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Metal distribution and environmental problems related to sulfide oxidation in the Libiola copper mine area (Ligurian Apennines, Italy)

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Abstract

Metal mobility and distribution in water and sediments in the surroundings of the pyrite–chalcopyrite–sphalerite mine of Libiola, in the Gromolo Valley near Sestri Levante (Genova), are investigated to evaluate the environmental hazard in the area. The mineralisation, related to Apennine ophiolites, was already known in the Bronze Age (about 2500 yr BC), but economic exploitation started in the XVII century. Open galleries, waste dumps and acid drainage testified the past mining activities which ended in 1965.

Mine waste material, covering an area of about 0.5 km^2, is reddish–yellowish, generally coarse-grained and stratified. The waste is a mixture of basalt, ultramafic-derived and iron-rich phases, with relatively high concentrations of S (mean 0.3% S) and Cu (mean 0.3% Cu), and significant contents of Zn, As, Mo and Se.

Acid drainage, with pH values as low as 2.5, is quite rich in dissolved Fe, Al, Cu, Zn, Mn, Ni. Repeated sampling revealed marked chemical variations, particularly in the mine waste area, depending on water flow conditions. Where low-pH water mixes with normal (pH 8) surface water, reddish amorphous iron phases (e.g. ferrihydrite, schwertmannite) precipitate, favouring the scavenging of many elements carried by the acid waters and providing a natural way of remediation for the stream waters. The rapid flocculation causes anomalous contents of Fe, Cu, Zn, Co, Sc, Y, La, Ce, and to a lesser extent of Cr and Ni, in the sediments. Although the ochreous colloids are important components of the Gromolo River sediments for about 8 km from the mine, preliminary results indicate that, unless natural conditions change, remobilisation of heavy metals should not be expected.

Keywords: mine waste; acid drainage; geochemical barriers; metal pollution

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1. Introduction

Sulfide waste disposal is an important environmental threat either in extensively mineralised areas or in localised spot sites. The wastes from mining activity, still having high metal concentrations, represent a source of metal pollution for a long time after extraction (Davies, 1980, 1983). The fragmentation and incoherence of the waste material enhance chemical reactions (Robertson, 1994) and, when iron sulfides are present, oxidation produces acid mine drainage (Salomons, 1995). Acidic waters can favour the mobilisation of large amounts of pollutant elements, only partially adsorbed by secondary phases. Downstream of pollution sources, metal concentration in the water decreases due to several

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physical and chemical factors, which include dilution, dispersion, precipitation, adsorption and ion-exchange reaction, sedimentation of suspended particulate (Chapman et al., 1983). However, metals released by water can be stored, through normal biogeochemical pathways, in sediments, soils and biomass, and finally enter the food chain.

For the evaluation of the environmental impact of both active and abandoned mining sites, the characterisation of the chemical composition of tailings is only the first fundamental step; it must be followed by studies directed to the identification of metal dispersion patterns in the surroundings, through analyses of soils, stream sediments, waters and plants.

In this paper, we discuss surface water chemistry and stream sediment composition of a drainage basin, in the Ligurian Apennines (Italy), impacted by past mining activities. The effects of excavation are still evident in the stream bed, coated by ochreous sediments some kilometres downstream from the mine, and sometimes also in the sea water in front of the river mouth, made red by ochreous colloids floated by violent discharges. This work is a contribution to the evaluation of the environmental hazard in this area, defining the sources, tracing the pathways and identifying the sinks of heavy metals released by sulfide oxidation and water–rock interaction. Studies on the isotopic characteristics of waters and of sulfides, and experimental investigations of plant–soil interaction are in progress.

2. Study area and ore characteristics

The study area is located in the drainage basin of the Gromolo River, near the village of Libiola (Genova), about 8 km NE from the town of Sestri Levante (Fig. 1). Sandstones and shales (Gottero Sandstones, Val Lavagna Formation and 'Palombini' shales; Decandia and Elter, 1972; Abbate et al., 1980–1992) crop out in the lower part of the Gromolo basin, while basalts, serpentinites, gabbros, cherts and limestones (Diaspri di Monte Alpe and 'Calpionelle' limestone; Decandia and Elter, 1972; Abbate et al., 1980–1992) dominates in the upper basin (Fig. 1).

Ore deposits related to the Apennine ophiolites occur in rocks that were affected by submarine hydrothermal metamorphism (Bonatti et al., 1976) and suffered intense tectonic deformation. The Libiola mine area (Fig. 1) is associated to the Mesozoic ophiolitic rocks of the Internal Ligurides cropping out in the Eastern Liguria (Brigo and Ferrario, 1974; Zuffardi, 1977; Cabella, 1994). The mineralisation is hosted in pillow and brecciated basalts, and partially involves tectonically overlaying serpentinites (Ferrario and Garuti, 1980). Pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and sphalerite (ZnS) are the main ore forming minerals, hosted in a quartz and/or calcite gangue (Bertolani, 1952).

The mine was already known in the Bronze Age (about 2500 yr BC, Campana et al., 1996). Economic exploitation started in the XVII century and ended in 1965. Mining operations were active both in open pit and underground shafts. Nowadays several open galleries and waste dumps testify the past mining activities.

