

## Soil contamination by heavy metals at Libiola abandoned copper mine, Italy

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*Exploitation of ores has surely represented a risk for contamination of environmental matrices for a long time. This paper reports the results of a study concerning soil contamination by heavy metals at Libiola abandoned copper mine (Italy). This deposit has surely got special importance in Italy because of its historical, environmental and mining features. From a historical viewpoint, Libiola deposit was known since Copper Age, with maximum exploitation at the end of the 19<sup>th</sup> century. Our investigation plan was elaborated in order to characterize the environmental matrices there, and it provided for inspection of the zones (included in the valley of Gromolo stream) which, according to our preliminary studies and according to literature, could be most affected by past mining activity. Within our selected zones, some soils (even cultivated) were collected in order to check their contamination by heavy metals. Results from the analysis of the collected soil samples showed that the content of heavy metals often exceeds limits provided by the Italian Law 152/06. The knowledge of situation concerning pollution can give useful indications about the influence of mining activities on the surrounding environment, and it can also be valid support in order to organize an optimal future use of the studied mining area, which has been abandoned since its closure (1962).*

**Keywords:** contamination, dump-field, heavy metals, soil, pollution, abandoned mines.

### Introduction

The abandoned Libiola sulfide ore deposit is located in the valley of Gromolo stream, near Sestri Levante (Liguria), and it is one of the several deposits whose mineralization is related to Jurassic ophiolites (gabbros and diabases, Vara Supergroup) of Northern Apennine (Faccenna et al., 2001; Buccheri et al., 2014; Andráš et al., 2016). Surface covered by mine is about 4 km<sup>2</sup>, including more than 30 km of underground passages plus extensive open-cut mines that facilitate drainage of rainwater (Capello et al., 2016).

Libiola deposit may be classified as a strata-bound volcanic-associated massive sulfide deposit (VMS), and it occurs both as massive lens-shaped bodies which are concordant with pillow basalts and as scattered mineralization, done of small aggregates of sulfides, either filling vesicular cavities or concordant with pillows' textures (Andráš et al., 2017). Libiola ore deposit was formed because of convective circulation of seawater through hot rocks at spreading ridges; the successive metamorphic and tectonic processes because of Apennine orogenesis, caused the formation of this ore deposit (Scott, 1997). Sulfide mineralization at Libiola area is mainly associated to pillow basalts and basaltic breccia and, subordinately, to serpentinitic rocks of ophiolites of Internal Ligurian Units belonging to the Supergruppo della Val di Vara Unit (Fig. 1).

According to texture and setting (Andráš et al., 2017), we can distinguish three types of mineralization at Libiola mine:

- a) massive mineralization with pyrite and chalcopyrite as strata and lenticular bodies in basaltic rocks;
- b) mineralization in stockwork-veins, not economically important, with pyrite and chalcopyrite in pillow lavas;
- c) scattered mineralization consisting of millimetric pyrite crystals inside a serpentine (lizardite and chrysotile), chlorite, and magnetite matrix, in basaltic and serpentinitic rocks (tectonically overlying basalts).

The sulfide mineral assemblages consist of pyrite and chalcopyrite, with minor sphalerite and pyrrhotite, in a gangue of quartz, chlorite, and minor to accessory calcite in both massive lenses and mineralized veins. Disseminated mineralizations within the serpentinites consist almost exclusively of millimetric pyrite crystals scattered in a serpentine (lizardite and chrysotile), chlorite, and magnetite matrix (Marescotti et al., 2010).

At Libiola mines, oxides and hydroxides show themselves as massive crusts of variable colors from ochre-yellow to intense red (Marescotti et al., 2010).

Ca<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup> and Cu<sup>2+</sup> sulfates show themselves as surface efflorescences, which are formed by water evaporation of interstitial water or by precipitation of circulating solutions. Besides hydroxides, sulfates, and phyllosilicates, it is also possible to observe some Cu<sup>2+</sup> and Ca<sup>2+</sup> carbonates, cuprite, native copper and secondary sulfides such as chalcocite.

