

Mine waste dumps and heavy metal pollution in abandoned mining district of Boccheggiano (Southern Tuscany, Italy)

M. Benvenuti · I. Mascaro · F. Corsini · P. Lattanzi · P. Parrini · G. Tanelli

Abstract Mining activity in the Boccheggiano-Fontalcinaldo area (Southern Tuscany) dates back at least to the 16th century AD and lasted up to very recent times. Copper-rich hydrothermal veins, massive pyrite deposits, and their gossans were exploited. Two mine waste dumps (Fontalcinaldo, Fontebona), one flotation tailings impoundment (Gabellino), and one roasting/smelting waste dump (Merse-Ribudelli) in the study area were selected to ascertain the environmental effects of such protracted mining activity. Primary waste mineralogy is mainly characterized by pyrite, gypsum, quartz, carbonates, chlorites, and micas. Secondary oxidation mineralogy includes Fe and Cu sulfates and hydroxy sulfates, Cu carbonates, Fe and Al oxyhydroxides, and other phases [neogenic cassiterite at Fontalcinaldo; probable calkingsite, $(\text{Ce,La})_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$, at Fontebona]. Mine waste samples show extremely variable contents of toxic elements (Cu, Pb, Zn, Bi, Cd, As), with average values in the order of hundreds to thousands of parts per million (except for Bi and Cd). In some samples, the abundance of proper minerals of these metals cannot account for the entire metal load. Conceivably, either solid solution substitutions or adsorption processes contribute to the intake of released metals into newly formed minerals. Release and transport of pollutants was affected to variable degrees by acid-neutralization processes. The highest metal and acid concentrations occur close to the investigated wastes and rapidly decrease moving downstream some hundreds of meters or less, with the partial exception for Mn and Fe. Other than dilution ef-

fects, this phenomenon may be ascribed to metal adsorption and precipitation of solid phases.

Key words Mine waste dumps · Heavy metal pollution · Italy

Introduction

Mining of base metal deposits in the southern Tuscany district dates back at least to Etruscan times (Cipriani and Tanelli 1983). Since then, and up to very recent times, a number of base metal (Hg, Sb, Fe oxides and pyrite deposits) have been intensely exploited in the district.

This study focuses on the area surrounding the old town of Boccheggiano. Here mining activity is historically documented since the 16th century AD, when Vannoccio Biringuccio (the author of "De la pirotechnia") supervised the mining of iron gossans. Exploitation of copper-rich hydrothermal veins began in the 18th century under Giovanni Arduino's direction, and reached its climax at the end of past century, when extensive exploitation of the so-called "Filone quarzoso cuprifero di Boccheggiano" took place. This yielded about 1.5×10^6 tonnes of ore at 4–8% Cu in the period 1889–1914. The lower grade ore was roasted and smelted in situ, leaving behind huge masses of slags and reddish roastings. Exploitation of pyrite bodies in the Boccheggiano-Fontalcinaldo area started in 1906 and continued up to the present, leading to the development of extensive mine workings (Baciolo, Bagnolo, Ballarino, Mulignoni, Rigagnolo, Fontebona, Fontalcinaldo, Campiano, and other minor deposits), with a total pyrite production on the order of some tens of millions of tonnes.

Such an extensive and protracted mining activity has left behind many abandoned mines and mine wastes, which can be of major environmental concern for problems such as acidic and metal-rich drainage (Benvenuti and others 1994; cf. Plumlee 1994a, b). Thus, the Boccheggiano-Fontalcinaldo area is an appropriate site to start a project of mineral-environmental geology, aimed to assess the environmental effects of mine wastes and to build on a predictive model of the evolution of acid- and metal-rich drainage (Jambor 1994).

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Geological background

The various lithologies cropping out in the Boccheggiano–Fontalcinaldo area may be grouped into four main units (Costantini and others 1994) (see Fig. 1): (1) Quaternary and Neoautochthonous (late Miocene–Pliocene) siliciclastic sediments; (2) arenaceous, phyllitic \pm carbonatic flysches of the Ligurian Domain (Cretaceous–Palaeocene); (3) anhydritic–carbonatic formation of Anidriti di Burano/Calcare Cavernoso (late Triassic), belonging to the Tuscan Nappe; and (4) anhydrites, phyllites, and siliciclastic formations of Triassic?–Palaeozoic age, formerly described (at least partly) as Filladi di Boccheggiano fnt. (AUCTT), and now grouped within the Monticiano–Roccastrada Unit.