The mine wastes, located between ~335 and ~230 m asl, extend over about 0.5 km^2 and are partially crossed by two tributaries of the Gromolo River (Rio di Boeno and Rio Cattan) (Fig. 1). They are clearly identified for the lack of vegetation cover and the typical reddish-orange–yellow colours due to iron-rich ochreous precipitates. Coarse-grained sterile rock fragments (mostly basalts and serpentinites), low grade mineralised fragments, ochreous-green weathering products and residual phases constitute the spoil heaps. High-angle stratification, favoured by the occurrence of an 'indurated' iron-rich surface layer, is a typical feature of the steep slopes of the waste area.

3. Materials and methods

Ten samples, representative of the mine waste material, were collected over the waste area. About 1 kg of the topsoil horizon (0–20 cm) was sampled and sieved retaining the <2 mm fraction. Fourteen samples of stream sediments, representative of the mined and unmined areas, were collected from the active river bed and sieved in the field to -80 mesh (0.177 mm) to obtain about 50 g of fine sediment. The grain size fractions chosen for soil and sediment follow the recommendations of UNESCO and IGCP (Darnley et al., 1995) for environmental and resource management geochemical investigations.

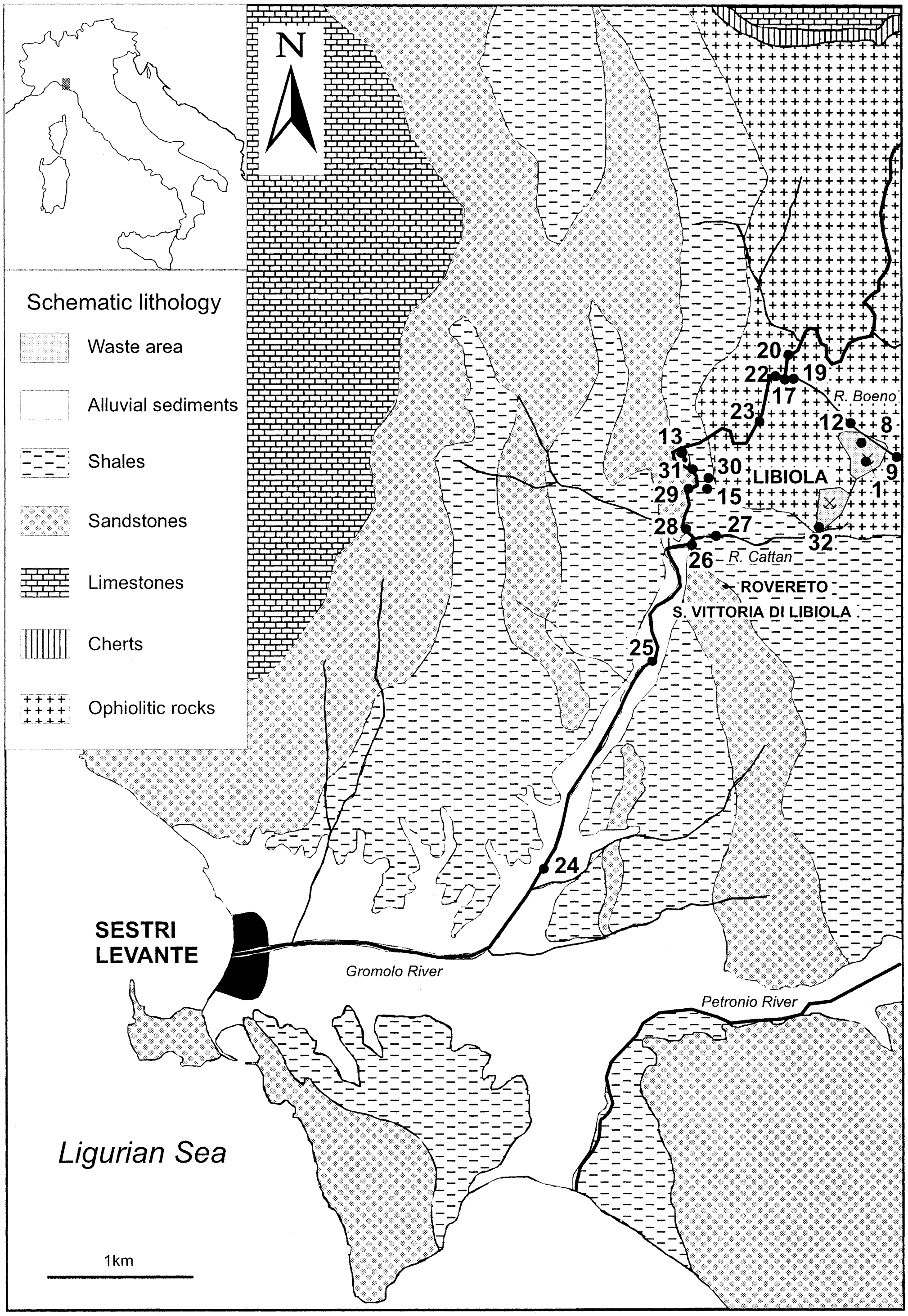

Fig. 1. Lithologic sketch of the Gromolo drainage basin and location of sampling sites.

