



# The impact of former mining activity on soils and plants in the vicinity of an old mercury mine (Vallalta, Belluno, NE Italy)

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**Abstract:** Exploitation of ore minerals (cinnabar, chalcopyrite, sphalerite) from the old mine in Vallalta (Belluno, NE Italy) has resulted in serious environmental impacts, including the acidification of water, and the contamination of soils and plants. Forty-eight soil samples and four wild plants were examined at four sites in the vicinity of the mine (<100 m), where mine waste was discharged. After digestion with aqua regia, chemical analyses were carried out on both soils and plants by inductively coupled plasma-optical emission spectroscopy (ICP-OES) for potentially harmful elements (Cr, Cu, Ni, Pb, Zn, Fe, Mn); the mercury concentration was directly ascertained by atomic absorption spectrometry (AAS). The levels of Ni, Cr, Mn and Zn in the soils were generally below the 'normal' levels for uncontaminated sites. Conversely, more than 50% of the examined samples presented Cu and Pb concentrations higher than the phytotoxic level (10 mg kg<sup>-1</sup>). Iron concentrations exceeded normal values (<300 mg kg<sup>-1</sup>) in 65% of the examined samples. The mercury concentration was high (6–21 mg kg<sup>-1</sup>) in all soil samples, mostly above the phytotoxicity limit (10 mg kg<sup>-1</sup>). *Chaerophyllum hirsutum* presented the highest Hg levels in roots, up to the phytotoxicity level (10 mg kg<sup>-1</sup>).

Micronutrients Cu, Zn, Fe and Mn showed translocation factors (TFs) of between 0.5 and 1, suggesting that these elements are taken up to a critical concentration and are then arrested in the roots. Iron is less mobile, particularly in *C. hirsutum*, with the lowest TF of 0.38. The TF for Mn and Hg is >1 in *S. nemorum* and *C. hirsutum*; a TF of <0.5 in *P. braunii*, and particularly in *T. officinale*, suggests that these metals are most likely to be arrested in their roots.

Soil contamination is confined to the proximity (<100 m) of the mine waste. Among the investigated plants, *Chaerophyllum* seems to be most suitable for phytoremediation of Hg-contaminated sites.

**Keywords:** mine waste; potentially toxic metals; environmental contamination; phytoremediation; Vallalta mine

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Soil is a key resource for the life of organisms in terrestrial environments; it is the basis of the ecosystem and of our farming system of food production (Chesworth 2008). Since soil is a resource subject to strong anthropogenic pressures, its degradation is one of the fundamental problems we face when trying to enable sustainable development and wise use of natural resources. Soil degradation can be physical, chemical or biological; chemical pollution of soil, in particular, can cause the transfer of the problem to other environmental media, such as surface water or groundwater, with a consequent spread of pollution over a wider area than the initial one (Davies 1992; Lal 2006). Pollutants in the soil can be partly absorbed by the plants that derive nutrients from it, with the risk of accumulation and toxic effects along the food chain and also to humans. Among the inorganic contaminants, potentially toxic metals are the most common (Bradl 2005; Alloway 2013). Some of them, at an optimum concentration, are essential for plant nutrition and are usually assimilated by plants (e.g. Fe, Cu, Mn, Co, Ni, Zn), while they become toxic when their concentration level exceeds the phytotoxicity threshold, which varies from species to species (Kabata-Pendias 2011). Other metals (e.g. Ag, Al, Cd, Hg, Pb, Sb) are not involved in plant nutrition and are potentially toxic at any concentration (Adriano 2001).

Human activity is considered to be the major source of pollution and contamination by potentially toxic metals in soils. Among the various causes of this type of contamination we can mention mining and the processing of metals, which are linked to several environmental problems (e.g. acid mine drainage, impact on the

landscape, and the pollution of water, soils and sediments). Moreover, in recent centuries, no due attention was paid to waste processing and disposal of mining waste, which was dumped on the ground and in turn became a source of potential pollution (Selim & Sparks 2001; Lal 2006; Bini *et al.* 2017a, b).

