies (Padoan et al. 2017). However, the two fractions did not differ in bioaccessible proportion, contrary to urban soils where the finer particles exhibit a higher bioaccessibility (Padoan et al. 2017), probably because of the unique source of contamination.

Correlations between bioaccessible and pseudo-total content of each metal in size fractions could help to clarify the processes underlying the sources of the bioaccessible fraction. In bulk soils, apart for Cu (Table SM3), the bioaccessible fractions were not correlated with the total content, suggesting that the bioaccessibility could be related to the physical structure of the particles rather than the chemical form of the metals, similar between all samples. Conversely, in the < 10 μm and in the 10–200 μm fractions (Table SM3), the bioaccessible portion of every metals was related to its total concentration (also for Cu) and the values of the two size fractions are correlated for most of the metals. This could suggest that the minerals degradation, or the extraction activities, leads to the production of finer particles that are more concentrated in metals (and more bioaccessible) due to the higher surface or other structural characteristics (Ajmone-Marsan et al. 2008) but do not differ in chemical properties.

Physico-chemical soil properties in Plassa

The PL soil samples had a sandy loam or loamy sand texture (Table 2). The granulometry was similar to CM soils, with a slightly higher quantity of clay and a slightly lower sand fraction. According to the USDA classification (Soil Science Division Staff 2017), the soils ranged from slightly acidic to slightly alkaline, while the majority of soils are neutral, the average being 6.2.

In the soil samples of PL, the C/N ratio varied from a minimum of 5 to a maximum of 21 with the average, excluding these two extremes, being 12.5 which is in line with the local land use as pastures and shrubs.

The pseudo-total concentration of the metals in the soils of the Plassa site is reported in Table 2.

All the soil samples had a Cd content much higher than the legislative limit for green areas. The highest Cd content was 493 mg/kg. Lead exceeded the legislation levels for green and residential areas except for one sample, whereas Zn content was always higher than the legislation limits of 0.15 g/kg soil dry weight, with a maximum content of 132 g/kg and a minimum of 7.1 g/kg. Other excess metal concentration was present in some samples for Co and Cu. These results revealed a very strong contamination from Cd and Zn due to the mining activity in the whole site, posing a serious risk to the environment in view of a likely translocation of particles due to wind (in bare soil areas) and run-off.

Conversely, Cr, Ni and Fe (data for Fe are reported in Table SM1 along with data for CM) showed constant values in all samples, indicating a likely natural origin, with concentrations correlated between them and negatively correlated with the total concentration of Cd and Zn (Table SM6).

The I_{geo} (Fig. 3) showed an extremely high pollution degree by both Zn and Cd in all samples, with values

Table 2 General soil properties and pseudo-total content of metals in PL soils (\pm standard deviations)

Sample	pH (KCl)	TC (%)	TN (%)	C/N	Clay (%)	Silt (%)	Sand (%)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (g/kg)
PL01	5.8	5.8	0.6	10	11.7	18.1	70.2	77 \pm 27	20 \pm 4	46 \pm 23	148 \pm 115	42 \pm 13	192 \pm 19	15 \pm 2
PL02	5.7	5.7	1.2	5	8.0	8.1	83.9	45 \pm 15	14 \pm 4	38 \pm 22	32 \pm 11	22 \pm 7	393 \pm 137	10 \pm 3
PL03	5.8	5.8	0.6	10	9.4	9.6	81.0	49 \pm 23	17 \pm 5	42 \pm 21	34 \pm 13	37 \pm 3	276 \pm 5	17 \pm 3
PL04	6.0	6.0	0.8	8	8.2	10.5	81.3	64 \pm 24	14 \pm 0.1	40 \pm 22	38 \pm 11	31 \pm 11	142 \pm 5	12 \pm 0.8
PL05	7.0	7.0	0.5	14	11.8	27.2	61.0	85 \pm 32	19 \pm 0.2	43 \pm 21	73 \pm 5	35 \pm 1	107 \pm 4	28 \pm 0.4
PL06	5.7	5.7	0.5	11	7.3	21.7	71.0	100 \pm 35	22 \pm 2	54 \pm 29	64 \pm 9	38 \pm 7	98 \pm 6	26 \pm 4
PL07	7.3	7.3	1.1	7	9.2	7.8	83.0	493 \pm 174	12 \pm 2	26 \pm 18	175 \pm 10	12 \pm 5	192 \pm 3	132 \pm 21
PL08	7.0	7.0	0.7	10	9.6	13.5	76.9	71 \pm 24	18 \pm 0.4	52 \pm 33	37 \pm 10	22 \pm 7	393 \pm 22	21 \pm 2
PL09	6.9	6.9	0.6	11	9.6	15.1	75.3	103 \pm 35	17 \pm 3	41 \pm 28	62 \pm 9	14 \pm 9	301 \pm 4	33 \pm 0.7
PL10	5.1	5.1	0.4	13	9.4	19.0	71.6	13 \pm 3	24 \pm 2	55 \pm 27	23 \pm 14	31 \pm 5	262 \pm 3	7 \pm 0.3
PL11	5.5	5.5	0.6	9	9.8	23.1	67.1	41 \pm 12	19 \pm 0.2	41 \pm 24	37 \pm 11	15 \pm 9	298 \pm 20	9 \pm 3
PL12	6.4	6.4	0.6	10	17.8	22.8	59.4	124 \pm 48	12 \pm 2	33 \pm 23	73 \pm 6	12 \pm 8	131 \pm 5	30 \pm 0.6
PL13	6.2	6.2	0.3	21	9.6	17.2	73.2	270 \pm 56	7 \pm 2	21 \pm 15	112 \pm 7	5 \pm 4	132 \pm 6	87 \pm 10
PL14	6.3	6.3	0.5	13	11.4	17.4	71.2	103 \pm 37	14 \pm 0.3	27 \pm 19	60 \pm 6	20 \pm 14	127 \pm 3	27 \pm 3
PL15	6.5	6.5	0.6	11	7.0	20.4	72.6	126 \pm 16	11 \pm 2	29 \pm 20	93 \pm 5	15 \pm 11	127 \pm 6	57 \pm 6
Limit A ^a								2	20	150	120	120	100	0.15
Limit B ^a								15	250	800	600	500	1000	1.5