Mineralogical analyses were carried out by X-ray diffraction (Philips PW1710 spectrometer, CuK_{α} radiation) by pressing powders into alumina holders; iron-rich samples were processed using a CoK_{α} source. Major and trace elements were analysed by X-ray fluorescence spectrometry (Philips PW 1480 with Rh tube) on pressed powder pellets following the methods of Franzini et al. (1972, 1975), Leoni and Saitta (1976) and Leoni et al. (1982) for matrix corrections; the net to background ratio method was applied for matrix correction for Mo determination. Long-term reproducibility for major elements is better than 7%. The estimated precision and accuracy for trace elements are better than 5% except for those elements at 10 ppm and lower (10–15%); the detection limit for the most trace elements is 3 ppm (Leoni and Saitta, 1976). For Se, working standards were obtained by adding known selenium concentrations to a clay sample; to test the procedure, international reference standards was used (NBS 1633a). Cu-rich samples required working standards in the range 0.9–20% CuO; five samples, analysed by atomic absorption, were used to test the calibration curve. Details on the analytical procedures are in Dinelli et al. (1996). LOI (Loss on ignition) was evaluated after overnight heating at 950°C in platinum crucibles.

Samples of natural and mining-related water were collected in polypropylene bottles from flowing streams both in November 1996 and April 1997 to represent periods of heavy and moderate rains respectively. Temperature, pH, Eh, and electrical conductivity were measured on-site, whereas chemical determinations were carried out by flame atomic absorption spectrometry (Perkin–Elmer 5000) on samples filtered through 0.45 μm Millipore® filters, according to the standards conditions listed by Perkin–Elmer (1976), with experimental detection limit 0.01 mg/l.

The location of sampling sites for stream sediments and stream waters in Gromolo drainage basin is reported in Fig. 1.

4. Waste material

The most common phases of the waste material are: serpentine, talc and plagioclases derived from the barren rock fragments (mostly basalts and serpentinites); quartz derived from the gangue of the mineralisation; goethite and other iron oxy-hydroxides originated from sulfide oxidation. Sulfide fragments are rare.

The chemistry of the waste material (Table 1) is dominated by Fe_2O_3, MgO as expected by the mineralogical composition. High Cu, Zn and Se values derive from ore minerals, whereas the large amounts of Cr, Ni, Co and V largely depend on the type of barren waste material. The relative contribution of the main components (basaltic and serpentine-derived rock fragments, and iron oxy-hydroxides) to the waste material can be evaluated through the Al_2O_3–MgO–Fe_2O_3 diagram of Fig. 2.

Table 1
Mean chemical composition and range for the Libiola waste rock pile (average of 10 samples)

	Mean	Range	
wt%			
SiO_2	32.62	23.38	36.97
TiO_2	1.19	0.85	1.39
Al_2O_3	9.68	7.82	13.57
Fe_2O_3	25.59	18.35	34.92
MnO	0.10	0.07	0.14
MgO	13.77	8.35	20.19
CaO	1.10	0.68	2.13
Na_2O	0.42	0.13	0.82
K_2O	0.21	0.04	0.36
P_2O_5	0.10	0.07	0.13
LOI	15.10	12.71	18.69
ppm			
S	2953	610	12000
V	267	208	302
Cr	1454	329	2267
Co	127	103	164
Ni	512	78	1325
Cu	3225	2300	4800
Zn	567	159	2100
Ga	21	14	26
As	14	4	33
Se	13	6	18
Rb	13	7	22
Sr	21	6	40
Y	16	10	31
Zr	136	95	168
Mo	13	6	24
Pb	23	11	43

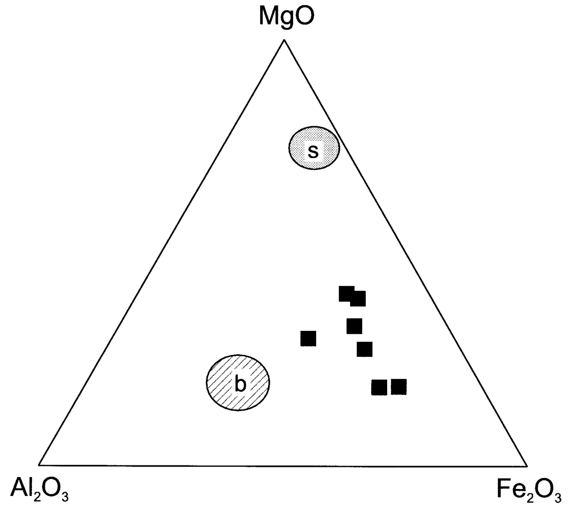

Fig. 2. Al_2O_3–MgO–Fe_2O_3 plot of waste rock pile material from the Libiola mine. Field data of Northern Apennines serpentinite and peridotite area (s) and basalt area (b) are reported for comparison (sources from Giammetti, 1968; Beccaluva et al., 1973, 1975, 1977).

5. Stream waters

The main features of the stream waters in the Gromolo drainage basin (Table 2) are governed by both the basin lithology and the sulfide oxidation process taking place in the Libiola mine area.

The occurrence of limestones, cherts, mafic and ultramafic rocks gives rise to weakly alkaline waters (pH up to 8), common in nearby areas with similar geological setting (Marini and Ottonello, 1997) and generally observed in areas where weathering of ophiolitic sequences is taking place (Drever, 1988). However, water–sulfide interaction lowers the alkaline pH values of the natural waters, and in the most polluted sites strongly acidic waters (pH close to 2.5) occur. In these waters, anion chemistry is dominated by sulfate (Fig. 3a), whereas bicarbonate prevails in the unpolluted (e.g. sample 20 in Fig. 3a and Table 2) or less impacted samples. Both in natural and polluted waters, major cation chemistry (Fig. 3b) is dominated by Ca and Mg, reflecting the basin lithology, but Mg contents are higher in the most acidic waters (Table 2) for their intense leaching action on the mafic silicates (serpentine, talc, chlorites, pyroxenes and amphiboles), abundant in the waste material and in the host rocks.