The main purpose of our study was to assess the degree of contamination of soils by potentially toxic metals, associated with the ore mineralogy, in the vicinity of an abandoned Hg–Cu–Pb–Zn mine, and to investigate the translocation of metals from soil to plants, with reference to phytoremediation.

## Study area

Vallalta is an old mine located in the mountain district of Belluno (46°16'55" N, 12°02'09" E; NE Italy), in the valley of Mis creek, at an elevation ranging between 543 and 990 m asl (above sea level). The present vegetation cover is consistent with the climatic conditions of the region (mean temperature = 9°C, mean precipitation = 1440 mm), and is composed mostly of mixed forests, with oak prevailing over hornbeam.

The geological substrate of the valley consists of the Alpine metamorphic basement of early Permian age, surmounted by Permian clastic sediments (Verrucano and Quartz-Porphyrite formations); while at the top, in unconformity with the previous geological formations, the calcareous–arenaceous complexes (Val Gardena Sandstone and Dolomia: Upper Permian–Lower Triassic) crop out (Caneve 1987; Frizzo & Ferrara 1994; Campana *et al.*

2007; Giordano 2008). The whole area has been intensely disturbed by the tectonic activity of the Valsugana Fault, with folding, fracturing and displacement of the geological formations.

The Mis River crosses the valley; even if no settlements can be found in this area, many buildings and tunnel outlets still bear witness to the past mining activity. Part of the area lies within the National Park of the Belluno Dolomites. The mineralized area, which is located along the contact between the metamorphic basement and the sedimentary rocks, is a deposit of mixed sulphides, composed primarily of native mercury and cinnabar, with minor amounts of other metallic minerals (pyrite, sphalerite and chalcopyrite) (Frizzo & Ferrara 1994). Its exploitation has continued, with some interruptions, from AD 1740 until the year 1962. Metals were extracted and processed directly *in situ* through roasting; a method with a severe impact on the area due to acid rain and intensive wood clearing.

## Methods

### Sampling

The sampling was conducted during the period of spring–summer 2014. A preliminary soil survey allowed identification of four sites with similar environmental conditions (slope, aspect, vegetation cover), all affected by mine waste. Sites MIS 1 and MIS 2 are in the Verrucano Formation, while MIS 3 and MIS 4 are developed in the Quartz–Porphyrite Formation.

At every site, soils were described in the field according to the Soil Survey Staff (USDA 2014) guidelines, and four representative subsites were selected in order to have a significant coverage of the area. The soils are mostly shallow (30–80 cm) and scarcely developed, with A–C or A–AC–C horizons. According to the current taxonomy (IUSS Working Group WRB 2014), they are classified as Spolic Technosols (Skeletal, Toxic).

At every subsite, four samples, covering 4 m<sup>2</sup>, were taken at a depth of 0–30 cm (A horizon). Three replicates of soil samples (to total 48 samples) were collected and transported to the laboratory for routine soil analyses (pH, organic carbon (OC), cation exchange capacity (CEC) and texture) and for the determination of potentially harmful elements (potentially toxic elements (PTEs): Ni, Cr, Cu, Pb, Zn, Fe, Mn and Hg).

For each site, based on the phytosociological approach (Braun-Blanquet 1928), samples of the natural vegetation were taken, following the abundance and accessibility of botanical species, both herbaceous and shrubs in juvenile stages. The plant species most present at each site were: *Salix purpurea* L., *Salix caprea* L., *Salix eleagnos* Scop., *Acer pseudoplatanus* L., *Taraxacum officinale* Weber, *Plantago major* L., *Stachys alopecuroides* (L.) Benth., *Silene dioica* (L.) Clairv., *Stellaria nemorum* L., *Chaerophyllum hirsutum* L., and two ferns (*Gymnocarpium robertianum* (Hoffm.) Newman and *Polystichum braunii* (Spencer) Fee). Some of them (e.g. *Salix* spp., *T. officinale*, *P. major*) are already known as metal accumulator or indicator plants (Wahsha *et al.* 2012a, b), while others have not yet been fully investigated as potential indicators of environmental pollution. Our attention was paid to the latter, in order to find new accumulator plants.

