

Toxic elements at a disused mine district: Particle size distribution and total concentration in stream sediments and mine tailings

V. Giuliano^a, F. Pagnanelli^{b,*}, L. Bornoroni^b, L. Toro^b, C. Abbruzzese^a

^a Institute of Environmental Geology and Geoengineering (CNR), Via Bolognola, 7, 00138 Rome, Italy

^b Department of Chemistry, University of Rome "La Sapienza", P.le A. Moro, 5, 00185 Rome, Italy

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Abstract

Heavy metal and metalloid pollution at a disused pyrite mine was investigated. Five solid samples collected in the area (three stream sediments with different soil texture, a background soil sample and a mine tailing) were characterised by mineral and element composition, particle size distribution (by wet and dry sieving and laser diffraction) and total concentration by acid digestion (Mn, Zn, Cu, Pb, Hg, Cd, Sb and As). X-ray and element analyses denoted a common mineralogical and chemical composition of mainly quartz, clinocllore, muscovite, anorthite, and hematite. Particle size distributions of the five samples showed that stream sediments were characterised by larger percentage of sand range classes (2000–60 μm) while background sample and tailing are mainly characterised by gravel particles (>2000 μm). Wet and dry sieving procedures gave different particle size distributions, which can be interpreted by laser diffraction analysis and represented by Rosin–Rammmler model. Concentrations of Zn, Cu and Cd were higher in the stream sediments than the tailing and background soil, while Mn, As, Sb and Hg are mainly concentrated in the tailing sample. Metal concentrations in the three stream sediment samples are correlated with both particle size dimensions ($D_{63.2}$) and concentration of geochemical normalizers (iron and aluminium). These correlations are observed also for the pollutants that are mainly concentrated in tailing sample (Mn and As), denoting the importance of surface interactions also for the binding of these elements onto stream sediments.

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1. Introduction

Pollution in soil systems is strictly related to human activities such as industry, agriculture, burning of fossil fuels, mining and metallurgical processes and their waste disposal. Toxic elements, such as heavy metals and metalloids, can be retained by soils and/or mobilised to soil solution by biological and chemical mechanisms with a potential impact on human health (contamination of drinking water supplies, uptake by vegetation and input into the food chain).

Metal mobility in soil systems depends on the chemical form of soil–metal interactions: metals immobilised by adsorption and precipitation, can be released when the metal retention capacity is overloaded or there is a particular change in soil environmental conditions, enhancing metal mobility (degrada-

tion of organic compounds, change of pH, redox potential or soil solution composition) [1].

The evaluation of the total concentration of metals and metalloids in soils is generally used as the first reference indicator for comparing pollution level with legislative limits. Nevertheless the natural occurrence of toxic elements in soils, especially in disused mining areas, requires further analyses to detect mobilisation due to erosion and leaching to groundwater.

In this contest, several sequential leaching procedures have been developed to selectively remove metals and metalloids present in different geochemical forms [2]. These procedures are all based on the general principle of reacting a soil sample with chemical solutions with progressively increasing strength. In this way it is possible to distinguish pollutant metals from natural and intrinsic ones. However, these procedures are lab expensive, require optimisation for the specific soil case and present several drawbacks, such as low reproducibility with large particles and encapsulated pollutants, error propagations, strong susceptibility to operating conditions, and re-adsorption of met-

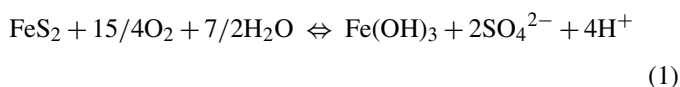
* Corresponding author. Fax: +39 06 490631.

E-mail address: francesca.pagnanelli@uniroma1.it (F. Pagnanelli).

als during extraction [3]. As a consequence, in a preliminary phase of pollution assessment, it can be useful to rationalize the information obtained by acid digestion for total concentration. This can be done by comparing the concentrations in different solid samples as representatives of various areas of a site: natural soils as background samples, tailings from mining and milling activities, stream or lake sediments. These comparisons can reveal mobilisation phenomena from source points, but also from one kind of solid matrix to others (e.g. from metal-bearing tailings to the surrounding soil). Further information can also be obtained by relating total concentrations to soil texture. In fact, particle size distribution is generally used for preliminary characterisation of soil samples, with a conventional classification as gravel (>2000 μm), sand (50–2000 μm), mud (2–50 μm) and clay (<2 μm) [4,5]. This kind of classification is based only on soil texture without taking into account the mineralogical composition of the different size fractions. It is quite generally observed that size fractions with lower dimensions present larger pollutant concentrations according to their higher specific area (grain size effect). Consequently, significant correlations between particle size distribution of soil samples and total concentrations can show how surface interactions, associated with anthropogenic contributions, predominate [6–8].

“Geochemical normalizers” can be also used to reveal pollution effects by normalising natural trace metal variability by the concentration of other elements [7,8]. Iron and aluminium can be used as normalizers, assuming that iron oxides and aluminosilicates are the main responsible for metal binding by surface interactions [8].

In this paper heavy metals and metalloid (As) pollution in an abandoned sulphide ore mining area is investigated. The site of interest, the Boccheggiano mine, is located in the South of Tuscany (Italy) in a wider area (Colline Metallifere), which saw an intense mining exploitation since the XV century. In particular the Boccheggiano area is characterised by different kinds of sulphide ores (mainly pyrite (FeS_2) and chalcopyrite (CuFeS_2) plus traces of Pb and Zn sulphides), magnetite (Fe_3O_4) and pyrrhotine (FeS). The mining, milling and metallurgical processes for the production of copper, iron and sulphuric acid from sulphide ore deposits generated large amounts of sulphide-bearing waste rocks which were heaped along the Merse river bank. These mine tailings present significant concentrations of heavy metals, which can be mobilised to soil water by acid mine drainage (AMD). AMD is a biologically enhanced phenomenon caused by the sulphur oxidation of metal-sulphide minerals (such as pyrite) and by the subsequent oxidation and precipitation of iron according to the global reaction [9]:



The release of H^+ and Fe^{3+} ions in soil solution generates a powerful leaching agent causing the secondary release of heavy metals and metalloids, such as As, from sulphur tailings.