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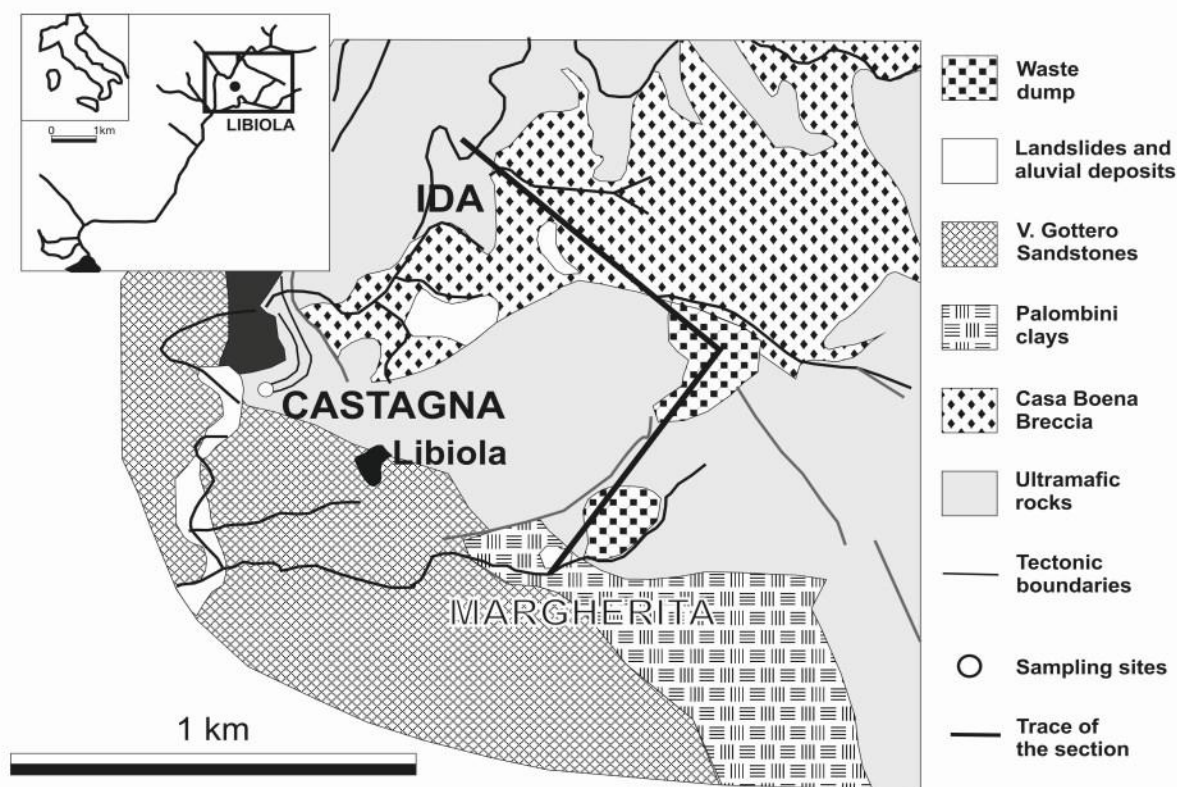


Fig. 1. Geological sketch map of Libiola mining area (Dinelli et al., 2007). About Ligurian Domain, it includes both tectonic units deriving from the Jurassic oceanic lithosphere (Ligure-Piedmont oceanic basin) and their sedimentary covers (Jurassic-Paleocene). The Internal Ligurian Units outcrop between the north-western side of Northern Apennine and the southern border of the western Alps. They are divided (from the bottom) as it follows: 1) a peridotitic basement (more or less serpentized ultra-mafites) associated to gabbros; 2) a volcano-sedimentary complex, characterized by presence of tectonic and sedimentary ophiolitic breccias, and massive or pillow effusive basalts at its bottom, and by a cover of fine oceanic sediments; 3) torbiditic deposits; 4) schist.

From a historical viewpoint, Libiola mine is one of the most ancient and important heritage of copper extraction activity in western Europe, together with Monte Loreto mine (near Castiglione Chiavarese, Liguria). According to radio-carbon analysis on the discovered pre-historical tools, first excavations at Libiola were dated around 3500 B.C. (Marescotti et al., 2018). Such rests testify early exploitation of iron and copper from Jurassic ophiolitic succession.

Ligurians, the enemy of Romans, built their weapons with copper coming from Libiola. Libiola mine was also exploited during the Roman Age. Around 1840, the interest for mines got higher again because of funds from Savoia administration. Libiola mine was thus exploited at an industrial level (important enrichment plants were built), and this fact contributed to the cancellation of the most ancient extraction traces. Mining activity kept on flourishing until the first thirty years of the 20<sup>th</sup> century, and its maximum production was achieved at the beginning of the 20<sup>th</sup> century (Buccheri et al., 2014).

After the Second World War, mining activity at Libiola fell into a crisis. In 1955, after its passage to Montecatini Society, this mine was closed, and then it was abandoned (1962). Closure of the mine left a degraded and polluted landscape. As a matter of fact, such long exploitation left a considerable amount of waste as heaps without vegetation covering a total area of ~ 500,000 m<sup>2</sup>. Mine waste is poorly sorted, either sterile or mineralized rock fragments, mainly serpentinites and basalts, and secondary mineral phases produced by weathering (mainly Fe oxy-hydroxides, brown-reddish-orange in color) (Marini et al., 2003; Marescotti et al., 2010; Carbone et al., 2005, 2013).

