

CHARACTERIZATION OF A METAL-CONTAMINATED WASTE ROCK DUMP USING FIELD PORTABLE X-RAY FLUORESCENCE (FPXRF) SPECTROMETRY

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INTRODUCTION

Waste rocks dumps are chemically heterogeneous deposits piled up during mining exploitation over tens of years (Jambor & Blowes, 1994 and references therein; Marescotti *et al.*, 2008, 2010). They contain non-mineralized rocks and low-grade mineralizations and are typically characterized by significant vertical and lateral heterogeneities in grain size, lithology, mineralogy and chemistry. Waste rock dumps are often sites of environmental concern because they commonly contain high concentrations of metals and metalloids which may be released to the circulating waters during weathering. Moreover, the metal leaching may be exacerbated by Acid Mine Drainage (AMD) processes (Jambor & Blowes, 1994; Jambor *et al.*; 2000; Jambor, 2003).

With this work we investigated the chemical composition and the metal distribution within a sulphide bearing waste rock dump using a Field-Portable Energy Dispersive X-ray fluorescence (FP-EDXRF). Thanks to the possibility of analyzing a large number of samples by means of FP-EDXRF, in a cost-efficient and timely manner, the entire analytical data set were processed in QGIS for spatial analysis, in order to recognize the spatial relationships among the different variables.

The site chosen for this study is a small-sized dump from an abandoned Cu-sulphide mine (Rio Bansigo mine, eastern Liguria, Italy), which was extensively exploited from 1904 to 1926.

MATERIALS AND METHODS

Study Area

The Rio Bansigo mine is located about 4.5 km ENE of Casarza Ligure (Eastern Liguria, Italy). The mine covers an area of about 30,000 m² and comprises 7 galleries located at an altitude between 326 and 494 m.a.s.l. Mine wastes were dumped in one major pile located close to the main mine adits.

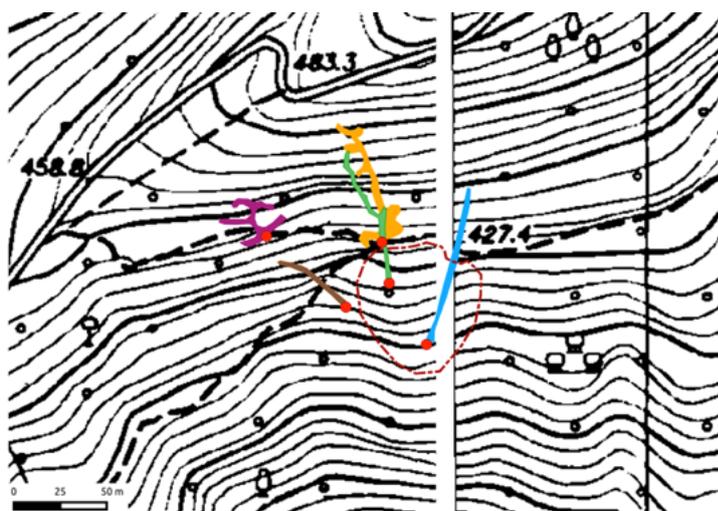


Fig. 1 - Topographical maps with the superimposition of the main mine galleries and the perimeter of the waste-rock dump (red dashed line).

Through georeferencing the historical maps, the galleries and the waste-rock dump were compared to present day satellite imagery and maps (Fig. 1). The waste-rock dump (Fig. 2) has a horseshoe shape, is about 34 m in height, cover a surface of about 3,400 m² and has a mean wall slope of about 30°. The dump is characterized by intense erosive processes that cause several debris-flow. The dumped materials are granulometrically heterogeneous (varying from boulders to silt) and are slightly cemented by iron oxides and oxyhydroxides. Centimetric to decimetric hardpans are present in several part of the dump where enrichment of sulphide are present.



Fig. 2 - The waste-rock dump of the Rio Bansigo mine.

have not been detected during the three years survey. However, dripping waters commonly occurs within the mine galleries, which are locally awash. The diffuse presence of iron-oxides concretionary formations indicates that sulphide-oxidation processes are still active, even if AMD processes resulted possible but non-persisting over time, as also evidenced by the net acid producing potential (NAPP) calculations.

Sampling (waste-rock materials and surrounding soils)

Two sampling plans were developed on the basis of GIS maps and of the data collected during the survey campaigns. The first sampling plan allowed the collection of 38 samples (19 waste-rocks, 4 undisturbed soils, and 15 outcropping rocks; Fig. 3) and was based on a 15 x 15 m square cell-grid designed using the open source GIS software GRASS GIS 6.4.