Values above legislative limits are in bold

^aLegislative limits currently adopted in Italy for metal concentration in the soil⁴², limit A is intended for green and residential areas, while B for commercial and industrial areas

ranging from 6 to 12. The very high values could have been enhanced from the use of the UCC concentrations. Furthermore, with respect to the UCC concentrations, also Pb and Cu were enriched in PL soils. These values are probably due to the presence of galena (PbS) and chalcopyrite (CuFeS₂) in the ore deposits (Dino et al. 2018a).

Sequential fractionation

In PL soils, the BCR sequential extraction procedure was performed to investigate the fractions of the three most concentrated metals (Zn, Cd and Pb). Results are reported in Fig. SM1.

Zinc and Cd fractionation was very similar in all soils, with extractable concentrations in the *exchangeable* and *reducible* fractions higher than 50% in most of the samples. This trend was more pronounced for Cd, where the *reducible* was the most prominent fraction, accounting for more than 40% (on average) of the total concentration, similar to what was found in other contaminated areas (Li et al. 2015). This very high *exchangeable* pool, probably due to the association with carbonates (Pascaud et al. 2014; Li et al. 2015), could be of particular interest for its mobility and possible toxicity and a factor of risk for the downward migration of the contamination to the aquifer.

Zinc soluble concentrations in the *exchangeable* fraction were also much higher than the legislation limit for the total