The aim of this paper is to investigate and detect pollution by relating total content of toxic element to particle size distribution of samples taken from mine tailings and soil samples

in the disused mine district (stream sediments and background soil samples). Because the natural occurrence of heavy metals and arsenic in this mining area, pollution could be evidenced by comparing stream sediment samples and mine tailing samples for their total concentration of heavy metals and metalloids. Solid samples were preliminary characterised (mineralogical and element composition, particle size distribution by wet and dry sieving and laser diffraction) to relate their properties to the total concentration of toxic elements obtained by acid digestion. Previous research papers about pollution mobilisation in this disused area used sequential extractions to obtain an operative speciation (or fractionation) of metal in soil phases [10] and also the titration modelling of a simulating mixture in order to identify the specific mineral soil constituents involved in metal binding [11]. In this paper this previous knowledge was combined with conventional polluted soil analysis of natural soils and tailings (particle size distribution and total concentration) to deduce possible significant trends and correlations to measure and assess pollution.

2. Materials and methods

2.1. Sample collection and preparation

Five-kilogram samples of different type were collected in the Boccheggiano mine district from the surface horizon (20 cm) near tailings dump and the Merse river. In particular:

- Sample 1: stream sediment collected along river bank (fine grain size).
- Sample 2: stream sediment collected along river bank (medium grain size).
- Sample 3: stream sediment collected in the river bed.
- Sample 4: background soil collected near the river.
- Sample 5: mine tailing.

These five samples have been selected from a large quantity of samples (stream sediments, soils and mine tailings) collected during a geochemical survey aimed to the creation of geochemical maps of the area. Sampling sites of the field survey have been identified on the basis of the mineralization douse, the mining landfills location, the geo-morphological features of the area controlling pollutants migration. More specifically, stream sediments samples were collected (with water samples) along the fluvial network, preferably near stream confluences; soils samples were collected at a distance (min. 100 m away) from roads and civil constructions; mine tailings samples were collected at the foot of dumping hills. The five samples under study were chosen in a way to ensure the representative characterisation of the pollution setting of the area. The samples should be able to give a significant picture of migration processes of the heavy metal pollutants from sources to receptors.

Samples 1, 2, 3 (stream sediments) come from a stretch of Merse river interesting for the significant concentration of heavy metals; sample 4 has been chosen as blank background sample; sample 5 is a mine tailing coming from a mining dumps near the Merse river.

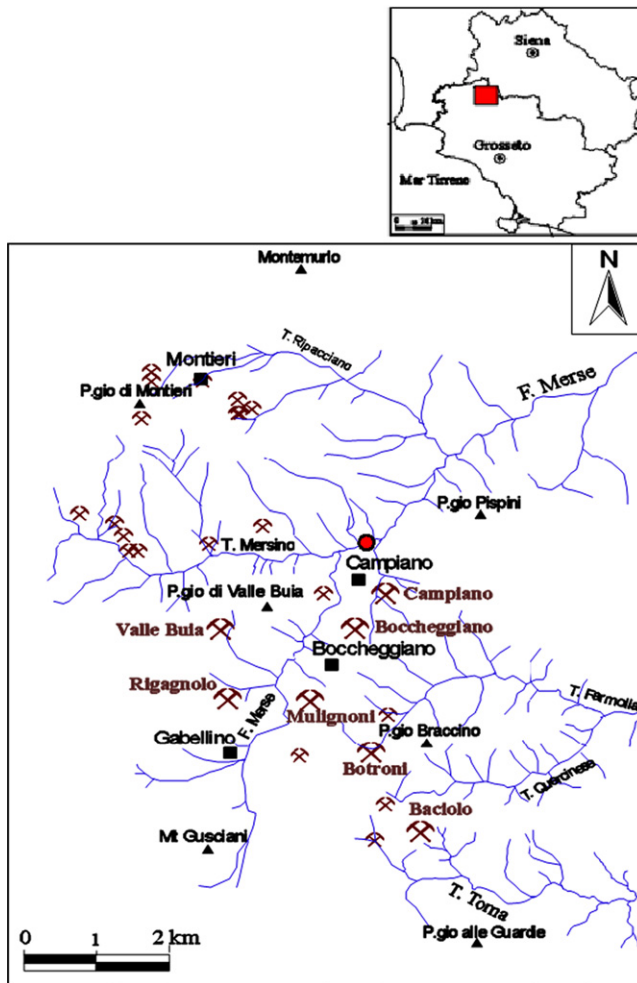


Fig. 1. Map of the mining district and sampling locations.

The samples location is shown in Fig. 1.

Samples were dewatered, placed in plastic bags, sealed, numbered and carried to the laboratory. Each sample was divided into representative sub-samples for the determination of the particle size distribution and, after grinding, for the other characterisation analyses.

2.2. Sieving and particle size distribution

Dry sieving of 500 g samples was performed by an automatic testing sieve shaker. The different size fractions are identified as >5000, >2000, >1000, >495, >355, >150, >73, >38, <38 μm meaning that the particles of the >2000 μm class have diameters larger than 2000 μm , but smaller than 5000 μm , which is the minimum value of the previous class. For the extreme classes only the minimum and maximum values of particle diameters are known (for >5000 μm and for <38 μm , respectively).

Wet sieving of 500 g samples was done by hand: 5000, 2000, 1000, 495, 355, 150, 75 and 38 μm sieves were used collecting the undersize solid particles and the water passed to the lower dimension sieve.

Lower dimension fractions (<38 μm) from dry and wet sieving were analysed with a laser granulometer (Sympathec Helos,

Clausthall-Zellerfeld, Germany) by suspending solid samples in water.

2.3. Acid digestion

0.1 g of homogenous and grounded (<74 μm) samples placed in a Teflon recipient were digested using 4 ml of an oxidising mixture of HNO_3 (65 wt.%) and HCl (37 wt.%) ($\text{HNO}_3:\text{HCl}=3:1$) and 6 ml HF (48 wt.%) in a microwave oven (800 W, 4 min; 400 W, 4 min; 800 W, 4 min; 20 min of ventilation). After complete digestion of solid samples, 5.6 g HBO_3 was added to avoid silica evaporation and each liquid sample was diluted to 100 ml with deionized water [12]. Metal and metalloid concentrations in the solution were determined by an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (detection limits: 0.001 ppb for Mn, Zn, Cu, Pb, Hg, Cd, Sb and 0.1 ppb for As).