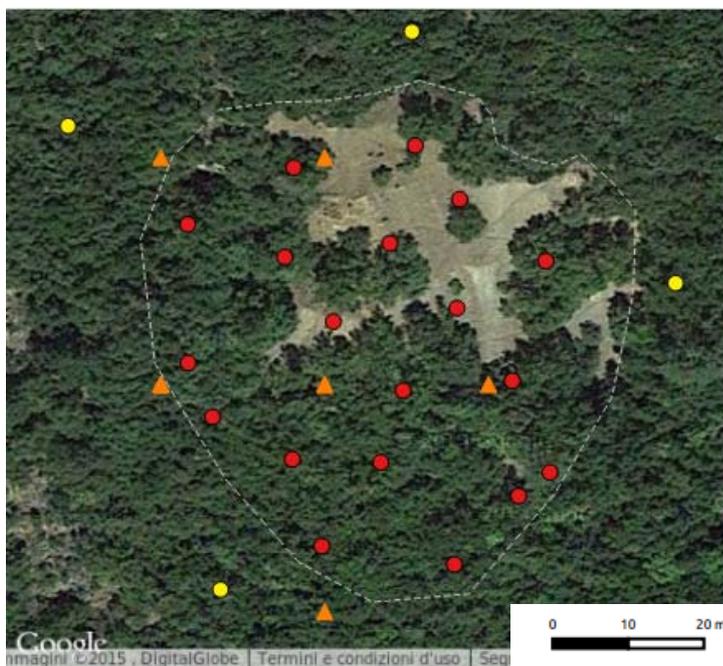


Fig. 3 - Samples location of outcropping rocks (orange triangles), undisturbed soils (yellow circles), and waste-rock materials (red circles).

The sulphide ore occurs within the Jurassic ophiolites of the Northern Apennine (Vara Supergroup; Abbate *et al.*, 1980) which consist of an ultramafic/gabbroic basement overlain by a volcano-sedimentary sequence (ophiolitic breccias, pillow basalts, and cherts). The sulphide-ore occurs within pillow basalts and has been classified as stockwork ore type 4c (Ferrario & Garuti, 1980; Garuti *et al.*, 2008). The sulphide mineral assemblage consist of chalcopyrite \pm pyrite \pm sphalerite in a gangue of quartz with minor chlorite and calcite (Zaccarini, 2006).

In the entire mining area, outflow of mine waters from the gallery addicts

Moreover, 4 samples from the uncontaminated soils surrounding the waste rock dump were analyzed to determine the natural background of the studied area.

According to the current national and international guidelines, for each sampling point about 1.5 kg of material was taken by digging a trench (about 30-40 cm in depth) and by removing the upper 20 cm from the ground level. After sieving, the granulometric fraction < 2 mm was split into three identical portions for the mineralogical and geochemical analyses.

The second sampling campaign was performed to increase the sampling density by reducing the sampling grid from 15x15 m to 5x5 m; sampling points were chosen by an "adaptive sampling" based on the geochemical results

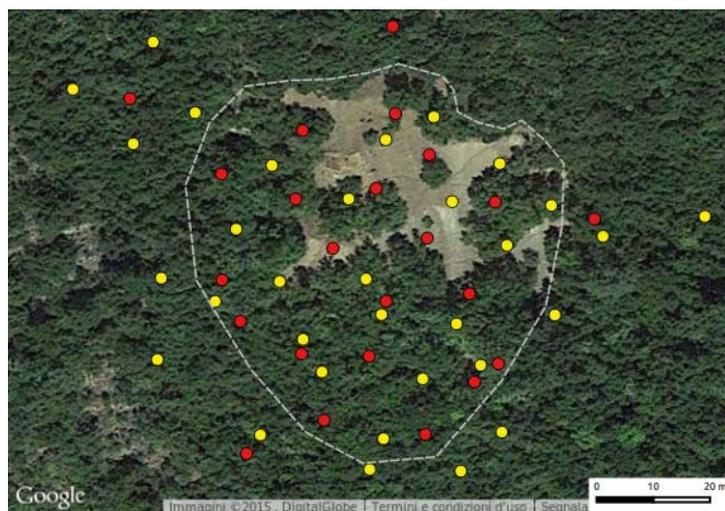


Fig. 4 - Samples location of first (red circles) and second (yellow circles) sampling campaigns.

obtained with the previous sampling campaign. At this stage 32 new sampling sites were selected and analyzed *in situ* by means of FP-EDXRF (Fig. 4). The sampling points of both campaigns have been georeferenced by means of GPS satellite receiver with 12 channels (model Garmin eTrex Vista HCX), an iPad device (using MotionX GPS App), and an Android device (using the Geopaparazzi App). The simultaneous use of these instruments allowed to directly map *in situ* the sampling points thus reducing significantly the error rate. The relative cartography and the associated database were realized by means open source software (GRASS GIS 6.4 and QGIS 1.8-2.2).