According to Costantini and others (1994), these sequences were folded and thrust during the compressional stage of the Apenninic orogeny (late Oligocene–middle Miocene), and subsequently (early Tortonian–Pliocene) offset by a number of extensional lineaments,

among which the Boccheggiano fault is especially prominent. This is a high-angle, normal fault, dipping 45° NE and striking from NNW–ESE to NNW–SSE (Fig. 1). At a regional scale, this extensional episode was accompanied by magmatic activity, leading to the emplacement of both intrusive and volcanic bodies (making up the Tuscan Magmatic Province) (cf. Innocenti and others 1992; Serri and others 1993). In the study area, the only direct evidence of this Tertiary magmatism is represented by a small granitic dike discovered at the Ballarino mine (Mazzuoli 1967). However, the occurrence of an intrusive body at a depth of about 1500–2000 m below the Nicciolenta–Boccheggiano area is concurrently suggested by the high geothermal gradient and a series of geophysical surveys carried out in the region (Ricceri and Stea 1992). In the Boccheggiano–Fontalcinaldo area, some pyrite deposits, namely Campiano, and most polymetallic mineralization (in particular, the Filone quarzoso cuprifero di Boccheggiano) are spatially associated with these late extensional structures, particularly the Boccheggiano fault (Fig. 1). Other pyrite deposits (e.g., Ballarino, Baciolo, Mulignoni, etc.) are located at the contact between basement rocks of the Monticiano–Roccastrada unit and the overlying Calcare Cavernoso formation of the Tuscan Nappe (Tanelli and Lattanzi 1983). Even if general consensus exists about the late-Cainozoic, hydrothermal origin of copper-rich polymetallic veins, several alternative models have been proposed for the genesis of the pyrite deposits. Some authors (Tanelli and Lattanzi 1983; Lattanzi and others 1994) favor a multistage process, in which Palaeozoic(?)–Triassic(?) pyritic protodes would have undergone strong remobilization during the tectonometamorphic Apenninic event.

Mine wastes

Three main types of mine waste have been identified in the study area (Badini 1994): waste rock dumps, flotation tailings, and metallurgical wastes.

At this stage of the research, we have selected four wastes, including at least one of each type: two waste rock dumps containing materials discharged from pyrite mines (Fontalcinaldo and Fontebona); one impoundment (Gabellino) filled with flotation tailings from beneficiation of ores from adjoining pyrite deposits (Rigagnolo, Mulignoni, etc.), and one accumulation of roastings and slags formed after metallurgical processing of ores from the Filone quarzoso cuprifero di Boccheggiano (Merse-Ribudelli).

Sampling and analytical procedures

Both near-surface (0–15 cm) and deeper samples (15–45 cm) of waste materials were collected by driving a