2.4. X-ray analysis

Diffraction analyses by X-ray were performed on bulk samples after grinding of representative sub-samples. Operational parameters: Cu tube, $K\alpha$ 1.506 \AA radiation, graphite crystal monochromator, and sparkler detector; instrumental conditions used are: voltage 40 kV; current 30 mA; slit 1, 1, 0.5 mm).

3. Results and discussion

Detailed information about particle size distribution can be used to identify possible relations between toxic elements and soil texture properties. In particular the increase of metal concentration for decreasing particle dimensions (with larger specific area) is important in detecting the nature of heavy metal/soil interactions. In fact polluting elements are generally bound by surface interactions such as physical sorption, ion exchange and complexation. If metal specific amounts increase in size fractionated samples of lower dimensions, these surface interactions can be mainly the result of pollution phenomena.

As a result particle size distribution was specifically addressed to characterise the different solid samples and find possible relations with total concentrations obtained by acid digestion.

Particle size distributions determined by dry sieving for the five samples are reported in Fig. 2 as weight percent amount in each size fractionated sample. The characteristic ranges of conventional type of soil texture (gravel, sand, mud, clay) are also reported in Fig. 2 as the secondary abscissa axis.

The analysis of the histograms by dry sieving shows that:

- Sample 1 and sample 2 (collected on the river bank) present similar bell-shaped distributions and sandy texture with about the 80% distributed between the classes >1000 and >150 μm .
- Sample 3 (collected in the surface horizon of the river bed) is characterised by an asymmetric distribution with about the 80% distributed between the classes >5000 and >1000 μm (gravel/coarse sand texture) and by very small amounts of the lower dimension classes.

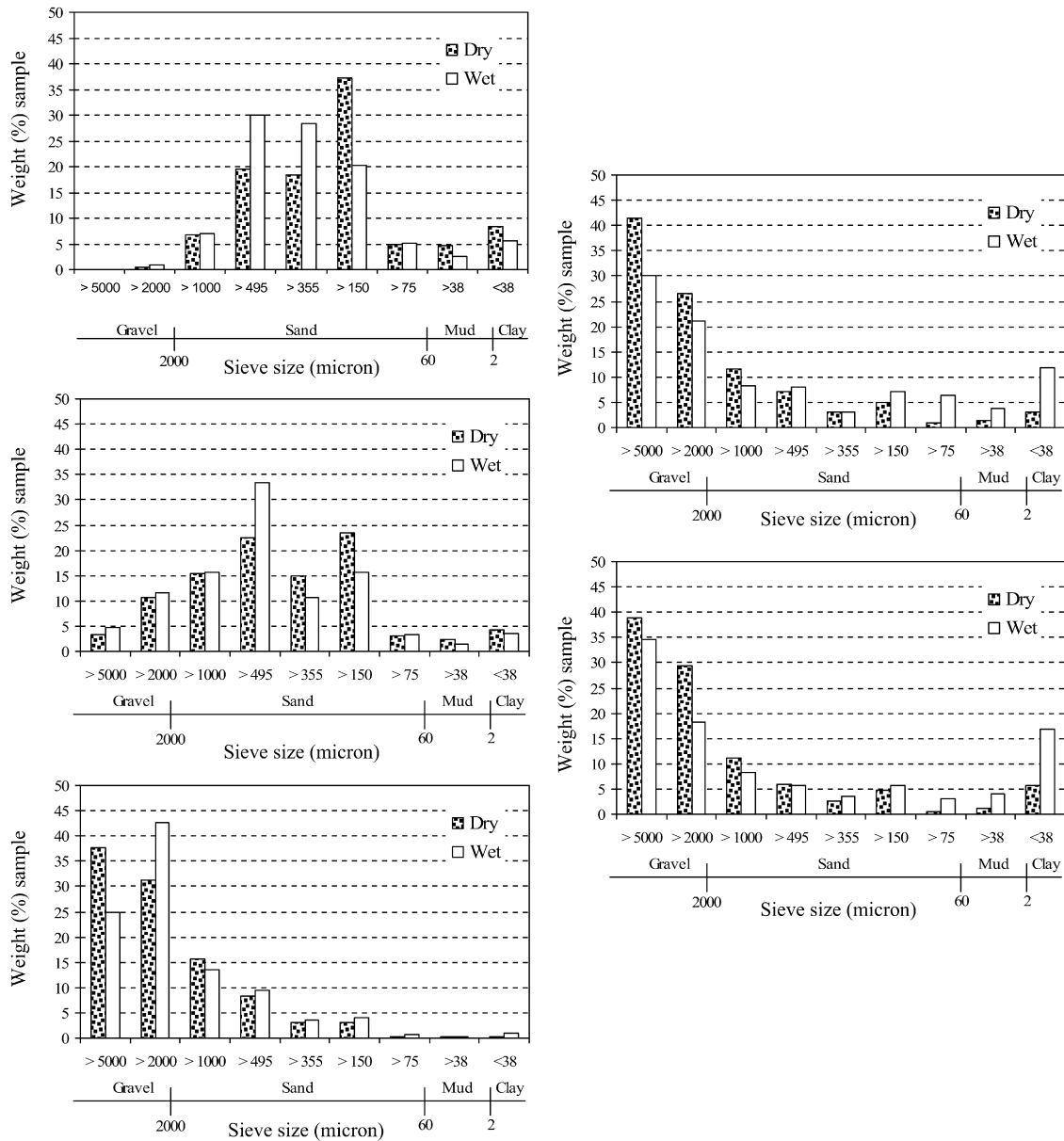


Fig. 2. Particle size distribution obtained by wet and dry sieving for the five soil samples.

- Sample 4 (background soil near the river) and sample 5 (mine tailing) show a right-hand sided distribution with about 65% in the >5000 and $>2000 \mu\text{m}$ classes (mainly gravel/coarse sand texture region with little amounts in mud and clay range).