Analytical methods

The chemical parameters of soil (pH, Eh) were analyzed by means of portable pH meter “WTW PH330i”, equipped with “SenTix41” and “SenTix ORP” electrodes.

The mineralogy of the samples was determined using several techniques that included transmitted- and reflected-light optical microscopy, scanning electron microscopy and microanalysis (SEM-EDS; SEM VEGA3_TESCAN equipped with the EDS detector APOLLO XSDD). The thin sections of the incoherent samples were carried out on the granulometric fraction 0.177-0.350 mm since it represents the best compromise between a statistically significant number of grains and the possibility to observe polimineralic grains suitable for the identification of textural and lithological characteristics. Quantitative analyses were performed by point counting and image analysis.

Bulk-rock chemistry (major, minor, and trace elements) were carried out using the OXFORD X-MET7500 FP-EDXRF with a FP (Fundamental Parameter) calibration built-in by the factory. With the used analytical conditions (counting time = 120s; X-ray tube 45 kV), it is able to identify and quantify all elements with atomic number between 12 (Mg) and 92 (U). Confirmatory analyses were performed by means of ICP-MS (AcmeLabs®, Canada) which allowed to verify the high quality of the FP-EDXRF results ($SD < 10\%$; $R2 0.7-1$) for all the analyzed elements with the exception of those occurring in concentrations close to the detection limit.

Considering only the environmentally significant elements and according to the USEPA protocol (1998) for the evaluation of the data quality level, Cu and Zn fall in the Class 1 (definitive data quality level) whereas Mn, Ni, Pb fall in the Class 2 (quantitative data quality level). Only Cr and V fall in the Class 3 (qualitative screening data quality level).

Finally, statistical analysis ANOVA (analysis of variance) and MDS (MultiDimensional Scaling) were respectively performed to determine if there is a statistical compatibility between the analytical results obtained with the two techniques (ICP-MS and FP-EDXRF) and to highlight potential correlations between the main chemical variables.

To display the distribution of the environmentally most significant chemical elements (Co, Cr, Ni, Pb, Cu, Sn, V, Zn) contour maps were drawn with Inverse Distance Weighted Interpolation (IDW) method.

RESULTS AND DISCUSSION

Mineralogy and lithology

All waste-rock and soil samples were well sorted and, according to the Shepard (1973) classification, they were found to be sandy and silty-sandy sediments, respectively.

According to the results of the mineralogical and petrographic analysis the following lithological and mineralogical classes were distinguished: 1) sulphide mineralizations; 2) Fe-rich oxidation crusts; 3) carbonates; 4) host rocks; 5) other components. The quantitative results are reported in Fig. 5.

The sulphide mineralizations (class 1) consist of pyrite and chalcopyrite with minor to trace amounts of sphalerite in a gangue of quartz and chlorite with minor to trace amounts of calcite. Pyrite and, in lesser extent, the other sulphides are partially to completely replaced by micro- to crypto-crystalline Fe-oxide (hematite) and -oxyhydroxides (mainly goethite).

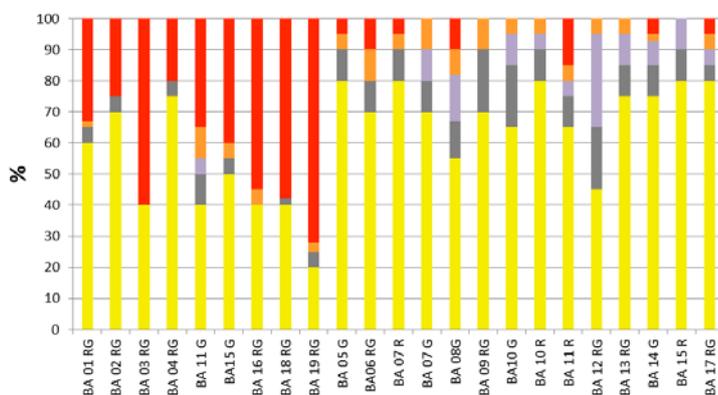


Fig. 5 - Modal abundance of the lithological classes within soils and waste-rock sediments: 1) sulphide mineralizations (dark grey); 2) Fe-rich oxidation crusts (orange); 3) carbonates (violet); 4) host rocks (yellow); 5) other components (red).

plagioclase, pyroxene, olivine, magnetite, and spinel. The class 5 (other components) includes clay minerals, which are widespread but, with the exception of the soil samples, always minor constituents. Moreover this class includes anthropic and biological materials.