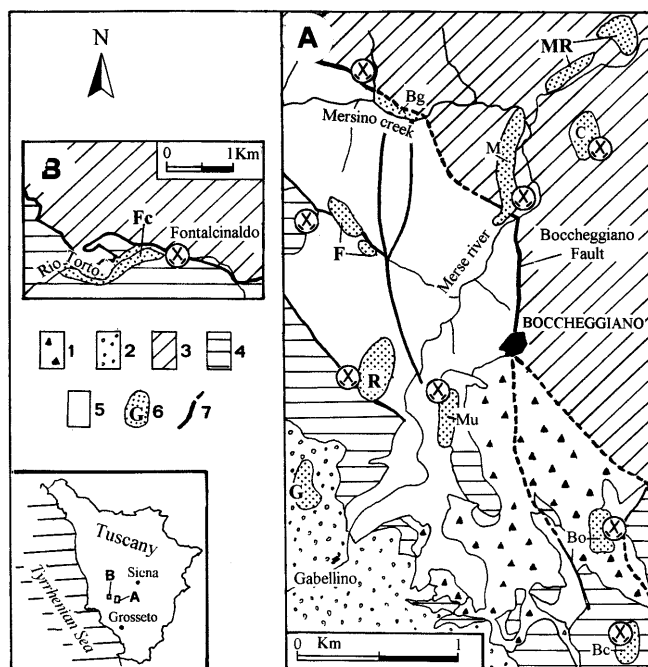


Fig. 1

Schematic geologic map of the Boccheggiano–Fontalcinaldo area (modified and simplified after Olivero 1965; Costantini and others 1994). Key to legend: 1. detritus; 2. Quaternary and Neoautochthonous sediments; 3. flysches of the Ligurian Domain; 4. Tuscan Nappe (mainly Anidriti di Burano/Calcare Cavernoso fnt.); 5. basement rocks of the Monticiano–Roccastrada Unit; 6. mine wastes [G = Gabellino flotation tailings, F = Fontebona mine waste dumps (mwd), Mu = Mulignoni mwd, Bo = Botroni mwd, Bc = Baciolo mwd, Bg = Bagnolo mwd, R = Rigagnolo mwd, M = Merse mwd, MR = Merse-Ribudelli roasting and smelting wastes, C = Campiano mwd, Fc = Fontalcinaldo mwd]; 7. major extensional lineaments. Location of main (abandoned) mines is also reported. The Ballarino mine, occurring about 1 km south of Baciolo mine, is not shown on the map

small-diameter pipe vertically through the wastes. Waters were sampled in winter and summer at various sites, up- and downstream of the mine wastes. After in-situ measurements of pH, water samples were filtered with 0.45- μm cellulose acetate filters, and subsequently acidified. In addition, a few samples of ochre precipitates in drainage waters were also collected.

Mineralogy of solid samples was examined under a binocular microscope and by transmitted and reflected light microscopy, SEM/EDS, and x-ray powder diffraction. Solid samples were then analyzed by XRF to determine the contents of the following pollutants: Cu, Pb, Zn, Bi, Cd, and As. We utilized a Philips PW 1480 instrument equipped with a Mo tube and LIF 220 analyzing crystal. Operating conditions were as follows: 40 mA (current), 60 kW (accelerating potential), 20/40 s (counting times for background and peaks, respectively). The measurement of Compton peak intensities was used to determine mass absorption coefficients for our samples (cf. Willis 1989). Due to the lack of suitable international standards, we have analyzed a few selected samples by different methods (ICP, NAA, and AAS) in different laboratories (Dipartimento di Scienze della Terra di Firenze, Italy; Nuova Solmine S.p.A., Grosseto, Italy; and Actlabs, Ancaster, Ontario, Canada), and used the averaged interlaboratory results as standard values for our correction curves.

Water samples were analyzed by atomic absorption spectroscopy flame and graphite furnace AAS.

Results and discussion

Mineralogy of the four investigated wastes is reported in Table 1. Following Jambor and Owen's (1993) criteria of classification, we have distinguished three classes of minerals: (1) primary (including ore, gangue, and pyrometallurgical phases); (2) secondary (i.e., minerals that formed in situ within the waste disposal area); and (3) ternary and quaternary minerals, developed only after collection and oven-drying at $\geq 60^\circ\text{C}$.

Primary mineralogy is mainly characterized by Fe, Cu, Zn, Pb and sulfides; Fe oxides; quartz; gypsum; calcite; micas; and chlorites. Pyrite is very abundant in all wastes studied except at Merse Ribudelli, where hematite, partly derived from roasting processes, is dominant. Minerals such as carbonates and (subordinately) aluminosilicates, which have the highest acid-buffering capability for tailings pore waters (see below), are relatively common in the Fontalcinaldo and Gabellino wastes, rather scarce in the Fontebona waste rock dump, and almost absent at Merse Ribudelli.

Secondary minerals are present in minor and variable amounts. In addition to prevailing Fe and Cu sulfates and hydroxy sulfates, Cu carbonates, Fe and Al oxyhydroxides, and unique phases such as neogenic cassiterite (Fontalcinaldo) and probable calkingsite [(Ce,La)₂(CO₃)₃·4H₂O] (Fontebona), have been observed. Tertiary and/or

Table 1
Mineralogy of waste samples¹

Locality	Primary minerals										Secondary minerals				Tertiary + Quaternary						
	qz	gyps	calc	mus	chl	dol	py	sp	po	ccp	gn	hem	goe	jar	cop	al	clay	gyps	minor phases		
Gabellino (flotation tailings)	XX	XX	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	fb, S, ang, cop	bs	
Fontebona (waste rock dump)	XX	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	fb, S(?), di, az, chrys, bis(?), mc, calk(?)	sd(?)	
Merse Ribudelli (metallurgical waste)	XX		X	X	X					XX				X	X	X			calc, ba, py, px, ov, ccp, po, Cu	sd	
Fontalcinaldo (waste rock dump)	XX	X	X			X	X			X	X	X	X	X	X	X	X	X	sp, mag, rhod, sid, asp, cs, clay	lp(?), cs	bs, ma