One of the most interesting aspects characterizing Libiola mines is due to water flowing out of the old galleries, which are a typical example of Acid Mine Drainage (AMD). Originated by oxidative dissolution of pyrite, and subordinately of other metal sulfides, as well as by processes of mixing, dilution, and especially neutralization through water-rock interaction, we can observe two distinct groups of water at Libiola: red and blue water, up to the color of the deposited solid phases. Red water is acidic (pH 2.4 – 3.5), whereas blue water pH is close to neutral (Andr  s et al., 2017).

Libiola mining area is included in the hydrographic basin of Gromolo stream. Its path starts about 10 km from the coast and debouches in Mar Ligure, covering an area of about 21 km<sup>2</sup> (Provincia di Genova, 2013).

The hydrographic network is asymmetric with respect to the main river course. Distribution of rivers inside the network is rather homogeneous. Among the most important tributaries on the left bank, Rio Boeno and Rio

Cattan are the most important ones from our viewpoint because they represent confluence points of mining waters, continuously coming from the northern and the southern slopes of the mining area respectively. Hydrologic regime of the area including Libiola abandoned mine is very affected by mining activities. As a matter of fact, acid water is constantly flowing out of the several galleries (in particular in correspondence with downward galleries Margherita, Ida, Weirs, and Castagna) and discharged into Gromolo stream, thus representing a threat for the surrounding environment (Consani et al., 2017). This feature is due to the presence of an extended network of interconnected galleries and wells, which facilitates drainage of raining water. At higher quotes, extended open excavations (showing a sink-like morphology) are moreover present: they increase drainage of water and represent important artificial basins for water collection (Buccheri et al., 2014).

Precipitation of ferrihydrite and schwertmannite (Dinelli et al., 2001; Asta et al., 2015) takes place upon mixing between acid mine waters and surface waters. Most of these solid phases remain in suspension in river waters. Although precipitation of these minerals may scavenge some metals, river waters are heavily polluted, especially during the dry season, when their flow rate decreases.

The end of mining activity there left many questions about the probable pollution of environmental matrices there and the instability of excavations, galleries, and dumps. The waste-rock dumps are very heterogeneous from mineralogical and geochemical viewpoints, with significant lateral variations and vertical heterogeneity, because dumps were formed within a period of over 50 years, during which different exploitation techniques were used, and several lithotypes and economic minerals were extracted (both underground and by open-air excavations). Waste materials that were piled up during exploitation included both host rocks and not economic mineralization derived from handpicking, milling and other treatments (Marescotti et al., 2008).

### Materials and methods

After studying past literature and after inspecting the interested mining area, we could confine our largest investigation area within the hydrographic basin of *Gromolo* stream, starting from identification of potential danger centers present in the area.

Potential danger centers can be related to: extraction activities (i.e. mining excavations, discharges for tracing deposit or for mining research), mineral processing (i.e. basins for mine steriles, banks of fine rests, steriles from gravimetry) and presence of different waste (i.e. reagents used at plants, oils, coverings or detritus with concrete-asbestos).

In the case of *Libiola* mining area, primary contamination sources are represented by dumps, excavations, and galleries. They can undergo erosion, powders emission and solid transport to soils and river sediments as well as infiltration, percolation and leaching, causing hydro-geological instability. Secondary contamination sources are there represented by hydro-geological instability and by soil (and sediments), which can move pollution to surface and groundwater (by solid transport or in solution) and wind/atmosphere (by the emission of powder).

After identifying the possible polluting sources present in the area, we could also identify the potential migration pathways of contaminants from sources to targets, according to features of the sources themselves and according to geologic, hydro-geologic and geomorphologic features of the site. It allowed us to build up a preliminary conceptual model (MCP).

We could thus realize our investigation plan in order to obtain a correct definition of features of danger centers and quality status of environmental matrices within our investigation area. We decided for a “reasoned” sampling strategy (Fig. 2), thus based on knowledge of the site itself (morphology, type of materials, active erosion, results of past investigations, etc.), which allowed us identification of the most vulnerable areas and the most probable contamination sources. Sampling operations were documented by pictures showing collecting points of each sample and the area in its context. Each sample was identified with univocal initials.

Soil and techno-soil samples (about 10 kg in weight) were collected by using manual tools down to 30-50 cm in depth. Samples were then saved in labeled containers, after taking out vegetable rests and roots, till laboratory analysis.