Dry sieving is especially used for soil samples with low amounts of fine particles, as otherwise aggregate formation between coarse and fine particles can lead to underestimates of the finest classes [4]. Even though dry sieving seems to be the suitable procedure for the five samples analysed here (because of the low percentage amount in mud and clay ranges), wet sieving was also performed to evaluate possible underestimates of the finest classes. Histograms obtained by wet sieving (Fig. 2) denoted some differences with respect to the classification by dry sieving. In particular stream sediments (samples 1, 2 and 3) present significant differences in the classes of sand (1 and 2) and gravel

(3) texture, while background soil and tailing (samples 4 and 5) especially differ in the clay, mud and lower side of sand ranges.

Linear correlations between wet and dry sieving data are reported in Fig. 3: Percentage weight of the i th size class obtained by dry sieving ($y_{i,\text{dry}}$) is reported as a function of the percentage weight of the same class by wet sieving ($y_{i,\text{wet}}$) for each j th sample. A linear regression is then performed to evaluate significant differences between the sieving procedures:

$$y_{\text{dry}} = a_j y_{\text{wet}} \quad (2)$$

Numerical coefficients obtained for the different samples (a_j) and the regression coefficients (R^2) are reported in Table 1. Differences between the sieving procedures are denoted by a_j and R^2 deviations from units [13]. It is possible to note that all the samples present significant deviations. In particular, samples 1 and 2 due to the large differences observed in the more abundant

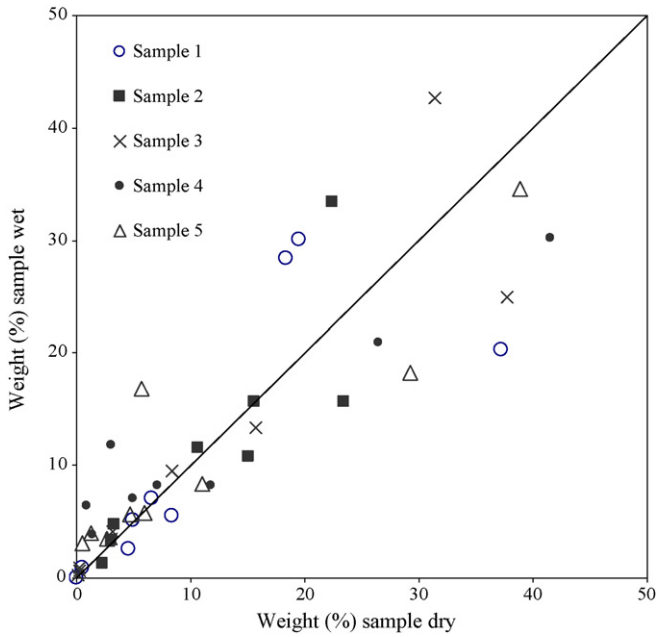


Fig. 3. Correlation between weight percent amount of each size fractionated samples obtained by wet and dry sieving.

Table 1
Correlation between weight percent amount of each size fractionated samples obtained by wet and dry sieving (Eq. (2)) and Rosin and Rammler parameters (Eq. (3)) for particle size distributions obtained from manual sievings (dry and wet) and laser diffraction

Sample	$a (y_{wet}/y_{dry})$	R^2
1	0.8815	0.5729
2	1.0082	0.7238
3	0.9463	0.8217
4	0.7733	0.7559
5	0.8273	0.7574

Sample	Separation method	$D_{63.2} (\mu\text{m})$	α
1	Manual dry sieving	64	1.25
2		104	0.97
3		424	1.37
4		628	0.78
5		678	0.69
1	Manual wet sieving	596	0.80
2		657	0.77
3		817	1.06
4		151	0.61
5		144	0.48
1	Laser diffraction (finest class from manual dry sieving)	4.5	2.00
2		5.9	1.82
3		6.2	1.82
4		20.2	1.55
5		17.0	1.76
1	Laser diffraction (finest class from manual wet sieving)	7.8	1.48
2		12.1	1.48
3		17.3	1.62
4		3.5	0.61
5		9.1	0.62

classes (>495, >355 and >150 μm), while sample 4 and sample 5 for the observed larger abundance of the finest particles (>150, >75, >38 and <38). Sample 3 is the sample whose dry and wet sieving histograms are more similar being characterised by very low percentage of finest classes.

In order to obtain further information about the lower dimension size fractionated samples from both sieving procedures, laser diffraction analysis of the five samples was also performed (Fig. 4). The analysis of the particle size distribution from dry sieving (Fig. 4A) denoted an inversion of the relative abundance of the finest particles in the different samples: gravel-like samples (samples 3, 4 and 5) present larger amounts in the finest size fractionated samples than sand-like samples (samples 1 and 2). These data coincide perfectly with the results already obtained by comparing dry and wet sieving: gravel samples (4 and 5) are those with larger amounts in the finest fractions observable by wet sieving. For these samples the finest particles were probably aggregated with coarse ones in dry sieving leading to an underestimate of the % amount of the size fractions with lower dimension.

Particle size distribution by laser diffraction of the finest class (<38 μm) from wet sieving (Fig. 4B) can give further insight. In this case it is not observable the distinct trend of inversion of dry sieved sample because fine particle aggregation was avoided by wet sieving. Nevertheless even in this case the gravel like samples (4 and 5) present the largest amounts of the finest classes (starting from 2.2 μm class). This would confirm that samples 4 and 5 are those characterised by the largest amounts of the finest classes even though they are mainly made up of gravel particles (60–70%) (Fig. 2).

Sample heterogeneity denoted by particle size distributions from dry and wet sieving was further addressed modelling the experimental data by an empirical model representing the distribution function of the particle size, the Rosin–Rammler model [14]

$$P(D) = 1 - \exp[-(D/D_{63.2})^\alpha] \tag{3}$$

where D is the dimension characteristic of each class (sieve dimension), $P(D)$ is the mass fraction of particles with dimensions lower than D (undersize), $D_{63.2}$ and α are two adjustable parameters representing the first a characteristic dimension of the population $P(D_{63.2})=0.632$ (samples that are mainly characterised by fine particles have lower $D_{63.2}$ than samples made up of coarse fractions) and the second the dispersion of the distribution (if α decreases, the heterogeneity of the particle size increases). Model predictions and adjustable parameters by non-linear regression are reported in Fig. 5 and Table 1, respectively.