### Sample preparation and analysis

#### Soil samples

According to the procedures described by the manual of the Italian Ministry of Agriculture and Forestry (MIPAAF 2000), the soil samples were air-dried and sieved to 2 mm. For the fine fraction (<2 mm), the following parameters were determined: particle size (pipette method), pH (1:2.5 soil–water suspension), CEC (BaCl<sub>2</sub> + ethanolamine, titration), exchange acidity (BaCl<sub>2</sub> + KCl, titration),

total CaCO<sub>3</sub> (gas volumetric) and OC (Walkley & Black 1934). Specific analyses were carried out at the Laboratory of Earth Science at the Ca' Foscari University of Venice, in order to characterize the soil geochemistry (major and trace elements). For the elemental analysis, the samples previously sieved to 2 mm were milled to a fine powder (<100 µm) with an agate mill, and 0.2 g of the powder obtained was subjected to a complete digestion in the microwave (Milestone model 1600-Ethos) in closed containers made of Teflon. Based on Nadimi-Goki *et al.* (2014), the breakdown was performed in 5 ml of aqua regia (1:3 HNO<sub>3</sub> + HCl) and 1 ml of HF, and then 1 ml of cold supersaturated H<sub>3</sub>BO<sub>3</sub> was added, based on the method of Leita & Petruzzelli (2000). Two standard certified reference materials (CRM) (SOIL5 from the International Atomic Energy Agency and MESS3 from National Research Council Canada) were analysed as a part of the quality control.

#### Plant samples

Five specimens of four selected wild plants (three of those not yet investigated for phytoremediation, and *T. officinale* as reference) were collected at the same sites as the soils. The samples were rinsed gently with tap and distilled water, and then washed in an ultrasonic bath with deionized water in order to remove the adhering soil as completely as possible. Leaves and roots were separated manually, dried in a ventilated oven at 50°C for 2 days, and then ground in an agate mill. Afterwards, 0.5 g of the sample was digested in an acid mixture (5 ml HNO<sub>3</sub> + 3 ml H<sub>2</sub>O<sub>2</sub>) in open vessels on the hot plate, followed by filtration with filter cellulose Whatman Grade 42 (Rodushkin *et al.* 1999; Zang *et al.* 2002; Keresztúri *et al.* 2003).

#### Chemical analyses

Samples of both soil and plants were analysed by inductively coupled plasma–optical emission spectroscopy (ICP-OES) for potentially harmful elements (Cr, Cu, Ni, Pb, Zn, Fe and Mn). The mercury concentration was directly ascertained by atomic absorption spectrometry (AAS) (AMA 254 Instruments) at the ENEA Laboratory, Rome. Detailed information about the materials and methods used is published elsewhere (Margesin & Schinner 2005; Fontana *et al.* 2010; Wahsha *et al.* 2012a).

#### Statistical analysis

The linear correlation coefficients were calculated on the whole set of 48 samples to determine the strength and direction of linear relationships between elements. Statistical significance was declared when the *P* value was equal to or less than 0.05. Statistical analyses were performed with the software Statistica, Version 9.

## Results and discussion

As previously stated, the soils are mostly shallow (30–80 cm) and scarcely developed, and are referred to as Spolic Technosols (Skeletal, Toxic) (IUSS Working Group WRB 2014). The pH varies from about 4 to nearly 8, depending on the nature of the substrate; the highly acidic pH values found in some soils are likely to be due to the alteration processes of the metal sulphides in the soil and substrate (Delgado *et al.* 2009; Vittori Antisari *et al.* 2014; Bini *et al.* 2017b). The texture is typically loamy, sandy-loamy or silty-loamy. The CEC is low for all the soil samples, with the exception of subalkaline, silty-loamy samples. The soil skeleton is abundant and consists of waste material from the processing of ferrous minerals, which shows a clear anthropogenic influence and reshuffling (ICOMANTH 2007).