The lowest pH values and the highest values of electrical conductivity and of dissolved metals (Al, Fe, Cu, Zn and Mn) mark the input of acid drainage into the Gromolo River (samples 30, 17 in Table 2, and Fig. 4). These acidic vents come from narrow galleries located in the bottom of the valley, relatively far from the main waste area and at a lower altitude (Fig. 1), and the discharge, rather constant throughout the year, is always higher at site 30 than at site 17. The site locations, the constancy of discharge and the physico-chemical features of these waters are consistent with a long underground path and extended water–sulfide interaction. In spite of the low flow rate of the acidic vents, the anomaly in dissolved metal content and pH value can be detected in the Gromolo River for about one kilometre downstream from the confluence (e.g. Zn at site 30), whereas other more conservative ions (Mg, SO_4) still record high values more than two kilometres from the acidic discharge (Fig. 4).

Variations in pH strongly control the mobility of dissolved heavy metals with a typical inverse relationship (e.g. Plumlee et al., 1992), and in Libiola mine area the increase of the pH value of the acidic mine waters mixing with normal alkaline waters creates alkaline geochemical barriers (Perel'man, 1986). Significant changes in water and sediment compositions are produced by the precipitation of colloidal phases, but the extent of the geochemical effects of water mixing are conditioned by the water flow rate. In fact, comparing the parameters measured on waters collected on November 1996 and on April 1997 (Table 2), values did not change significantly where fairly constant water flow discharge has been observed (e.g. site 30), but they change passing from high (November) to moderate (April) water flow. This mainly concerns the sites located at higher elevation within the mine waste area, where fluctuation of the water table leads to marked variation of chemical features, apparent for all the elements except for the more conservative ones. For example, at site 1 (Fig. 1), the mine adit with active water emission located at higher elevation, pH changed from 3.8 to 6.2 and was accompanied by a dramatic decrease in Fe, Cu, Al dissolved contents (Table 2). This was also reflected on land by a change in the colour and composition of the stream bed

Table 2

Chemical data of waters samples from the Gromolo drainage basin. Samples 1–30 represent acid mine waters; samples from 20 to 24 represent river waters and are arranged according their downstream location along the Gromolo River (Fig. 1) (n.d.: not detected)

Site sampling	1		8		12		17	30	
	Nov-96	Apr-97	Nov-96	Apr-97	Nov-96	Apr-97	Apr-97	Nov-96	Apr-97
pH	3.8	6.2	6.6	4.2	6.9	6.2	2.7	2.8	2.6
Eh (mV)	455	210	247	360	146	230	610	595	590
Cond (μS/cm)	1775	1550	600	576	584	511	5200	7950	8000
Cl (mg/l)	18	11	12	4	9	12	53	350	533
SO_4	1500	1300	210	240	230	190	3500	6000	7000
Alk	0	31	26	3	20	18	0	0	0
Na (mg/l)	22	18.3	6	4.7	6	4.3	42.0	25	41.3
Mg	159	167	39	59	43	54	484	801	1080
Ca	289	249	38	23	44	24	252	333	149
K	5.00	5.7	0.50	n.d.	0.26	0.02	0.54	0.20	0.21
Al	42	n.d.	0.11	0.30	0.72	0.09	99	210	230
Fe	9.84	n.d.	n.d.	0.04	n.d.	0.03	225	99	775
Cu	32	6.98	0.87	0.03	0.25	0.01	46	154	175
Zn	5.66	3.22	0.52	0.23	0.33	0.16	21	26	35
Ni	0.73	0.34	0.10	0.21	0.27	0.13	2.05	5.77	8.50
Cr	0.10	n.d.	0.02	n.d.	0.04	n.d.	0.29	1.18	1.23
Mn	1.91	1.32	0.20	0.10	0.20	0.03	3.86	8.75	9.15
Site sampling	20 (Apr-97)	22 (Apr-97)	13 (Nov-96)	31 (Apr-97)	29 (Apr-97)	28 (Apr-97)	26 (Apr-97)	25 (Apr-97)	24 (Apr-97)
pH	8.3	6.5	8.2	8.9	5.9	6.9	7.3	8.1	8.0
Eh (mV)	280	290	138	360	289	5	20	250	260
Cond (μS/cm)	223	465	302	349	511	457	420	434	435
Cl (mg/l)	11	14	12	14	11	12	14	18	11
SO_4	20	170	120	110	190	180	170	140	170
Alk	92	40	66	73	46	27	49	49	58
Na (mg/l)	4.1	4.6	8	6.9	6.4	6.3	7.0	9.5	6.2
Mg	26	52	21	34	49	50	46	40	42
Ca	17	30	36	32	63	47	45	51	53
K	n.d.	n.d.	0.09	0.07	0.08	0.09	0.09	0.12	0.10
Al	0.02	0.01	0.19	n.d.	0.02	0.13	n.d.	0.01	0.05
Fe	0.05	0.04	n.d.	n.d.	0.06	0.05	0.02	0.12	0.04
Cu	n.d.	0.02	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.
Zn	0.01	0.69	0.01	n.d.	0.54	0.34	0.14	0.03	0.02
Ni	n.d.	0.07	0.13	n.d.	0.15	0.12	0.07	0.04	0.01
Cr	n.d.	n.d.	0.04	n.d.	0.01	0.01	0.02	0.01	n.d.
Mn	n.d.	0.15	0.06	n.d.	0.18	0.17	0.11	0.04	0.01

sediments: orange and iron-rich in the November sampling, blue-green copper-rich in the April sampling (Dinelli and Tateo, 1999).