¹ Relative abundance of investigated phases: XX = abundant; X = minor; x = accessory. Mineral abbreviations: al: aluminite, ang: anglesite, asp: arsenopyrite, az: azurite, ba: barite, bis: bismuthite, bs: bassanite, calc: calcite, calk: calkingsite, ccp: chalcocopyrite, cel: celestite, chl: chlorites, chrys: chrysocolla, clay: clay minerals, cop: copiapite, cs: cassiterite, Cu: native copper, di: diasporite, dol: dolomite, fb: fibroferrite, gn: galena, goe: goethite, gyps: gypsum, hem: hematite, il: ilmenite, jar: jarosite, lp: lepidocrocite, ma: meta-aluminite, mag: magnetite, mc: malachite, mus: muscovite, ov: olivine, po: pyrrhotite, px: pyroxenes, py: pyrite, qz: quartz, rhod: rhodochrosite, S: native sulfur, sd: siderite, sid: siderite, sp: sphalerite

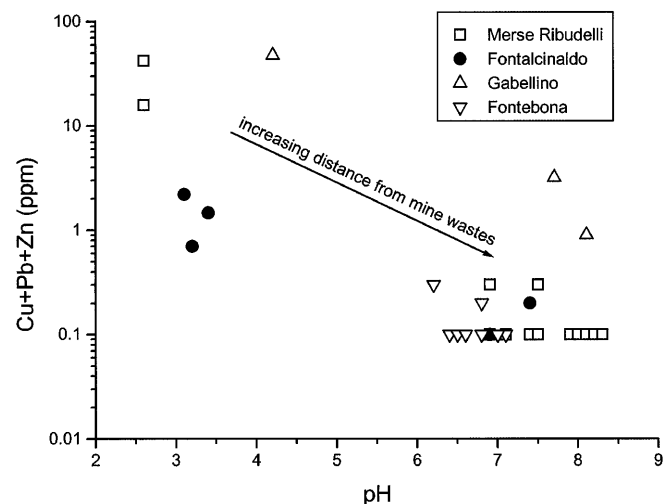
Table 2Toxic elements contents of solid samples from mine wastes (in ppm)¹

Mine waste	n	Pb		Bi		As		Zn		Cu		Cd	
		Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range
Fontebona	5	6750	672–29200	38	3– 80	268	88– 429	524	154– 807	678	264–1080	4	2–6
Fontalcinaldo	8	219	106– 346	26	7– 37	705	55–1075	311	29– 460	177	29– 460	4	bdl–8
Merse Ribudelli	8	747	53– 783	446	13–885	166	36– 386	256	89– 2280	709	252–2280	9	bdl–16
Gabellino	25	2450	449– 5670	9	bdl–44	138	50– 388	6080	154–16750	299	81–1470	18	3–59

¹ Geochemistry of waste rock dumps, flotation tailings, and roasting/smelting wastes in the Boccheggiano area. The contents of analyzed elements are expressed in ppm. n: number of analyzed samples; bdl = below detection limits

quaternary minerals are present only in trace amounts and include siderotil, bassanite, and metaluminite. Waste samples show relatively high, although extremely variable contents of analyzed elements (Table 2): As and Pb are dominant in waste rock dumps at Fontalcinaldo and Fontebona, Zn and Pb in the Gabellino impoundment, and Cu and Bi in the Merse-Ribudelli waste. A comparison between mineralogy and geochemistry of waste samples indicates that a high metal concentration is frequently matched by the presence of primary and/or secondary proper minerals containing this specific metal. For instance, Cu-rich samples from Merse-Ribudelli waste include primary chalcopyrite and native copper; base metal-rich flotation tailings at Gabellino contain primary sphalerite, galena, and chalcopyrite and secondary angle-site. Apparently, other samples lack such a correlation: this feature may be ascribed to metal incorporation, either by solid solution or adsorption mechanisms (cf. Jambor 1994; Bigham 1994), into primary minerals, organic materials, and/or secondary minerals, rather than to the undetected presence of submicroscopic metal-bearing phases. In fact, thin, reddish and/or ochre precipitates are commonly associated with waters draining mine waste dumps. Semiquantitative SEM/EDS analyses of some of these precipitates (made up of iron oxyhydroxides and sulfates) indicate metal contents of up to 0.7 wt% Ni, 1.2 wt% Cu, 4.7 wt% As, and 6.7 wt% Pb. Table 3 reports the acid and metal loadings (Fe, Mn, Cu, Pb, and Zn) of the Boccheggiano-Fontalcinaldo drainage waters. As a rule, the highest metal and H⁺ concentrations occur close to the investigated wastes and rapidly decrease moving downstream some hundreds of meters or less (Fig. 2). Other than dilution effects, the rapid water quality improvements downstream of mine wastes should be also ascribed to metal adsorption and precipitation of ochre minerals and microbial bioaccumulation. The persistently high Fe contents of water samples, often in excess of the solubility value at the pH-temperature-Eh boundary conditions, may be due to differences in the particle size distribution or chemical composition of naturally occurring colloid iron. In agreement with experimental results (cf. Byrne and Kester 1976), it is likely that 0.45- μ m filters do not remove the smallest colloid particles present in the analyzed waters.