**Table 1.** Concentration of metals ( $\text{mg kg}^{-1}$ ) in soils of Vallalta and the Mis creek valley

Sampling site	Ni	Cr	Cu	Pb	Zn	Fe	Mn	Hg
MIS 1	24 ± 2	93 ± 3	28 ± 2	40 ± 3	29 ± 2	33 200 ± 87	560 ± 12	10 ± 1
MIS 2	14 ± 1	56 ± 2	40 ± 2	49 ± 3	46 ± 3	35 200 ± 98	479 ± 10	21 ± 2
MIS 3	55 ± 2	95 ± 3	1122 ± 18	373 ± 5	734 ± 12	68 500 ± 124	1076 ± 46	6 ± 1
MIS 4	13 ± 1	32 ± 1	224 ± 9	571 ± 8	817 ± 18	14 800 ± 39	182 ± 8	8 ± 1
I.A.*	46	100	51	21	89	10 130	900	–
R.L.*	120	150	120	100	150	–	–	1
I.L.*	500	800	600	1000	1500	–	–	5

\*I.A., Italian average; R.L., residential limits; I.L., industrial limits (adopted from Wahsha *et al.* 2012b and Angelone & Bini 1992). All concentrations are the mean of three replicates ± SD.

**Table 2.** Linear correlation coefficients calculated on metal concentrations in soils

	Ni	Cr	Cu	Pb	Zn	Fe	Mn
Ni	1.00						
Cr	0.31	1.00					
Cu	–0.13	<b>–0.74</b>	1.00				
Pb	–0.41	–0.42	<b>0.69</b>	1.00			
Zn	–0.09	<b>–0.81</b>	<b>0.79</b>	<b>0.70</b>	1.00		
Fe	<b>0.80</b>	–0.42	<b>0.79</b>	<b>0.80</b>	<b>0.75</b>	1.00	
Mn	<b>0.86</b>	<b>0.70</b>	<b>–0.63</b>	<b>–0.37</b>	<b>–0.48</b>	<b>–0.59</b>	1.00

Values shown in bold are significant at  $P < 0.05$ .

### Metals in soils

The concentrations of potentially toxic metals in soil samples are shown in Table 1.

The soils at sites MIS 1 and MIS 2 (developed on the Verrucano Formation) present metal concentrations generally below the contamination threshold reported in the Italian Legislative Decree (Decreto Legislativo 152/2006), with the exception of Hg. The levels of Ni, Cr, Mn, Pb and Zn at these sites are generally within the mean values reported in literature (Ni and Cr  $< 50 \text{ mg kg}^{-1}$ ; Mn  $< 900 \text{ mg kg}^{-1}$ ; Pb  $< 50 \text{ mg kg}^{-1}$ ; Zn  $< 70 \text{ mg kg}^{-1}$ , respectively) (Kabata-Pendias 2011). Mn and Zn concentrations, moreover, are below the phytotoxic levels (500 and  $100 \text{ mg kg}^{-1}$ , respectively) indicated by Madejon *et al.* (2002).

Conversely, the soils at sites MIS 3 and MIS 4 (developed on the Quartz Porphyrite Formation) are seriously contaminated with Cu, Pb and Zn (mean values of 1122, 571 and  $817 \text{ mg kg}^{-1}$ , respectively), and slightly contaminated by Hg ( $6\text{--}8 \text{ mg kg}^{-1}$ ).

Nickel and Cr are below the contamination threshold at all four sites. Copper concentrations are overall above normal levels ( $20 \text{ mg kg}^{-1}$ ), and more than 50% of the examined samples present Cu concentrations higher than the phytotoxic level ( $\text{Cu} > 40 \text{ mg kg}^{-1}$ ). Lead concentrations are overall above the phytotoxic level ( $\text{Pb} > 15 \text{ mg kg}^{-1}$ ). Iron concentrations exceed

normal ranges ( $10\ 000\text{--}30\ 000 \text{ mg kg}^{-1}$ ) in 65% of the examined samples; this is likely to be due to the high Fe concentration in the parent material. The mercury concentration is high (range  $6\text{--}21 \text{ mg kg}^{-1}$ ) in all soil samples, as expected given the exploited ore, mostly above the phytotoxicity limit ( $10 \text{ mg kg}^{-1}$ ). Comparing the values found in this study with those of the contamination threshold reported in the Italian legislation (D. L. n° 152/2006), the surveyed area seems to be uncontaminated by Ni, Cr and Mn, while there is a moderate contamination by Zn, and a high contamination by Cu, Pb, Fe and Hg.