6. Stream sediments

The geochemical features of the stream sediments in the Gromolo drainage basin are not homogeneous (Table 3), reflecting the different control of the basin lithology and the effects of the geochemical barriers. According to the downstream variations (Fig. 5) the elements with coherent patterns can be grouped as follows.

One main group includes iron and other elements (Al, S, Sc, Co, Cu, Zn, Y, La, Ce) and LOI, all enriched in the sediments of the Gromolo River just downstream the confluence of acidic, metal rich waters (Fig. 5a). Their behaviour is strongly controlled by the precipitation at the geochemical barriers of ochreous phases, represented for the largest part by ferrihydrite and schwertmannite. Although no peculiar Al-bearing phases have been detected in these sediments (Dinelli and Tateo, 1999), a direct incorporation of aluminum into ochreous phases substituting iron, as invoked by some authors in similar cases (Fuge et al., 1994; Alpers et al., 1994), is suggested by mixing calculations (see below). However, high Al_2O_3 content of the sample at about 8000 m may reflect the increasing importance of sedimentary clastic rocks in the lowermost section of the Gromolo River. With regard to the other elements, Cu and Zn display the most important and wide anomalies: concentrations about 1000 × background values (50 ppm) for Cu and about 20 × (background 50 ppm) for Zn at two kilometres downstream of the acidic water immission, with higher Zn values generally recorded further away from the source compared to Cu. The peculiar behaviour of Sc, Y and REE has been discussed in Dinelli et al. (1999), who suggested the use REE to evaluate the intensity of water/rock interaction in the Libiola area.

Another group includes some elements strongly controlled by the transition from the ophiolitic rocks and the overlaying cherts and limestones to sandstones and clays. This transition occurs at about 5000 m from the coast along the Gromolo River. Representatives of this group are MgO, CaO, Ni, Cr (Fig. 5b) and SiO_2, whose concentrations markedly decrease downstream of acidic discharges for the dilution operated by the precipitation of ochreous phases, but all record a strong decrease at the ophiolite/sedimentary cover transition. As a consequence of their conservative behaviour in water, MgO and CaO directly reflect the lithological change and, considering

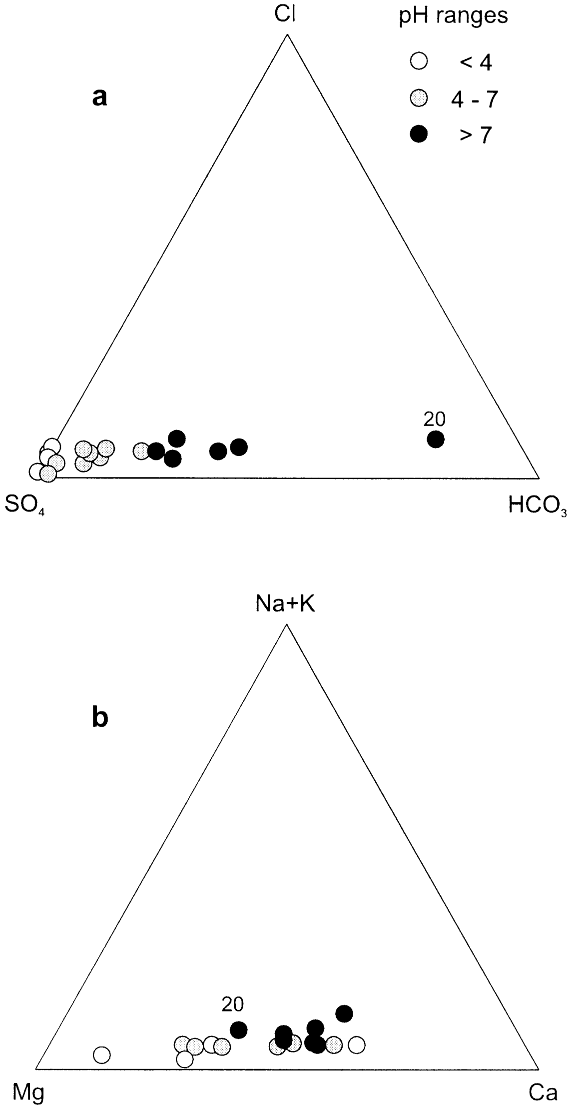

Fig. 3. Triangular plots relative to major anions (a) and major cations (b) for the stream waters collected in the Gromolo drainage basin. In both diagrams the position of sample 20, an unpolluted waters sample, is indicated. Low-pH waters in the (a) diagram are strongly enriched in sulphate.