Waters derived from tailings and waste-rock dumps owe their high concentrations of dissolved constituents mainly to sulfide-oxidation reactions occurring in the higher vadose zone of waste impoundments. In addition, bacterial sulfide oxidation can not be excluded. Attenuation of these high acid and metal loadings may occur through buffering reactions with reactive solid phases in the tailings and in underlying bedrock. The principal acid-neutralization mechanisms are represented by dissolution of carbonates, hydroxides, and aluminosilicates. At present, the chemical evolution of waste pore waters is difficult to establish on a quantitative basis, because many of the interrelated factors involved (e.g., the physical setting of the impoundment, the mineralogy and relative abundance of the pH-buffering solids, the sequential nature of pH-buffering reactions, the reaction rates under conditions of dynamic flow) (cf. Blowes and Ptacek 1994) still have not been comprehensively evaluated. However, a rough estimate of buffering capabilities of various waste systems can be obtained from simple consideration of the mineralogy of both wastes and underlying/adjacent be-

**Fig. 2**

Plot of the pH and dissolved metal content (given as the sum of copper, lead and zinc) of waters draining mine wastes in the Boccheggiano-Fontalcinaldo area

Table 3
Metal contents and pH of drainage waters¹

Sample		Fe		Cu		Pb		Zn		Mn		pH	
w	s	w	s	w	s	w	s	w	s	w	s	w	s
Gabellino creek													
F6		<u>22</u>		0.82		<u>0.32</u>		46.5		<u>15.1</u>		<u>4.2</u>	
F7	FC16	<u>0.7</u>	<u>1.9</u>	<0.05	0.01	<0.004		<u>3.2</u>	0.18	<u>3.2</u>	<u>0.75</u>	<u>7.7</u>	8
F8		<u>0.35</u>		<0.05		<0.004		0.93		<u>0.93</u>		<u>8.1</u>	
Rigagnolo creek (Fontebona)													
VB1		<u>1.2</u>		<0.5		<0.004		0.3		<u>0.5</u>		<u>6.2</u>	
VB3		<0.1		<0.5		<0.004		0.2		<u>0.8</u>		<u>6.8</u>	
VB4		<0.1		<0.5		<0.004		<0.03		<u>0.3</u>		<u>6.4</u>	
VB5		<u>1.7</u>		<0.5		<0.004		0.1		<u>0.6</u>		<u>6.8</u>	
VB7		<0.1		<0.5		<0.004		<0.03		<0.05		<u>7.1</u>	
VB10		<u>2.1</u>		<0.5		<0.004		0.08		<u>0.5</u>		<u>6.5</u>	
VB12		<0.1		<0.5		<0.004		0.03		<u>0.4</u>		<u>6.6</u>	
VB14		<0.1		<0.5		<0.004		<0.03		<u>0.2</u>		<u>7</u>	
Merse Rivers (Merse Ribudelli waste and others)													
F9		0.12		<0.05		<0.004		<0.03		<0.05		<u>6.9</u>	
F10		0.13		<0.05		<0.004		0.06		<0.05		<u>7.9</u>	
R1	FC13	<0.1	<0.1	<0.05	0.01	<0.004	<0.004	0.3	0.29	<u>0.5</u>	<u>0.56</u>	<u>6.9</u>	6.9
R2P		<u>717</u>		<u>11.3</u>		<u>0.02</u>		<u>30.5</u>		<u>14</u>		<u>2.6</u>	
R2C	FC12	<0.1	<0.1	<0.05	0.03	<0.004	<0.004	<u>0.3</u>	0.30	<u>0.7</u>	<u>0.75</u>	<u>7.5</u>	7.7
F14M	FC11	<0.1	<0.1	<0.05	0.029	<0.004	<0.004	<0.03	0.17	<0.05	<u>0.21</u>	<u>8</u>	<u>6.8</u>
F14D		<u>430</u>		<u>3.5</u>		<0.004		<u>12.3</u>		<u>2.2</u>		<u>2.6</u>	
F14V		<0.1		<0.05		<0.004		<u>0.04</u>		<0.05		<u>7.4</u>	
R4	FC10	<0.1	<0.1	<0.05	0.015	<0.004	<0.004	<0.03	0.86	<u>0.3</u>	<u>0.19</u>	<u>8.1</u>	7.7
R5	FC9	<u>1.7</u>	<0.1	<0.05	0.5	<0.004	<0.004	<0.03	0.24	<0.05	<u>0.23</u>	<u>7.5</u>	<u>6.8</u>
F17	FC5	<0.1	<0.1	<0.05	0.08	<0.004	<0.004	0.05	0.21	<u>0.13</u>	<u>0.21</u>	<u>8.2</u>	<u>7.7</u>
F18	FC6	<0.1	<0.1	<0.05	0.01	<0.004	<0.004	0.05	0.15	<0.05	<u>0.06</u>	<u>8.3</u>	
R6	FC4	<0.1	<0.1	<0.05	0.01	<0.004	<0.004	0.03	0.17	<u>0.2</u>	<u>0.11</u>	<u>7.1</u>	
Rio Torto creek (Fontalcinaldo)													
F1		<0.1		<0.05		<0.004		0.12		<u>0.25</u>		<u>6.9</u>	
F2		<u>0.35</u>		<0.05		<0.004		0.23		<u>0.4</u>		<u>7.4</u>	
F3	FC1	<u>155</u>	<u>804</u>	<u>1.1</u>	<u>8</u>	<0.004	0.028	1.1	<u>14</u>	<u>4.3</u>	<u>68</u>	<u>3.1</u>	<u>2.3</u>
F4	FC2	<u>50</u>	<u>164</u>	<u>0.62</u>	<u>3.5</u>	<0.004	0.029	0.85	<u>11</u>	<u>3</u>	<u>69</u>	<u>3.4</u>	<u>2.7</u>
F5		<u>60</u>		<u>0.69</u>		<0.004		0.85		<u>3.4</u>		<u>3.2</u>	