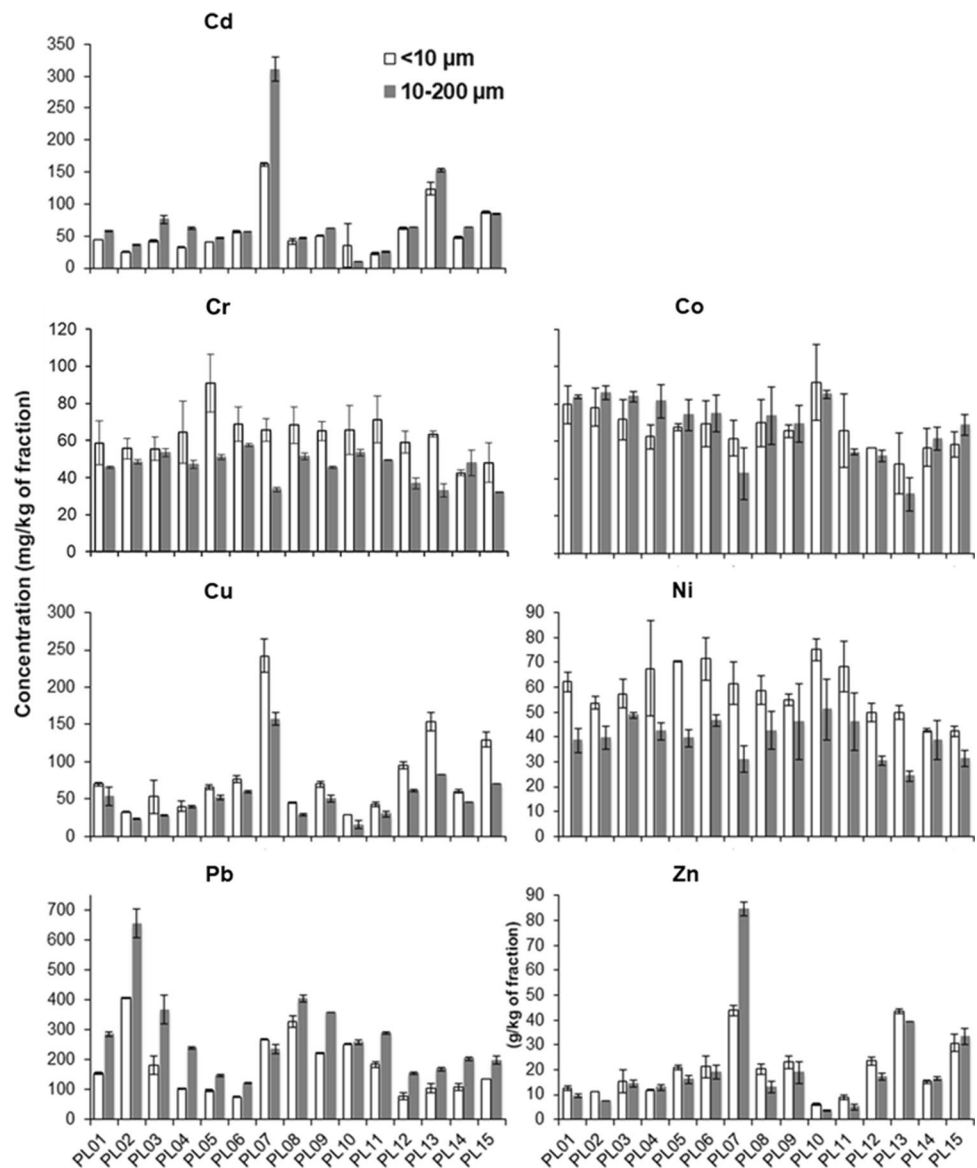
concentration in green areas (150 mg/kg), with a range of 238–17,628 mg/kg.

Lead, on the contrary, had a very low *exchangeable* fraction (Fig. SM1), with most of the metal being extracted in the *reducible* or in the *oxidisable* fraction. This reactivity will limit its direct risk for the environment in oxic conditions but could pose a risk if the soil particles eroded from the slope end up in anoxic environments such a water body. Soil oxides and organic matter that seem to retain the metals could release them in case of an abrupt decrease in the soil redox potential (Ajmone-Marsan et al. 2019).

Size fractionation and bioaccessibility in Plassa

In the PL samples, the size distribution of the metals leads to three different trends (Fig. 6). The elements that were not enriched, thus mainly not influenced from the mining activities, such as Cr, Ni and Cu, presented concentrations not statistically different in the two size fractions, although slightly higher in the < 10 μ m, with values similar to ones reported for the bulk soil. The natural origin was also strengthened from the high correlation between the Ni and Cr in all the fractions (Table SM6). Lead appeared to be enriched in the coarse fraction of the soil, with high concentrations in some sites, suggesting a contribution from mining activities, but it was the only metal not correlated with the others.

Fig. 6 Pseudo-total content of metals in PL in the < 10 and 10–200 μm fraction and in the bulk soils (expressed in mg/kg of fraction; bars represent the analytical standard deviation)



The trend of Cd, Co and Zn was towards a similar concentration in both fractions of the soils, with Cd slightly enriched in < 10 μm particles and Zn in 10–200 μm particles. Interestingly, both sizes presented values similar or lower than ones reported for the bulk soil. This, together with the very high absolute quantities (almost always above 10,000 mg/kg for Zn), suggests that at least part of the particles in both size fractions were in fact Cd or Co or Zn minerals rather than soil particles. Looking into Pearson's correlations (Table SM6) confirmed Cd and Zn as deriving from the same mineral source, with $r_{\text{Cd-Zn}}$ coefficients higher than 0.95 in all the fractions and in bulk soil.

The bioaccessible proportion of the more concentrated metals was particularly high for Cd, Zn and Pb (Fig. 7), followed by Co, Cu, Ni and Cr, that is, the less

bioaccessible of the measured elements. The complete data are reported in Table SM7.