The mineralogical and lithological composition of the sediments confirms that most of the materials deposited in the waste-rock dump correspond to rocks fragments arising from excavations carried out during the ore mining operations.

The mineral chemistry analyses evidenced that Cu, Zn, Pb, As, Cd and, subordinately, Ni (few occurrences of Ni-bearing pyrite) are clearly related to the sulphide mineralizations and their oxidation products (Fe-oxides and -oxyhydroxides). Conversely, Ni and Cr are almost exclusively related to the rock-forming minerals of the basalts and subordinately serpentinites. Chromium occurs either within primary minerals (magnetite, chromian-spinels, and chromite) or authigenic minerals (Fe-oxyhydroxides and clay minerals); nickel occurs as subordinate to trace constituent within olivine, pyroxene, and chlorite.

Chemistry

The analyses of the elemental bulk composition of the outcropping rocks, soils and waste-rocks are given in Table 1. The geochemical signatures of the waste-rock samples agreed well with the qualitative and quantitative results of the mineralogical analyses evidencing significant enrichments in Fe, S, Cu, and Zn. Soil and outcropping-rock composition are similar and differ from the waste-rocks mainly for the significant enrichments in Al, Ti, Sr, Ba, Cr, and Ni. Batch leaching experiments showed a different behaviour for the

The Fe-rich oxidation crusts (class 2) are represented by micro- to crypto-crystalline authigenic Fe-oxide and oxyhydroxides (mainly hematite and goethite) occurring as fractures and voids filling, pseudomorphosis after sulphides, and massive crusts.

The carbonates (class 3) mainly occur as filling of veins associated to sulphides and quartz. They are almost exclusively represented by calcite with subordinate amounts of Ba- and Sr- carbonates.

The host rocks (class 4) mainly consist of basalts with subordinate amounts of gabbros and serpentinites. The rock-forming minerals are mainly represented by (in order of decreasing abundance): chlorite,

ecotoxic metals; Cu and Zn are significantly released to the experimental medium (in good agreement with the weatherability of the sulphide mineralization in oxidizing condition) whereas the leachability of Cr, V, and Ti is very low or nil.

Table 1 - Bulk chemical composition of soils, rocks and waste-rocks (mean values)

Major el. (wt.%)	Soils	Rocks	Waste rocks
TiO ₂	0.86	1.39	0.89
Al ₂ O ₃	8.18	11.67	7.98
Fe ₂ O ₃ t	6.92	7.22	8.6
MnOt	0.15	0.17	0.2
MgO	4.16	7.05	6.77
CaO	1.85	4.37	1.53
K ₂ O	0.22	0.08	0.18
P ₂ O ₅	0.06	0.17	0.07
Minor and trace el. (ppm)	Soils	Rocks	Waste rocks
S	<1000	2200	3000
V	243	2125	250
Cr	250	1570	213
Co	50	60	60
Ni	137	80	113
Cu	144	1263	2922
Zn	114	182	552
Sr	95	66	72
Zr	73	84	101
Ba	53,75	9,75	37,84
Pb	40,65	2,85	28,27

Geostatistical analysis and mapping

The use of the FP-EDXRF ensured a very high sampling density which, suitably processed with statistical and geostatistical methods, were able to provide a picture of the spatial distribution of the elements of interest. The dump selected for this study is geometrically simple and limited in size and resulted particularly suitable for the purpose of this study.

Several contour maps were realized (Fig. 6) which allowed to easily identify the geochemical variations inside the dump perimeter and in the surrounding soils, the vertical and lateral heterogeneities as well as the presence of hot spots or other local criticality. In particular, Ni evidenced a general high concentration outside from the boundaries of the waste-rock dump, in good agreement with a general high baseline level for this element in the mafic and ultramafic soils of the area; conversely, Cr showed several hot spots inside the dump perimeter and anomalously high concentration restricted in an area of the surrounding soils.

The waste-rock dump is clearly distinguishable also by the spatial distribution of the two most representative chalcophile elements of the Rio Bansigo mineralizations (*i.e.*, Cu and Zn; Fig. 6); the ratio (*CuR*) among the Cu concentration in the waste rock samples and the Cu mean concentration in the surrounding soils also evidenced the evolution of the waste-rock dump due to erosion processes. Infact, the spatial distribution of the *CuR* values well evidenced the presence of one main (and other minor) erosion channels which redistribute the waste-rock debris downward along fan-shaped deposits.