Comparing the values of $D_{63.2}$ and α obtained for the different samples by the two sieving procedures it is possible to see that this simple model resembles the distribution characteristics already seen in Fig. 2.

In particular:

- stream sediments 1 and 2 present $D_{63.2}$ for dry sieving that are lower than the other gravel-like samples (3, 4 and 5);

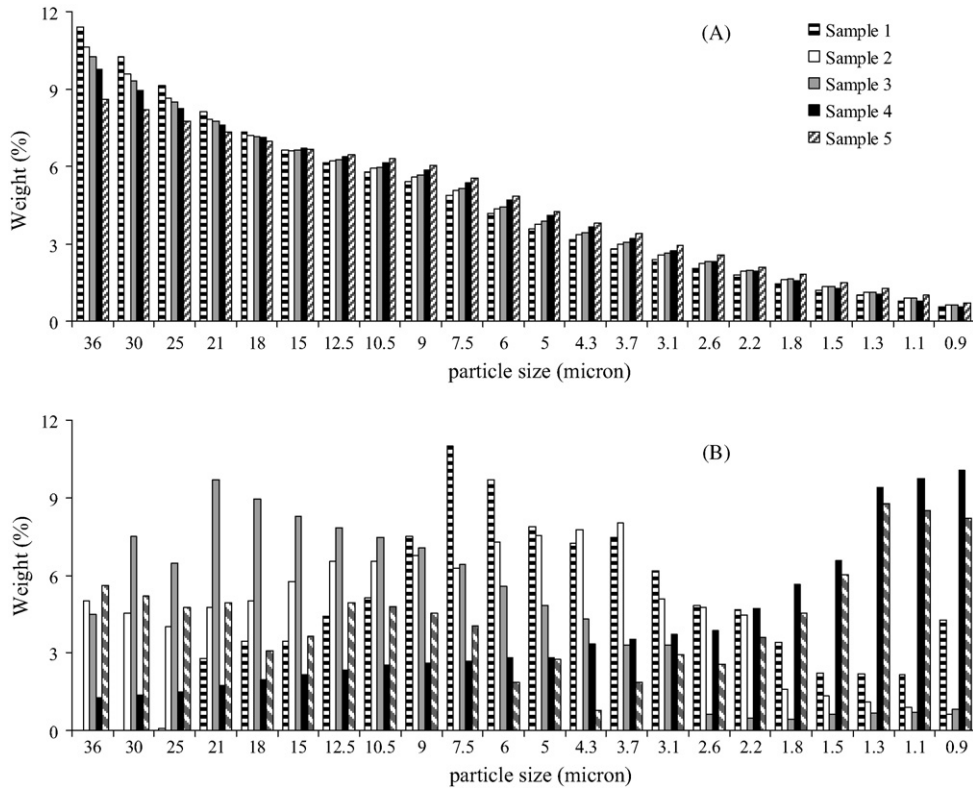


Fig. 4. Particle size distribution by laser diffraction for the five soil samples by dry (A) and wet sieving (B).

- samples 4 and 5 present a wider dispersion of particle size dimension with smaller α values, due to high percentage in both gravel and mud-clay ranges;
- sample 3 is the most homogeneous sample (highest α) with a gravel-like nature;
- stream sediments (1, 2 and 3) by wet sieving present larger $D_{63.2}$ than by dry sieving, in line with the increased portion obtained in larger dimension classes, while the opposite occurs for samples 4 and 5 where dry sieving underestimates lower dimension classes;

- all the particle distribution by wet sieving present lower α values than those obtained by dry sieving meaning that the intrinsic heterogeneity of samples revealed by wet sieving can be properly represented by this model.

The modelling of particle size distribution from laser diffraction denoted that:

- the values of the shape distribution parameter, α , are always lower for wet sieving than for dry sieving; the characteristic

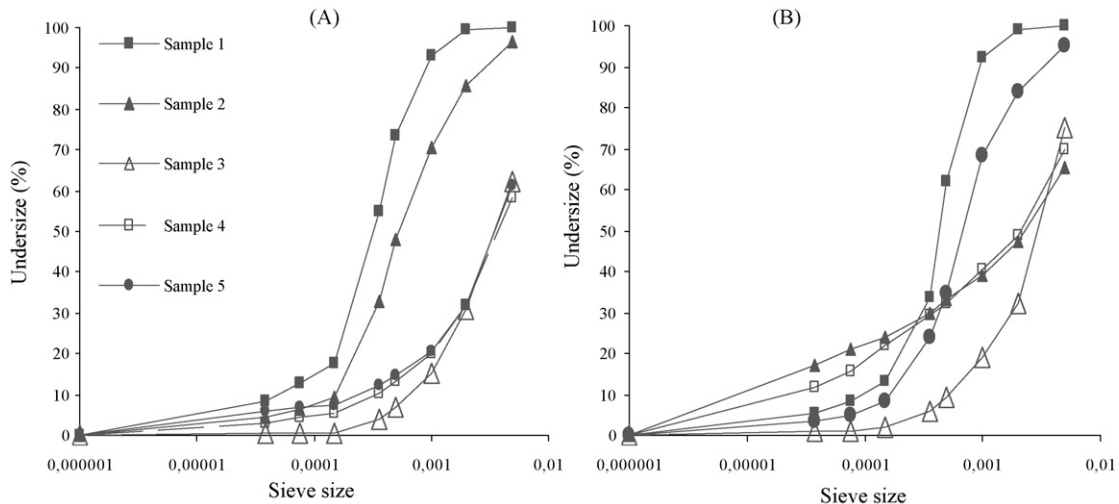


Fig. 5. Cumulative distribution for the five samples from dry (A) and wet sieving (B).