Soils sampled in the immediate vicinity of the Mis stream are less polluted than others in the valley, even though they are within the area of greatest influence of human activities (i.e. mining). This is probably due to the leaching of water and the establishment of periodic reducing conditions that increase the mobility of most elements considered, enhancing the removal from soil and amplifying the risk of water contamination (Adriano 2001; Bini 2012; Cidu *et al.* 2013).

Linear correlation coefficients between the concentrations of potentially toxic metals in the examined soils were calculated in order to assess if metals present similar geochemical behaviour, as listed in Table 2. The concentrations of Fe, Pb, Zn and Cu are significantly correlated, according to their calcophilous behaviour, since they all tend to form compounds with sulphur. In this study,

**Table 3.** Metal concentrations ( $\text{mg kg}^{-1}$ ) in selected plants growing on mine waste

Plants		Ni	Cr	Cu	Pb	Zn	Fe	Mn	Hg
<i>Stellaria nemorum</i> L.	L	*	*	5.6	10.9	48.1	255	78.9	4.00
	R	*	*	4.5	*	61.7	454	65.1	3.10
<i>Polystichum braunii</i> Spenn.	L	*	3.09	10.9	*	50.5	68	30.8	0.11
	R	*	*	16.2	*	67.3	114	65.4	0.23
<i>Chaerophyllum hirsutum</i> L.	L	*	*	8.8	*	50.2	123	30.6	8.00
	R	*	*	11.2	*	28.1	327	31.9	>15
<i>Taraxacum officinale</i> Web	L	*	3.76	10.6	*	40.1	268	60.4	1.10
	R	*	*	13.8	*	59.6	562	93.0	14.00

L, leaves; R, roots; \*below detection limit.

**Table 4.** Translocation factors (TF) for selected plants growing on mine waste

TF	Cr	Cu	Pb	Zn	Fe	Mn	Hg
<i>Stellaria nemorum</i>	n. a.	1.22	n. a.	0.78	0.56	1.21	1.29
<i>Polystichum braunii</i>	n. a.	0.67	n. a.	0.75	0.60	0.47	0.47
<i>Chaerophyllum hirsutum</i>	n. a.	0.79	n. a.	1.79	0.38	0.96	1.09
<i>Taraxacum officinale</i>	n. a.	0.77	n. a.	0.67	0.48	0.65	0.08

n.a., not available.

these elements are all present in the mineralized area of Vallalta. Our findings show that most of the Fe in soils of the study area derives from the alteration of pyrite and chalcopyrite, which explains its low correlation with Mn, although the latter usually tends to accompany Fe in rocks due to their similar geochemical behaviour (Bradl 2005). The same correlation between elements is found in soil. Accordingly, no element of the mineralization has been removed in a preferential way, since pedogenesis has acted for only a short time (some decades) in the investigated area, and thus the geochemical characteristics of the soil are still tied to that of the substrate.

### Metals in plants

None of the individual plants collected during sampling showed evident signs of toxicity. The concentrations of metals of interest in the plants examined are shown in Table 3.

Nickel, Cr and Pb concentrations both in leaves and roots are generally below the detection limits, with the exceptions being in leaves of *S. nemorum*, *P. braunii* and *T. officinale*. Concerning the other PTEs (Cu, Zn, Fe, Mn and Hg), the metal concentration is generally higher in roots than in leaves, with the exceptions being *S. nemorum* for Cu, Mn and Hg, and in *C. hirsutum* for Zn. Nevertheless, metal (Cu, Zn and Mn) concentration levels in both roots and leaves are within normal values (range 1–100, 5–200 and 5–2000 mg kg<sup>-1</sup>, respectively) suggested by Kabata-Pendias (2011).