¹ Geochemistry of drainage waters in the Boccheggiano-Fontalcinaldo area. The contents of analyzed elements are expressed in ppm. Underlined values exceed drinking waters levels established by Italian law (in ppm: Fe = 0.2; Mn = 0.05;

Cu = 1; Zn = 3; Pb = 0.05; pH < 6). Sampling was repeated twice a year (w: winter; s: summer) in order to demonstrate possible seasonal fluctuations (see text)

drock. On such a basis (Fig. 1, Table 1, and related text), the lowest acid-buffering capability would be shown by the Merse Ribudelli metallurgical waste (phyllitic/carbonatic bedrock; scarcity of carbonates and other pH-buffering minerals). Environmental risks of acid drainage should, however, be comparatively minor for this waste, given the low amounts of primary phases (e.g., pyrite) that may increase H⁺ pore water concentrations through oxidation reactions.

Seasonal fluctuations of acidic and metal contents have been observed, especially at the Fontalcinaldo and Merse-Ribudelli wastes, where the Rio Torto creek and the Merse river, respectively, drain various effluents flowing downslope through mine waste heaps. Such variations largely depend on morphologic (length, dip, and lifetime

of runoff paths) and climatic factors (temperature, abundance of rainfall, etc.).

Concluding remarks

The main results so far obtained, which constitute the first mineral-environmental data set for the Boccheggiano-Fontalcinaldo area (and for the whole southern Tuscany district), can be thus summarized:

1. Waste samples are notably enriched in toxic elements such as Cu, Pb, Zn, As, Bi, and Cd.
2. Primary waste mineralogy is characterized by variable amounts of pH-buffering phases (calcite, dolomite, si-

derite, chlorites, muscovite), which, together with the lithologic nature of underlying/adjacent bedrock, can accordingly influence to variable extent the acidic and metal output of mine wastes.

3. With the partial exception for Mn and Fe, drainage waters show high acid and metal contents only in close proximity of mine wastes.
4. The occurrence of soluble phases such as sulfates (copiapite, chalcantite, etc.) among secondary minerals may favor rapid increases of acid and metal loadings in the wet season.
5. Even if water quality improves moving away from waste sites, entrapment of metals (for instance, as ochre precipitates) may be only temporary; metal release may occur in response to changing chemico-physical conditions (e.g., photochemically induced redox reactions) (McKnight and others 1988) and microbial activities.

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