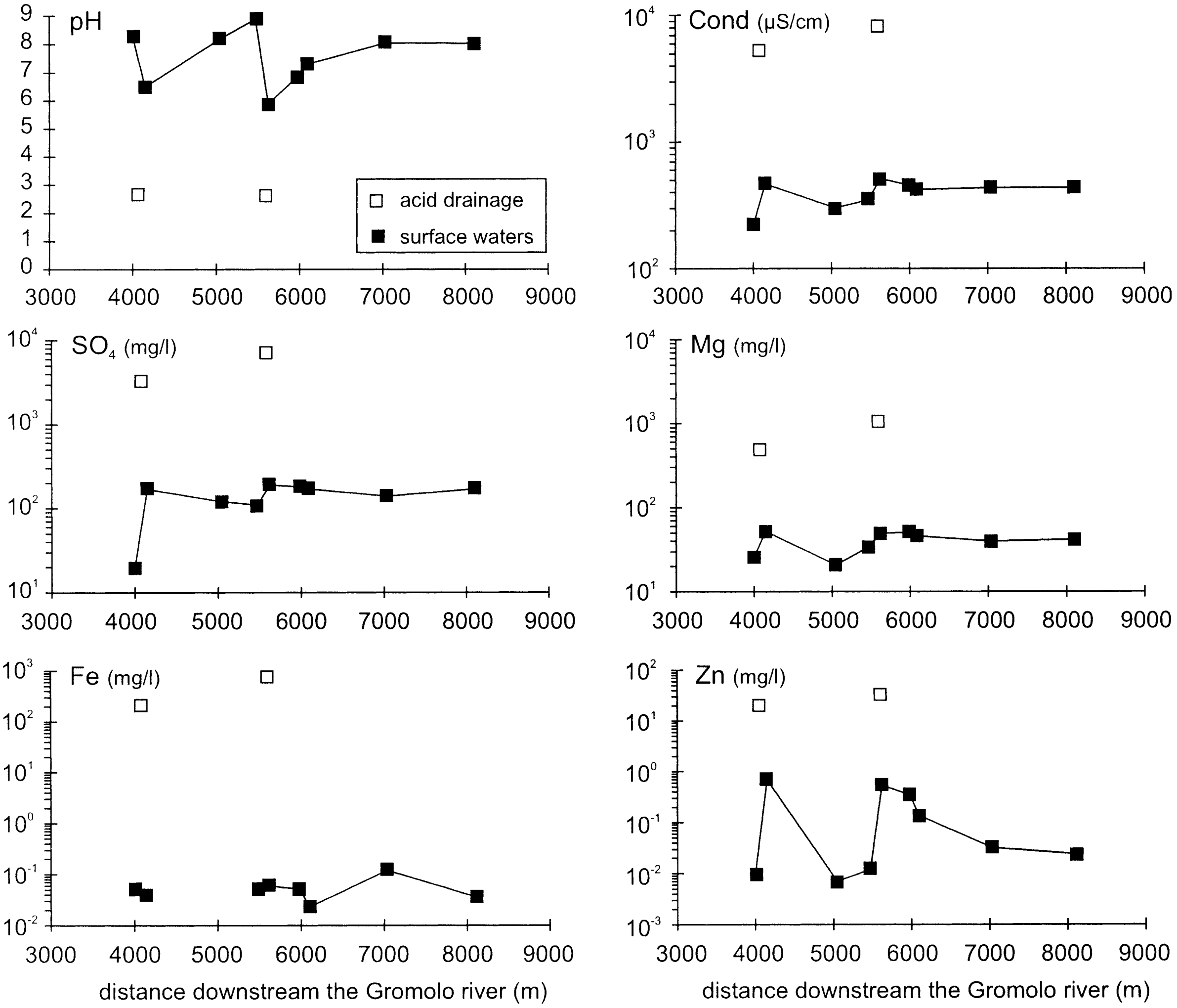

Fig. 4. Downstream variations of water features along the Gromolo River; open squares indicate the acid drainage inflows (sample 17 and 30 in Table 2). Some parameters tend to recover the pre-acid input values (pH, Fe, Zn) whereas other more conservative ions (SO_4 and Mg) settle to higher values. The increase in electrical conductivity records the presence of the acidic inputs.

the inverse relationship between Fe_2O_3 and MgO (Fig. 6a), the MgO content of the stream sediments can help to estimate the amount of the non-ochreous fraction of the sediment. Also Cr clearly reflects the lithological variation, because its relatively high concentrations in the acidic waters are not able to alter its distribution. Ni and Si might instead be partially involved in the precipitation of ochreous phases, although this effect is probably not so intense to significantly influence their downstream pattern. Actually the Ni distribution in the waters closely matches those of Fe, Cu, Zn, and Co, all strongly partitioned in the ochreous phases, so its incorporation into iron-rich phases cannot be excluded even if masked by the high background values typical of the upper course of the Gromolo River. However, its good correlation with MgO (Fig. 6b) suggests that mafic silicate minerals such as chlorite, serpentine and talc are the most important factors controlling the Ni distribution.