Iron concentrations, conversely, exceed normal values (30–250 mg kg<sup>-1</sup>), reported by Fergusson (1990), in roots and leaves of most samples. Mercury presents generally higher levels in comparison to normal values (0.005–0.02 mg kg<sup>-1</sup>), as expected, due to Hg mineralization of the area. In particular, *C. hirsutum* presents high Hg concentrations both in roots (>15 mg kg<sup>-1</sup>) and in the aerial parts (8 mg kg<sup>-1</sup>), close to the threshold that indicates hyperaccumulator plants (10 mg kg<sup>-1</sup>); *T. officinale*, however, displays a high Hg content (14 mg kg<sup>-1</sup>) in roots, suggesting that it behaves as excluder plant.

### Translocation factor

Based on the available data, the translocation factor (TF) (i.e. the ratio of metal concentration in leaves/metal concentration in roots), which expresses a measure of the plant's ability to transfer metals to its aerial parts or to block them in roots (Mendez & Maier 2008), was calculated for the investigated plants (Table 4). Data for Cr and Pb are not available, since these metals have been determined only in leaves of *P. Braunii* (Cr), *T. officinale* (Cr) and *S. nemorum* (Pb), probably due to an aerial contribution.

Most TFs are below 1, suggesting that the investigated plants are more prone to block metals in their roots than to translocate metals to the aerial parts: that is, a barrier effect by roots is likely to occur. Micronutrients Cu, Zn, Fe and Mn, show TFs in the range 0.5–1 in the examined plants, with some exceptions (Table 4), suggesting that these elements are taken up to a critical concentration and are then arrested in the roots. Iron (TF of 0.38) seems to be the least mobile in this group, particularly in *C. hirsutum*, with the lowest TF.

The translocation factor for Mn and Hg is somewhat contradictory: TF >1 in *S. nemorum* and *C. hirsutum* suggests an easy translocation from roots to leaves; conversely, TF <0.5 in *P. braunii*, and particularly in *T. officinale*, suggests that metals are likely to be arrested in the roots. These findings are quite surprising for *T. officinale*, since this species is known as an accumulator of selected metals (Bini *et al.* 2012).

It must be borne in mind that the assessment of the metal absorption ability of plants is difficult, because, to date, there are no univocal data in the literature that are related to 'normal' levels and those of phytotoxicity (Kabata-Pendias 2011). It should also be noted that the metal concentration within the plant is largely determined by the type of plant, the substrate, the bioavailability, the interaction between elements and many other environmental parameters, which makes a comparison between data collected under different conditions very complicated (Kabata-Pendias 2004). Nevertheless, it has been ascertained that plants tend to translocate micronutrients up to a critical concentration, and to exclude toxic elements by the barrier effect, as reported in previous papers (Bini 2010; Wahsha *et al.* 2012a). This is true of willows, which are able to accumulate and translocate metals, in particular Zn; qualifying them as good candidates for phytoremediation of polluted soils. Conversely, *Plantago major* shows very high metal concentrations in the roots and thus seems to qualify as an excluder species (Garbisou & Alkorta 2001). Translocation factors can also show how metals exhibit different mobility within the plant. Metals that are not essential for plant nutrition (e.g. Cr, Pb) tend to remain blocked in the roots, thereby suggesting an excluder strategy. Conversely, the essential nutrients (e.g. Cu, Zn, Fe, Mn) are present in similar concentrations in leaves and roots, which is typical of indicator plants, or even show higher concentrations in leaves than in roots, which is typical of accumulator plants (Adriano 2001).

### Conclusions

The soils of the investigated area present strong evidence of anthropogenic influence due to past mining activity, with high contamination of potentially harmful elements (Cu, Zn, Pb, Fe and Hg). Metals were released into the terrestrial ecosystem as a consequence of the weathering of waste material discharged in the proximity (<100 m) of the exploitation area during past mining activity.

The metal contents of the native vegetation show relatively high concentrations of these elements. Some of the selected plants (e.g. *S. nemorum* for Cu, Mn and Hg; *C. hirsutum* for Zn and Hg) seem to have good potential for use in land-restoration purposes with phytoremediation projects.

The area in question is part of the National Park of the Belluno Dolomites. Therefore, it could be used as a natural laboratory to raise awareness among park visitors about the impact caused by human activities.

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