Table 2
Mineral composition of the five solid samples by X-ray diffraction

Mineral	Formula	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Quartz	SiO ₂	✓	✓	✓	✓	✓
Clinocllore	(Fe)(SiAl) ₄ O ₁₀ (OH) ₈	✓	✓	✓	✓	✓
Muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	✓	✓	✓	✓	✓
Anorthite	(Na)(SiAl) ₄ O ₈	✓	✓	✓	✓	✓
Illite	(KH ₃ O)Al ₂ Si ₃ AlO ₁₀ (OH) ₂				✓	✓
Hematite	Fe ₂ O ₃	✓	✓	✓	✓	✓
Goethite	FeO(OH)				✓	✓
Calcite	CaCO ₃				✓	

heterogeneity of particle size can be preserved by wet sieving avoiding fine particle agglomeration;

- the values of the dimension parameter, $D_{63.2}$, are strongly dependent on the sieving procedure: stream sediments have the lowest values if samples come from dry sieving, while a different dimension order can be observed for samples from wet sieving.

X-ray analyses (Table 2) denote a common mineral matrix of quartz, aluminosilicates (clinocllore, muscovite and anorthite) and iron oxide (hematite) for all the samples of stream sediment, background soil and tailing. Specific differences are the presence of goethite and illite in the tailing sample, and calcite in the background soil sample.

Experimental results by acid digestion of the five samples are reported in Fig. 6 where the elements are grouped by specific concentration range. The elements that are characteristic of the mineral matrix revealed by X-ray (mainly Si from quartz, Al, Si, K, Na from aluminosilicates and Fe from hematite) present similar concentrations in all the samples (Fig. 6). The presence of specific minerals in sample 4 and sample 5 (calcite and goethite, respectively) is confirmed by the concentrations of Ca and Fe, which are larger in these samples than in the others.

As for toxic species found in these samples, the concentrations of Mn, Zn, Cu, As, Pb, Sb, Cd, and Hg are reported in Fig. 6. The background soil sample (sample 4) and the tailing sample (sample 5) feature lower concentrations of Zn, Cu and Cd than stream sediments, comparable concentrations of Pb were found in all samples, while Mn, As, Sb and Hg are more concentrated in the tailing sample. Grain size effect cannot explain such difference between stream sediment samples and background and tailing samples. In fact, percent amounts of clay and mud by wet sieving are even larger for samples 4 and 5 than in the three stream sediments (Fig. 2).

Another observable trend from Fig. 6 is that in sediment samples the concentration of Mn, Zn, Cu, Cd and As follows the order $Me_1 > Me_2 > Me_3$, resembling the particle size distribution of the stream sediment samples, with sample 1 the finest and sample 3 the larger (Fig. 2).

Previous data reporting the total concentrations in the different size fractionated samples of sediment (sample 1) also show the significant effect of particle size [10]. The total concentrations in the sediment are larger for the lower dimension particle classes (with higher specific area), while this effect was not

found for the tailing. This observation suggests that in sediment samples significant amounts of heavy metals and metalloids are bound to the solid matrix by surface interactions affected by sample specific area determining the adsorption capacity.

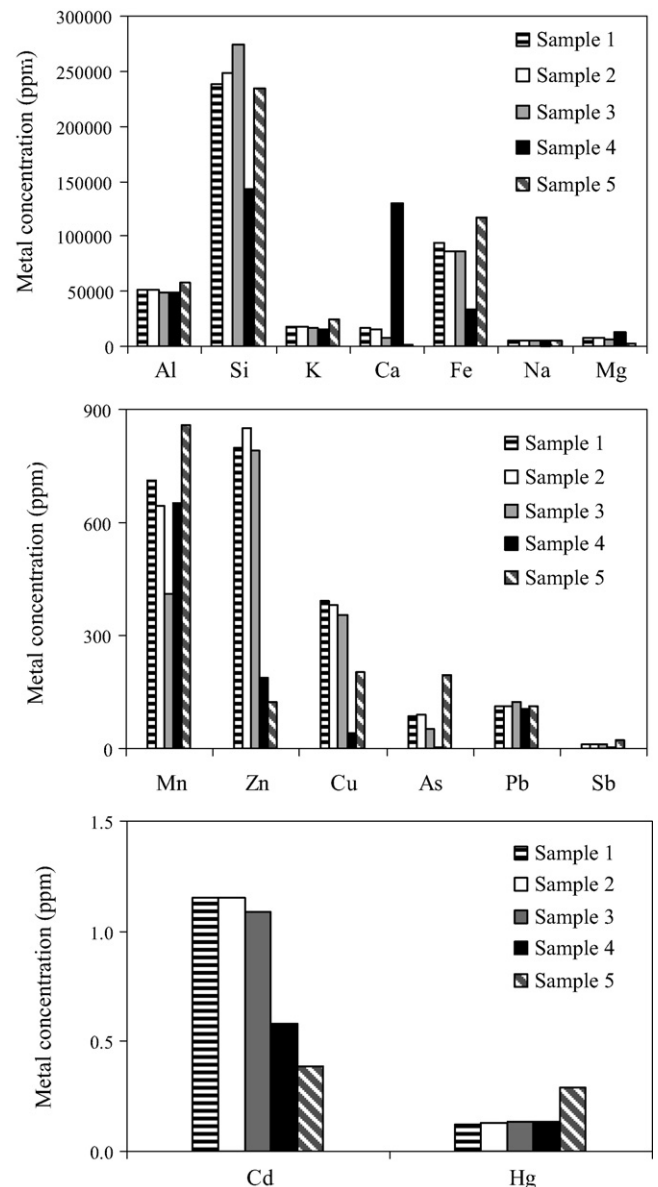


Fig. 6. Element concentrations by acid digestion for the bulk samples of the five soils.