ICP-MS analyses of heavy metal content in soil and techno-soil samples were carried out by ACME Laboratories in Vancouver (Canada), starting from samples of 50 g in weight. Samples were homogenized and dried at laboratory temperature. The grinding in agate mill was realized in the laboratory of UMB, Banská Bystrica (Slovak Republic). We are reporting results in the following paragraph (Tab. 1, 2).

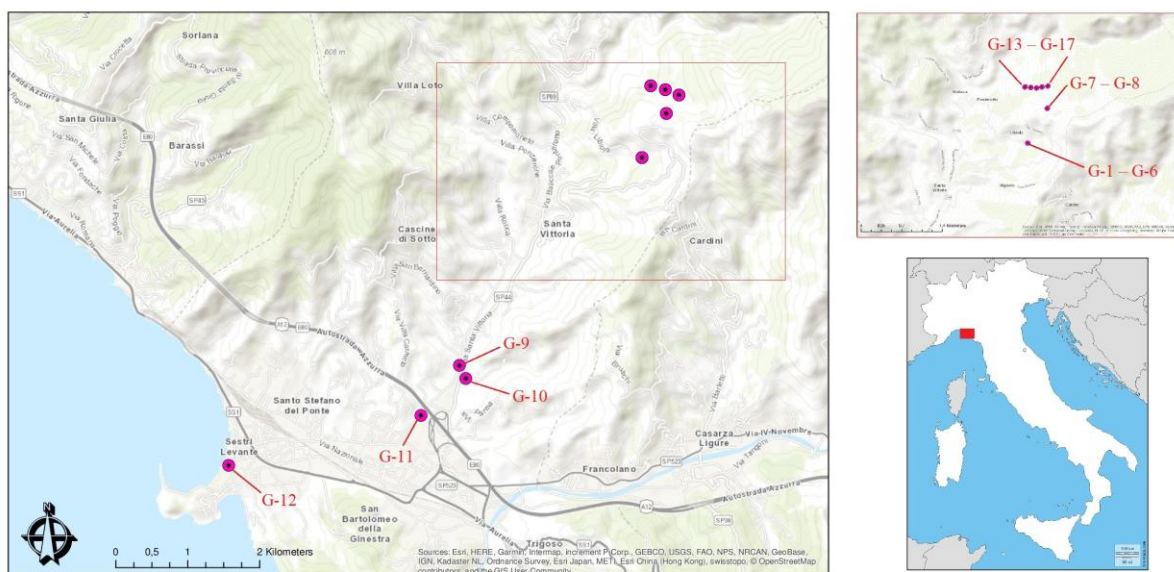


Fig. 2. Map with location of sampling points at Libiola mining area.

## Results and discussion

Table 1 reports concentration values concerning soil and techno-soil samples collected at Libiola mining site, compared with Italian law limits provided by the Italian Law 152/06 (Decreto Legislativo 3/4/2006, n. 152, Norme in materia ambientale).

Tab. 1. Concentration values concerning soil and techno-soil samples collected at Libiola mining site, compared with Italian law limits provided by the Italian Law 152/06. Concentration values exceeding the limit for residential/public green (A) are marked, whereas concentration values exceeding the limit for industrial/commercial sites (B) are both marked and underlined.