The third group also includes elements controlled

Table 3

Chemical composition of the stream sediments (<0.177 mm) in the Gromolo drainage basin. Gr: Gromolo River; Bo: Boeno river; Ca: Cattan river (dist m.: distance in meters from the Gromolo River source; values in italics among trace elements are wt%)

	Gromolo										Boeno			Cattan
Sample	20	22	23	13	31	29	28	26	25	24	19	12	9	27
Distance (m)	4000	4150	4400	5050	5475	5625	5985	6100	7035	8110				
wt%														
SiO_2	39.34	24.62	32.48	39.45	40.45	11.37	16.03	21.21	42.60	46.54	17.69	31.56	37.46	48.37
TiO_2	0.18	0.16	0.20	0.25	0.27	0.06	0.06	0.12	0.35	0.55	0.27	0.77	0.20	0.72
Al_2O_3	4.22	10.53	8.15	5.61	5.06	15.33	14.46	12.24	9.55	14.36	5.80	10.72	4.48	14.67
Fe_2O_3	8.20	24.52	14.60	9.39	9.75	32.51	30.84	25.30	10.72	9.86	44.05	23.74	8.69	9.02
MnO	0.13	0.13	0.14	0.13	0.14	0.07	0.08	0.11	0.15	0.24	0.32	0.11	0.15	0.23
MgO	28.28	14.17	20.52	27.67	27.45	4.42	4.68	6.66	18.63	8.54	6.00	14.24	27.21	4.83
CaO	4.54	2.01	3.36	4.89	4.11	0.85	1.09	2.35	2.74	2.16	1.38	1.17	0.99	2.95
Na_2O	0.03	0.06	0.10	0.14	0.12	0.01	0.11	0.27	0.34	0.55	0.28	0.13	0.09	0.67
K_2O	0.11	0.06	0.08	0.21	0.22	0.07	0.08	0.17	0.76	1.69	0.07	0.15	0.16	1.95
P_2O_5	0.03	0.03	0.02	0.03	0.04	0.04	0.04	0.05	0.05	0.13	0.06	0.07	0.07	0.13
LOI	14.94	22.11	19.11	12.24	12.39	31.34	28.32	28.57	14.11	15.37	22.72	16.38	20.50	16.44
ppm														
S	210	2185	1250	570	755	*1.20*	*0.90*	1905	620	440	2980	1850	460	870
Sc	18	45	32	20	22	59	59	51	26	26	46	41	19	26
V	66	695	74	75	81	29	29	42	90	122	95	178	72	138
Cr	2919	3342	3860	2792	3338	1288	1228	1187	1356	686	800	1355	1831	384
Co	94	147	131	100	99	125	153	191	125	127	425	149	155	105
Ni	1757	889	1327	1662	1608	260	385	616	1136	691	648	846	2029	441
Cu	53	*1.62*	*1.26*	650	820	*2.75*	*3.31*	*2.96*	*0.62*	*0.46*	*1.37*	*0.97*	200	*0.59*
Zn	56	1984	2700	157	223	1246	4400	6200	1250	967	6700	707	59	2600
Ga	n.d.	11	7	4	n.d.	16	17	13	7	10	23	20	n.d.	10
As	n.d.	n.d.	4	n.d.	3	6	n.d.	6	3	5	n.d.	10	n.d.	5
Rb	6	11	7	14	16	13	12	18	43	95	12	10	9	92
Sr	30	33	46	43	45	24	37	77	68	86	26	22	15	93
Y	6	39	28	9	9	51	52	43	20	28	41	30	10	40
Zr	39	67	61	42	53	9	9	16	64	107	22	86	34	110
Pb	7	10	5	9	15	11	13	9	17	6	24	24	24	34

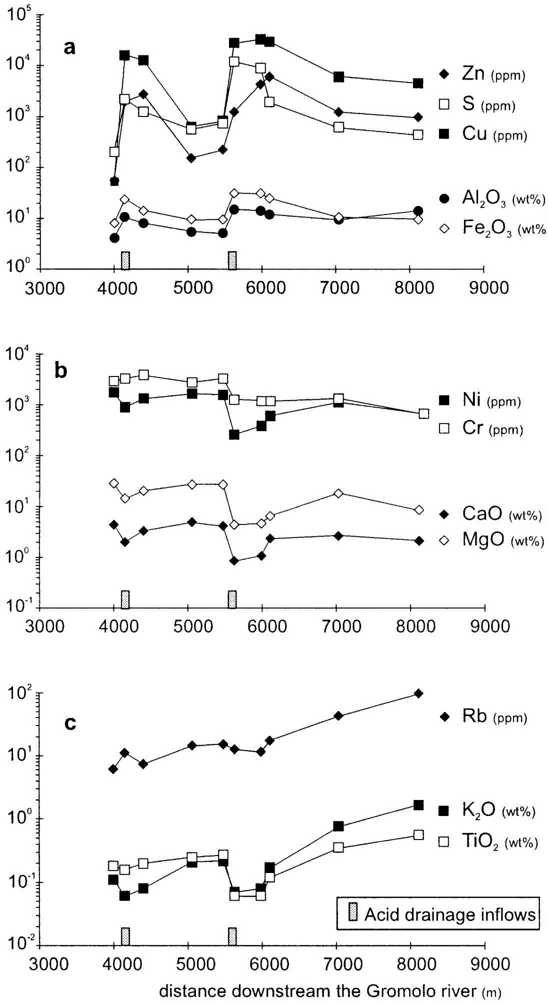

Fig. 5. Downstream variation of representative elements in the stream sediments of the Gromolo River: (a) include the elements which are strongly influenced by the ochreous phase formation associated to the alkaline geochemical barriers along the Gromolo River; (b) and (c) include the elements mostly controlled by lithological variations; (b) elements enriched in the upper section of the river and mainly associated to ophiolitic rocks and overlaying sedimentary cover (limestones and cherts); (c) elements enriched in the lower section of the river and mainly associated to sandstones and shales.

by the lithological change, but this time concentrations are higher in the lower section of the Gromolo River, indicating their association with clays and sandstones. TiO_2, Rb (Fig. 5c), but also K_2O, Na_2O, MnO, P_2O_5, V and Zr are all elements with common affinity for these rock types, and all display a dilution effect due to ochre precipitation.