Cadmium and zinc, in particular, showed a bioaccessible fraction close to the pseudo-total content in many soils, indicating that once they are released in the environment (as sulphides), they remain in the soil in very labile forms.

The bioaccessible portion of the metals in size fractions varied among elements (Fig. 7 and Table SM7). For all metals, the bioaccessibility of size-fractionated particles was higher than that of the bulk soil, while within fine particles, different trends were observed. Chromium, Ni and Co showed higher bioaccessibility in the finest particles, while Cd and Cu presented values not significantly different ($p=0.05$) between the particle sizes. Lead fine particles were more bioaccessible than coarser, but concentrations

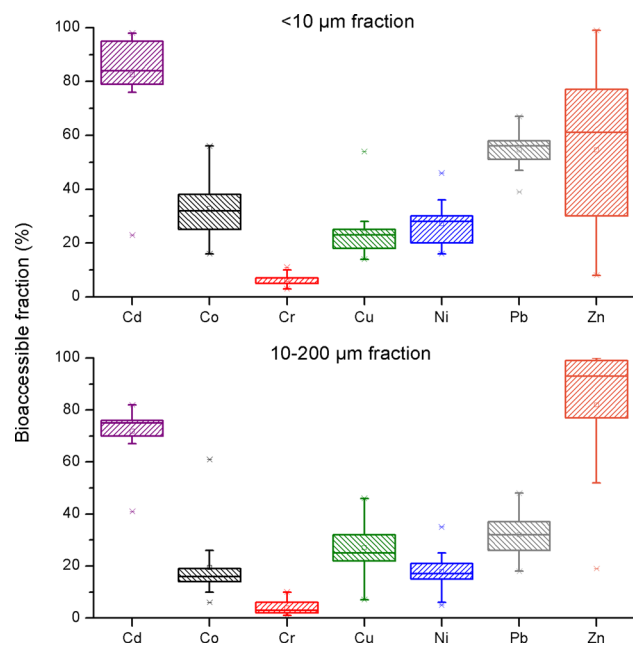


Fig. 7 Bioaccessible metals in size fractions of PL soils. Boxplot represents the proportion (%) of the pseudo-total content in each fraction; bars represent the interquartile range, while dots represent outliers

of all three fractions and their bioaccessible portion were significantly correlated (r values > 0.87 , $p = 0.01$), indicating a probable single source emitting coarse particles.

Zinc had very variable results between samples, especially in the fine fraction, with values of the bioaccessible fraction ranging from 8 to 99% of the total content; however, coarser grains resulted to have a higher bioaccessibility, on the average. This result could have been due to the diversity of the mining debris scattered along the studied area during the different mining phases, where different separation methods could have produced Zn particles of different sizes. This hypothesis is confirmed by a study done in a nearby mining area, where the mineralogy of rocks, mine tailings and of one sample of soil were studied (Mehta et al. 2020b). In that soil, near to the waste deposits, Zn was found in many different forms in the same sample: as zinc oxide, in a Cu–Fe–Zn–S phase, as hemimorphite, sphalerite, smithsonite, and embedded in clay minerals (Zn–K–Mg–Si).

Conclusion

The heritage of past mining activity in Northern Italy is a matter of serious concern for the consequences that mining activities and mining waste can pose to the surrounding environmental compartments. The soils of both areas are

heavily contaminated by potentially toxic metals that appear to be directly derived from the mining activities.

In CM, the major contaminants were Ni, Cu and Cr, although chromium high concentrations appeared to be mainly of natural origin. These elements showed higher concentrations and bioaccessibility in the finest fraction ($< 10 \mu\text{m}$) of the soils below the landfills and at the underlying valley sites, confirming the higher contamination potential of these particles.

In the Plassa mining site, the entire slope appeared to be contaminated, in particular from Cd and Zn at very high levels (up to 800 times the Italian legislative limit). This was due to the mining debris scattered during the centuries all along the slope, and to the probable translocation of particles due to wind and run-off. Here, the mobility of metals appears to be a factor of risk for the environment as almost the totality of the metals was bioaccessible. This very high bioaccessibility means that, once released from the minerals, the contaminants remain in the soil in a very labile and, consequently hazardous form, posing risks also in the case of the actual land uses of the area, as pastures or recreational zone.

In both sites, the slow dispersion of metal contaminants in surrounding and downhill areas observed in CM samples might result in an increased risk for the population.

The study of the fine, more reactive and mobile particles offered a close insight into the lability of contaminants. This would be helpful to understand the environmental risk appraisal and to improve the management plan for both areas.

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Data availability All data generated or analysed during this study are included in this published article (and its Supplementary Materials).

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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