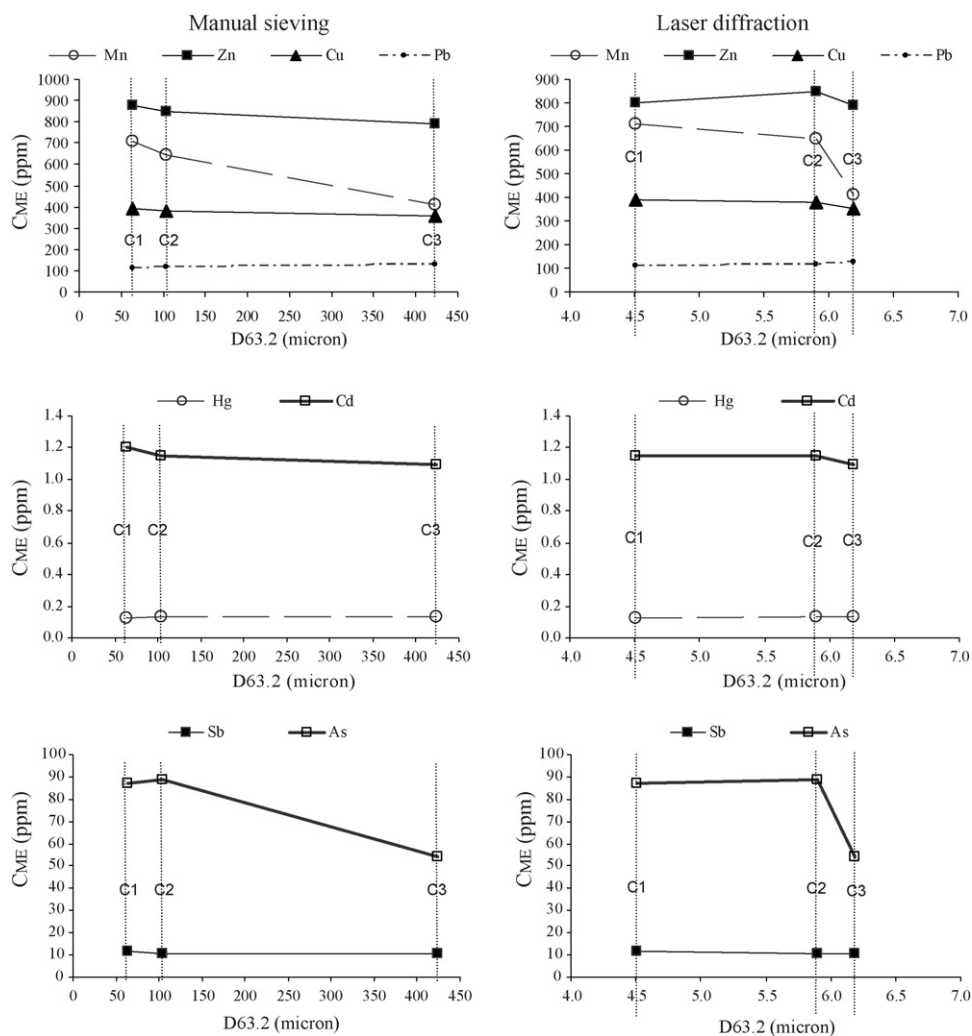


Fig. 7. Correlation between heavy metal concentration and particle size dimension parameters from Rosin and Rammler model for stream sediment samples (manual sieving and laser diffraction) (C1, sample 1; C2 sample 2; C3 sample 3).

Considering the information about size distribution, a correlation between the model parameter $D_{63.2}$ and total concentration in the three stream sediments (C_1 , C_2 and C_3) was also considered for particle distributions from both manual sieving and laser diffraction (Fig. 7). These figures denoted that concentrations are larger in the finest stream sediments (samples 1 and 2) than in the coarse one (sample 3) (grain size effect). This trend is also valid for the elements that are mainly concentrated in the mine tailing, i.e. arsenic and manganese, whose contents diminish passing from the finest (samples 1 and 2) to the coarsest sample (sample 3). Similar trends were observed both for samples from dry sieving (Fig. 7) and wet sieving (not reported here).

The effect of iron and aluminium amounts in the different stream sediments (C_1 , C_2 and C_3) was also considered to assess the effect of these normalizers on toxic element's binding onto stream sediments. Even though both iron and aluminium amounts in three stream sediment are very similar (Fig. 6), the stronger correlations are observed for the elements that are more concentrated in the tailing, Mn and As (Fig. 8).

The observed correlations for As and Mn concentrations with $D_{63.2}$ and Fe and Al amounts indicated that these elements are largely interacting by surface binding with the stream sediment phases of iron oxides and aluminosilicates. It is also noteworthy that these same elements are those presenting the highest concentrations in the tailings compared to the other samples (Fig. 6), as a confirmation that elements, which are mainly concentrated in the tailings, are bound to the stream sediments by surface interactions of different nature (ion exchange, surface complexation and surface microprecipitation).

In order to understand these findings the experimental data of element speciation in sample 1 and sample 5 (representing stream sediment and tailing, respectively) [10] were analysed. Because of the natural presence of heavy metals and metalloids in this mining area, and considering the large amounts of sulphides, pollutant mobilisation can be assessed by using a modified Tessier's procedure, which can distinguish the metal fraction bound to organic matter from that present in the sulphide form [15]. In particular, elements extracted by this procedure can be distinguished as exchangeable (I step), complexed by inorganic phases (II step), complexed by organic phases (III