Soil Sample	Latitude	Long	Cu	Pb	Zn	Ni	Co	As	Cd	Sb	V	Cr	B
G-1	44.299763	9.445048	<u>1794</u>	44	374	<u>982</u>	85	5	0.9	<3	75	<u>961</u>	<u>36</u>
G-2	44.299763	9.445048	<u>1624</u>	47	328	<u>732</u>	73	5	0.8	<3	65	<u>752</u>	<u>36</u>
G-3	44.299763	9.445048	<u>1765</u>	27	<u>402</u>	<u>1115</u>	<u>101</u>	4	1.1	<3	<u>121</u>	<u>989</u>	<u>43</u>
G-4	44.299763	9.445048	<u>&gt;10000</u>	14	<u>2851</u>	<u>574</u>	<u>87</u>	3	<u>5.3</u>	<3	<u>185</u>	<u>444</u>	<u>39</u>
G-5	44.299763	9.445048	<u>323</u>	<u>137</u>	22	9	2	10	0.7	<3	<u>231</u>	86	<20
G-6	44.299763	9.445048	3343	40	<u>219</u>	18	7	<u>110</u>	1.0	<3	<u>202</u>	117	<20
G-7	44.303712	9.448071	<u>&gt;10000</u>	<u>476</u>	<u>354</u>	<u>308</u>	<u>34</u>	<u>266</u>	<0.5	<u>84</u>	<u>176</u>	<u>1121</u>	<20
G-8	44.303712	9.448071	1383	38	113	32	<u>10</u>	12	0.8	<3	<u>266</u>	<u>190</u>	<20
G-9	44.281134	9.422246	<u>284</u>	55	<u>228</u>	<u>560</u>	<u>49</u>	5	<0.5	<3	53	<u>530</u>	<u>31</u>
G-10	44.280005	9.423046	<u>820</u>	<u>189</u>	<u>288</u>	<u>196</u>	<u>51</u>	3	<0.5	<3	<u>191</u>	<u>274</u>	<u>29</u>
G-11	44.276664	9.417445	<u>371</u>	98	<u>177</u>	<u>488</u>	<u>39</u>	8	<0.5	<3	43	<u>475</u>	<u>30</u>
G-12	44.273630	9.393970	<u>448</u>	32	<u>189</u>	<u>435</u>	<u>38</u>	6	<0.5	<3	73	<u>455</u>	<u>36</u>
Law limit A [mg/kg]			<u>120</u>	<u>100</u>	<u>150</u>	<u>120</u>	<u>20</u>	<u>20</u>	<u>2</u>	<u>10</u>	<u>90</u>	<u>150</u>	<u>2</u>
Law limit B [mg/kg]			<u>600</u>	<u>1000</u>	<u>1500</u>	<u>500</u>	<u>250</u>	<u>50</u>	<u>15</u>	<u>30</u>	<u>250</u>	<u>800</u>	<u>10</u>

Sample G-4 is a detritus containing blue patina near *Margherita* Gallery. It shows the highest values for copper (there, in fact, chalcantite is present) and zinc. Nickel also a little exceeds limit B. Cobalt, cadmium, vanadium and chromium exceed limit A. Content in cadmium in the sample G-4 could be due to the simultaneous presence of greenockite and sphalerite.

G-7 (southern dump, upper layer, Fig. 3) shows, together with G-4, the highest value as far as copper is concerned. It also shows high values as far as arsenic (over five times the allowed limit B), antimony (almost three times) and chromium are concerned. About the sample G-7, all elements are shown in Table 1, also exceed limit A (except for cadmium).

We can also underline that horizons of cultivated soil near *Margherita* Gallery (G-1, G-2 e G-3) show values over limit B as for copper (almost three times), nickel, chromium (only G-2 shows a value that is a little lower than the limit B) and boron. About high values in boron (between three and four times the allowed limit B), we must remember that ophiolites (basaltic volcanic rocks which were erupted in the submarine environment about 150 million years ago and which are present in the scaly clays) show high resistance against erosion in

comparison with clays. During their long geological story, lava flows were fractured. Mineralized waters could thus deposit on them salts with calcium, silicon, boron, and aluminum: thus, several minerals could be formed, also containing boron, i.e., datolite -  $\text{CaB}(\text{OH}/\text{SiO}_4)$ , a silicate, associated to basic ophiolitic rocks, which is formed by the action of hydrothermal fluids containing boron.

We must also underline that in samples G-1, G-2 e G-3 (collected under an olive tree), zinc and cobalt also exceed limit A (Law 152/06).



Fig. 3. Libiola southern dump.

G-5 (detritus from the dump, upper layer) is the least contaminated sample: only copper, lead, and vanadium exceed limit A. No metal there exceeds limit B.

Vanadium (together with copper) exceeds limit B only in the sample G-8 (lower layer, -50 cm, the sediment of the southern dump). As for G-8, cobalt and chromium exceed limit A.

About the sample G-6 (detritus from the dump, -50 cm), copper (over five times) and arsenic (more than twice) exceed limit B. Zinc, and vanadium exceed limit A.

If we move away from the mining area to the sea, while following *Gromolo* stream, the situation seems safer, even though, in the sample G-10 (orographic left of *Gromolo* stream, along with Provincial Street SP44), copper and boron (almost three times) exceed limit B. About G-10, lead, zinc, nickel, cobalt, vanadium, and chromium exceed limits A.

The situation of the sample G-9 (orographic right of *Gromolo* stream, locality *Villa Scorza*) results a little safer, on the average, but limit B for nickel shows low exceed. In G-9, copper, zinc, cobalt, and chromium also exceed limit A.

The sample G-11 (orographic right of *Gromolo* stream, *via Fabbrica a Valle*) shows a content in boron that is three times higher than limit B (Law 152/06). Moreover, copper, zinc, nickel, cobalt, and chromium also exceed limit A. Limit A concerning lead is almost reached there.

About the sample G-12 (sediments at the mouth near hotel "Grande Albergo"), copper, zinc, nickel, cobalt, and chromium exceed limit A.