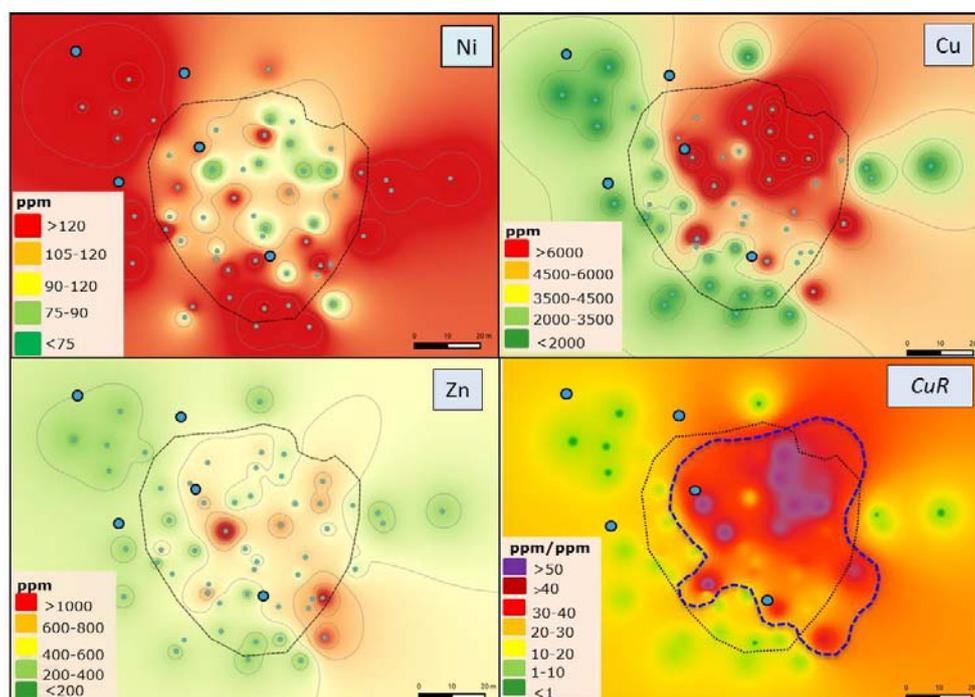


Fig. 6 - Contour maps of the spatial distribution of: a) Ni; b) Cu; c) Zn; d) CuR (*i.e.* the ratio among the Cu concentration in the sample and the Cu mean concentration in the surrounding soil). The black dashed lines in Fig. 6a-d represent the perimeter of the dump as resulted from historical maps and field surveys. The blue dashed line in Fig. 6d represents the “geochemical perimeter” of the dump as resulted from the spatial distribution of CuR.

CONCLUSIONS

The results obtained evidence the feasibility of a detailed evaluation of the metal hazard within waste rock dumps using field-portable XRF device (FP-EDXRF device), thus providing a powerful tool for quick decision-making in the field and reducing significantly the number of samples that need to be submitted for off-site laboratory analysis.

Moreover, the possibility to perform a large number of *in situ* analyses, in a cost efficient and timely manner, allows to realize geo-environmental models and detailed mapping of metal distribution as well as to easily recognize pollution hot spots.

In particular the main advantages can be synthesized as follow: *i*) the FP-EDXRF is a rapid and cost effective technology producing on site definitive data quality level for most of the investigated metals (Cu, Zn, Pb) and good quantitative (Ni) or qualitative (Cr) data quality level for the others; *ii*) the FP-EDXRF allows to determine in real-time the presence of hot spots areas and thanks to the possibility to increase significantly the density of the analytical grid, allows to recognize ‘spurious hot spots or to confirm actual hot spots at the time of the survey; *iii*) the FP-EDXRF associated with mobile devices with open-source GIS software allows to map immediately the spatial distribution of metal contamination across a site.

On the other hand, the main limitations are the following: *i*) although minimal, samples need preparation (sieving and homogenization) and require the use of apposite sample cups to avoid error related to physical matrix effects and to the inconsistent positioning of samples, respectively; *ii*) preliminary survey, sampling and confirmatory analyses are necessary for calibration corrections and to achieve an analytical quality comparable to the laboratory data; *iii*) the technique can be applied on site only when soil or sediment samples have a moisture content < 20% and in any case cannot be applied in samples saturated with water.

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