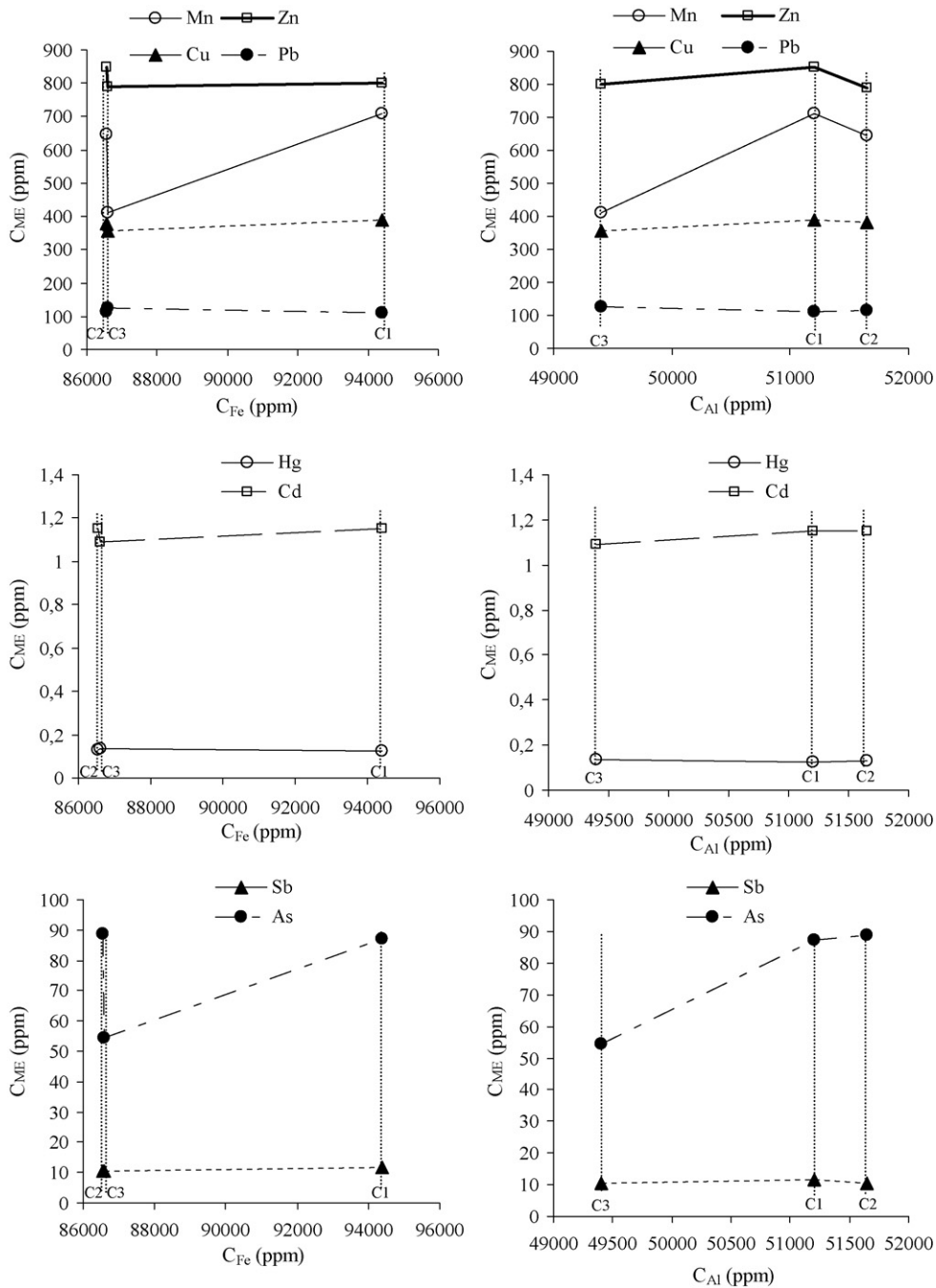


Fig. 8. Correlation between heavy metal concentration and Fe and Al amounts for river sediment samples (C1, sample 1; C2 sample 2; C3 sample 3).

plus IV steps), bound as sulphides (V step) and intrinsic of the mineralogical matrix (residue).

Experimental results showed that the larger amounts of toxic elements (Cu, Mn, Zn, Pb and As) found in sediment samples are mainly present as sorbed species (exchangeable, complexed onto inorganic soil phases, bound to organic matter), while toxic elements in tailing samples are present as bound to the sulphide phase and in the mineralogical matrix (intrinsic to the ore deposits) [10].

The correlation between metal concentrations and Fe amounts in soil samples should be representative of the metal

extracted by the II step, because iron oxides are one of the most important mineral phases responsible for metal complexation. The Al bearing phase (aluminosilicates) can retain metal both by ion exchange due to isomorphous substitution (I step) and by complexation onto surface hydroxyl groups (II step). The observed correlations Mn–Fe and Mn–Al are supported by the experimental data on sequential extractions, as manganese is mainly extracted from the sediment in the I and II steps. Nevertheless, As is present only as bound to the organic matter and in the mineral structure of the sediment not supporting the observed As–Fe and As–Al relations.

4. Conclusions

Heavy metal and metalloid pollution at a disused pyrite mine was investigated by considering five solid samples as representatives of the different soil systems in the area: three stream sediment samples with different soil texture, a background soil sample and a mine tailing sample.

X-ray and element analyses indicated a common mineralogical and chemical composition, of mainly quartz, clinocllore, muscovite, anorthite, and hematite. Particle size distributions of the five samples showed that the stream sediments were characterised by larger amounts of the finest classes (sand range, 2000–60 μm) than tailing and background soil samples (gravel range, >2000 μm). Wet and dry sieving procedures gave different particle size distributions: stream sediments presented significant differences in the classes of sand and gravel texture, while native soil and tailing (samples 4 and 5) differed especially in the clay, mud and lower end of sand ranges. These observations could be explained by applying laser diffraction analysis showing that samples 4 and 5 presented the largest amounts of the finest particle (<12.5 μm). The Rosin–Rammler model is used to represent these observed trends by means of two adjustable parameters ($D_{63.2}$ and α related to the mean dimension and distribution dispersion, respectively), which can reproduce the differences among wet and dry distribution.

Total concentration of Zn, Cu and Cd are larger in stream sediments than in tailing. In addition these metals are more concentrated in the finest stream sediment samples following the order ($M_1 > M_2 > M_3$). Mn and As are more concentrated in the tailing sample, but show linear correlation with both the particle size dimensions of the stream sediments ($D_{63.2}$) and Al and Fe amounts. This denotes that these elements, characteristic and intrinsic of the mine tailing, are now present also in stream sediments bound by surface interactions.

Experimental results are in accordance with previous results of heavy metal and metalloids speciation in stream sediment and mine tailing [10] and indicate both the accumulation in the stream sediments of the toxic elements released by mine tailings dump (because of AMD) and the significant effect of surface interactions in the binding of these pollutants.

Nevertheless comparing the speciation results by sequential extractions and the observed correlations with $D_{63.2}$, Fe and Al some contradictions emerged, in particular for As. This is a further proof of the complexity of metal pollution occurring in natural soil systems and indicates that it is better not to use conventional analyses (such as soil texture classification and acid digestion for total concentration) as stand-alone charac-

terisation for pollution assessment especially in mining area. Speciation and investigation of sorbing properties by simulating mixtures are therefore fundamental steps for the identification of the chemical and physical mechanisms involved in pollution mobilisation and migration [16].

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