An interesting high concentration of boron was found in many samples. It could also be due to the presence of datolite (to be confirmed by successive analysis), at least partially. Datolite is a mineral that we could mainly find in gabbro, and that could also be easily found in *Bargonasco* Valley (i.e., *Gallinaria* mine and at other outcrops), a parallel and eastern valley with respect to *Gromolo* Valley. Though we cannot exclude that presence of datolite at *Libiola* mining area could be responsible for an increase of boron content in our soil samples, we

must, therefore, underline that diffusion of datolite in this mining area is not expected to be so large to justify such a high content in boron.

It is also interesting to notice that a high concentration of boron has been found near *Margherita* Gallery and in soil samples collected out of *Libiola* mining area (till the mouth of *Gromolo* stream, *Sestri Levante*), whereas we couldn't find such a high boron concentration in dump-soils and detritus from mining discharge near *Margherita* Gallery. We find interesting to deepen reasons for such high concentration of boron.

We also focused our attention on the northern side of the mining area (Table 2), in the surroundings of the main building. There, soil samples G-13 to G-17 were collected (Fig. 4). As for G-15, we also differentiated soil horizons (A, B, C).

Tab. 2. Concentration values concerning soil and techno-soil samples collected at the northern side of Libiola mining site, compared with Italian law limits provided by the Italian Law 152/06. Concentration values exceeding the limit for residential/public green (A) are marked, whereas concentration values exceeding the limit for industrial/commercial sites (B) are both marked and underlined.

Soil Sample	Latitude	Long	Cu	Pb	Zn	Ni	Co	As	Cd	Sb	V	Cr
G-13	44.305623	9.448771	<b>946</b>	75	<b>411</b>	81	<b>34</b>	11	1,0	4,0	<b>282</b>	<b>222</b>
G-14	44.305701	9.448023	<b>2992</b>	17	<b>228</b>	<b>511</b>	<b>62</b>	7	<b>9,5</b>	0,6	<b>139</b>	<b>702</b>
G-15 A	44.305741	9.447636	<b>&gt;10000</b>	49	<b>606</b>	<b>1023</b>	<b>462</b>	8	<b>2,2</b>	1,7	<b>143</b>	<b>1118</b>
G-15 B	44.305741	9.447636	<b>&gt;10000</b>	70	<b>691</b>	<b>908</b>	<b>541</b>	15	<b>2,7</b>	3,1	<b>151</b>	<b>830</b>
G-15 C	44.305741	9.447636	<b>7346</b>	31	<b>436</b>	<b>1115</b>	<b>197</b>	12	1,4	1,9	<b>99</b>	<b>1158</b>
G-16	44.305833	9.447268	<b>5639</b>	34	<b>435</b>	<b>714</b>	<b>109</b>	9	<b>3,6</b>	4,8	<b>142</b>	<b>1374</b>
G-17	44.305775	9.446834	<b>3239</b>	<b>114</b>	<b>265</b>	<b>668</b>	<b>82</b>	15	0,5	7,7	<b>196</b>	<b>1145</b>
Law limit A [mg/kg]			<b>120</b>	<b>100</b>	<b>150</b>	<b>120</b>	<b>20</b>	<b>20</b>	<b>2</b>	<b>10</b>	<b>90</b>	<b>150</b>
Law limit B [mg/kg]			<b>600</b>	<b>1000</b>	<b>1500</b>	<b>500</b>	<b>250</b>	<b>50</b>	<b>15</b>	<b>30</b>	<b>250</b>	<b>800</b>



Fig. 4. Dumps on the northern side of Libiola mining area.

Among these samples, G-15 is the one showing the highest contamination because of copper, nickel, cobalt, chromium, and zinc. It also shows a high concentration of vanadium. High concentrations of copper, cobalt, chromium, and zinc can also be due to the presence of a small creek river draining a part of the dump-field and flowing in a small channel upstream of the main building (Fig. 5). As a matter of fact, it joins *Rio Boeno* stream more or less where G-15 is located. It could justify high concentrations of copper, cobalt, chromium, and zinc, which, on the contrary, should decrease westwards from sample G-13 to sample G-17, as sampling points are farther from *Rio Boeno* stream, with the consequence that dilution could be expected.



Fig. 5. Map (from Google) representing the northern side of Libiola mining area, also showing the location of Weirs Gallery. The arrow indicates water flow from Weirs Gallery, through a small channel, in the direction of the area where samples G-13 to G-17 were collected (fig. 4).

With regard to it, it is necessary to underline that some pools for copper cementation were present in the surroundings of the main building in the past: as a matter of fact, some iron shavings can be found in the surroundings of the area (probably used to activate oxido-reduction processes to water flowing out from Weirs Gallery). It is thus plausible that defluxe interesting this area shows very high concentrations that, without pools, can reach *Rio Boeno* stream and justify higher concentrations in that point. Whereas, in the past, water flowing out from *Weirs* Gallery passed through pools, nowadays this water directly reaches *Rio Boeno* stream.

G-16 shows high contamination of copper, nickel, cobalt, chromium, zinc, and vanadium. Copper, nickel, and chromium exceed limit B. A little bit better situation is shown by the sample G-17 as far as values over the limit are concerned, with the difference that in G-17 cadmium remains under the thresholds provided by Law 152/06, whereas lead shows there higher contamination in comparison with the sample G-16.

In the sample G-14, closer to the main building, most of the analyzed metals (especially copper and nickel) exceed. Zinc, cobalt, cadmium, vanadium, and chromium exceed limit A (Law 152/06). It must be noticed that G-14 shows the highest content in cadmium among all analyzed samples.

In the sample G-13, copper and vanadium show high values, whereas nickel remains under the thresholds provided by Law 152/06. Zinc, cobalt, and chromium also exceed.

### Conclusion

After results from analysis of soils collected in *Libiola* mining area and at surroundings, we can observe that:

- The content of heavy metals often exceeds limits provided by the Italian Law 152/06, and it is known that presence of heavy metals at abandoned copper mines, given by ore composition assemblage, can become a very important source of contamination for the surrounding environment. We must easily notice, for example, that sample G-12 (collected at the mouth of *Gromolo* stream) shows a content in chromium that exceeds three times the limit value provided by the Italian Law 152/06 for residential houses/public green.
- Sample G-7 is the only one in which antimonium exceeds according to the Italian Law 152/06 (limit B) and in which lead shows the most important deal. In any case, it is easy to obtain very different values when soils are collected from discharge, even within small distances, because of the extraordinary irregularity of the dumps, where concentrations of minerals are connected to the several extractive phases and the logistic points besides to the crossed lithotypes.

- We still find necessary to integrate our investigation plan by including other sampling points, in order to isolate anomalous compositions from the “average” ones, also taking into account that soils collected downstream of the mining area show concentration related to fluids that, after interacting with crossed materials, transport elements far away from the mine. Furthermore, transportation capability of these fluids depends on a) their physical and chemical properties, b) contribution of additional water streams not interacting with the mining area and c) seasonal fluctuation of stream flows. Additional sampling campaigns will have to consider all these variables in order to investigate better the area and related dynamics.
- About concentration values on the northern dumps, G-15 is the one showing the highest contamination because of copper, nickel, cobalt, chromium, and zinc. A cavity, upstream of the main building, acts as a drain for mineralized waters. As the leached part of the dump is a source for metals in solutions, we should expect that physical conditions gradually change westwards (pH, in particular, because of the confluence with secondary and neutral channels and because of interaction with more neutral soils), causing precipitation of part of metals. On the contrary, in our case, concentrations show an anomalous trend from G-13 and G-17, because they show a peak with the sample G-15. This anomalous trend can be caused by the presence of a source (i.e., the above mentioned small drain), flowing into *Rio Boeno* stream, that could also collect (because of infiltration) defluve water from *Weirs* Gallery which, in the absence of the pools that were used for cementation of copper, directly flow into *Rio Boeno* stream.

### References

- Andraš, P., Turisová, I., Buccheri, G., Matos, J.X., Dirner, V. (2016). Comparison of heavy-metal bioaccumulation properties in *Pinus* sp. and *Quercus* sp. in selected European Cu deposits. *Web Ecol.*, 16, 81–87, 2016; [www.web-ecol.net/16/81/2016/](http://www.web-ecol.net/16/81/2016/) doi:10.5194/we-16-81-2016.
- Andraš, P., Turisová, I., Matos, J.X., Buccheri, G., Andráš, P. Jr., Dirner, V., Kučerová, R., Castro, F.I.P., Midula, P. (2017). Potentially toxic elements in the representatives of the genus *Pinus* L. and *Quercus* L. at the selected Slovak, Italian and Portuguese copper deposits. *Carpathian Journal of Earth and Environmental Sciences*, February 2017, Vol. 12, n. 1, 95 – 107.
- Asta, M.P., Calleja, M.L., Pérez-López R., Auqué, L.F. (2015). Major Hydrogeochemical processes in Acid Mine Drainage affected estuary. *Marine Pollution Bulletin*, Vol. 91, Issue 1, 295-305. [10.1016/j.marpolbul.2014.11.023](https://doi.org/10.1016/j.marpolbul.2014.11.023)
- Buccheri, G., Andráš, P., Astolfi, M.L., Canepari, S., Ciucci, M., Marino, A. (2014). Heavy metal contamination in water at Libiola abandoned copper mine, Italy. *Rom. J. Mineral Deposits*, ISSN 1220-5648, vol. 87, No. 2, 65-70.
- Capello, M., Cutroneo, L., Consani, S., Dinelli, E., Vagge, G., Carbone, C. (2016). Marine sediment contamination and dynamics at the mouth of a contaminated torrent: The case of the Gromolo Torrent (Sestri Levante, north-western Italy), *Marine Pollution Bulletin*, 2016, 109, pp. 128 – 141.
- Carbone, C., Di Benedetto, F., Marescotti, P., Martinelli, A., Sangregorio, C., Cipriani, C., Lucchetti, G., Romanelli, M. (2005). Genetic evolution of nanocrystalline Fe oxide and oxyhydroxide assemblages from the Libiola mine (eastern Liguria, Italy) structural and microstructural investigations. *European Journal of Mineralogy*, Vol. 17, n. 5, 785-795. Editor: E. Schweizerbart'sche Verlagsbuchhandlung Science Publishers.
- Carbone, C., Dinelli, E., Marescotti, P., Gasparotto, G., Lucchetti, G. (2013). The role of AMD secondary minerals in controlling environmental pollution: indications from bulk leaching tests. *Journal of Geochemical Exploration*, Vol. 132, 188-200. Elsevier.
- Consani, S., Carbone, C., Dinelli, E., Balić-Žunić, T., Cutroneo, L., Capello, M., Salviulo, G., Lucchetti G. (2017). Metal transport and remobilisation in a basin affected by acid mine drainage: the role of ochreous amorphous precipitates. *Environmental Science and Pollution Research International*, ISSN: 0944-1344, doi: 10.1007/s11356-017-9209-9.
- Italian Law 152/2006. Decreto Legislativo 3/4/2006, n. 152, Norme in materia ambientale. In Italian language.
- Dinelli, E., Lucchini, F., Fabbri, M., Cortecchi, G. (2001). Metal distribution and environmental problems related to sulfide oxidation in the Libiola copper mine area (Ligurian Apennines, Italy). *Journal of Geochemical Exploration*, 74(1-3), 141–152.
- Dinelli, E., Perkins, W.T., Pearce, N.J.C., Hartley, S. (2007). IMWA Symposium 2007: Water in Mining Environments, R. Cidu & F. Frau (Eds), 27-31 May 2007. Cagliari, Italy.
- Faccenna, C., Becker, T.W., Lucente, F.P., Jolivet, L., Rossetti, F. (2001). History of subduction and back arc extension in the Central Mediterranean Geophys. *J. Int.*, 145, 809-820.



- Marescotti, P., Brancucci, G., Sasso, G., Solimano, M., Marin, V., Muzio, C., Salmona, P. (2018). Geoheritage Values and Environmental Issues of Derelict Mines: Examples from the Sulfide Mines of Gromolo and Petronio Valley (Eastern Liguria, Italy). *Minerals*, 8, 229.
- Marescotti, P., Azzali, E., Servida, D., Carbone, C., Grieco, G., De Capitani, L., Lucchetti, G. (2010). Mineralogical and geochemical spatial analyses of a waste-rock dump at the Libiola Fe–Cu sulphide mine (Eastern Liguria, Italy). *Environ Earth Sci* (2010), 61, 187-199. DOI 10.1007/s12665-009-0335-7.
- Marescotti, P., Carbone, C., De Capitani, L., Grieco, G., Lucchetti, G., Servida, D. (2008). Mineralogical and geochemical characterization of open-air tailing and waste-rock dumps from the Libiola Fe-Cu sulphide mine (Eastern Liguria, Italy). *Environ Geol* DOI 10.1007/s00254-007-0769-8.
- Marini, L. Saldi, G., Cipolli, F., Ottonello, G., Vetuschi Zuccolini, M. (2003). Geochemistry of water discharges from the Libiola mine, Italy. *Geochemical Journal*, Vol. 37, pp. 199 to 216.
- Provincia di Genova (2013). Ambito Regionale di Bacino 17. Piano di Bacino Stralcio sul rischio idrogeologico (ai sensi dell'art. 1, comma 1, del D.L. 180/1998 convertito in L. 267/1998) - Torrente Gromolo - Relazione Generale.
- Scott, S. (1997). Submarine hydrothermal systems and deposits. *Geochemistry of Hydrothermal Ore Deposits* (Barnes, H. L., ed.), 3<sup>rd</sup> ed., 797–875, Wiley, New York.