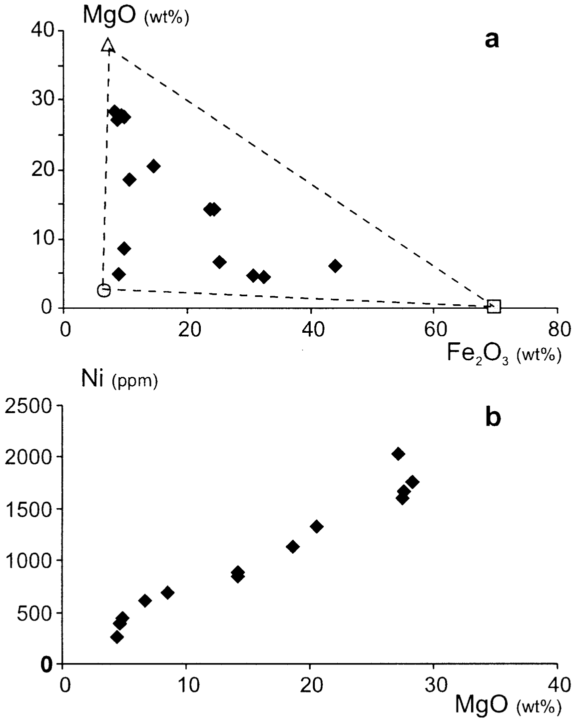

Fig. 6. Binary diagrams relating MgO to Fe_2O_3 and Ni contents in the stream sediments of Gromolo basin: (a) in the MgO vs Fe_2O_3 plot the samples fall in the field defined by the most representative rocks in the area (shales: circle; serpenitite: triangle) and by iron hydroxides (square); the negative correlation between Fe_2O_3 and MgO indicates that they represent respectively the ochreous and ultramafic fractions of the sediment; (b) the good positive correlation between Ni and MgO suggests that Ni might not be strongly partitioned into the ochreous phase precipitated at the alkaline barriers.

7. Conclusive remarks

The data so far outlined indicate that some environmental problems, mostly related to the acid mine drainage with high concentration of dissolved metals, occur in the Gromolo valley. However, heavy metal mobility in the aqueous phase are substantially controlled by pH variations: sometimes pH changes occur gradually without leading to intense heavy metal scavenging (Dinelli and Tateo, 1999); in another cases the mixing between acidic and normal surface waters leads to a rapid flocculation of ochreous phases which traps or at least favour the precipitation of many elements carried by the acidic waters. In this way the alkaline geochemical barrier

Table 4
Representative analyses of serpentinite, shales (Val Lavagna and 'Palombini' Formations) and colloidal products sampled in the Gromolo drainage basin (17: Fe colloid; 15: Al colloid; 32: Al–Cu colloid (numbers refer to site location in Fig. 1); values in italics are wt%)

	Serp.	Shale	Shale	17	15	32
wt%						
SiO_2	40.18	57.48	25.12	0.07	15.58	18.47
TiO_2	0.03	0.59	0.3	0.03	0.02	0.01
Al_2O_3	1.13	16.58	7.71	0.22	33.74	22.06
Fe_2O_3	7.09	5.98	2.61	69.73	0.85	1.51
MnO	0.13	0.13	0.09	0.02	0.02	0.03
MgO	38.06	3.42	1.22	0.18	2.00	1.95
CaO	0.06	3.42	31.79	0.18	1.68	1.78
Na_2O	0.06	0.92	0.3	0.08	0.21	0.68
K_2O	0.01	2.66	1.57	0.04	0.06	0.03
P_2O_5	0.01	0.1	0.03	0.03	0.03	0.05
LOI	13.24	8.72	29.26	27.42	43.03	32.41
ppm						
Cr	3011	84	43	175	246	52
Ni	2232	79	23	14	52	147
Cu	0	41	16	2500	3100	*17.40*
Zn	40	107	37	124	211	*2.03*
S	30	92	22	*2.00*	*2.80*	*1.60*

provides a natural remediation for the stream waters, although causing high metal concentrations in the sediments. A striking example is offered by the mixing between the metal-rich waters of site 30 with the alkaline waters of the Gromolo River leading to the anomalies recorded in the sediments of sites 29 and downstream (Figs. 1 and 5; Table 3).

To evaluate the contribution of the colloidal phases to the sediments, mixing calculations have been tested using as end members serpentinite and shales, the most representative rocks in the area, and some colloidal products collected at the geochemical barriers (Table 4). The choice of these end members is suggested by Fig. 6a, where the Gromolo sediments plot inside a triangle defined by the points of shales, serpentinite and iron hydroxide; however, to account for the high contents of Cu, Zn and Al in the sediments, also products more complex than simple iron hydroxide, representative of variable pH conditions (Dinelli and Tateo, 1999), have been involved in the calculations. The results indicate that the content of the colloidal phases in the sediments decreases from 89% at site 29 (44% Fe–Cu and 45% Al–Cu colloids; 9% serp, 2% shales) to 66% at site 26 (33% Fe–Cu and 33% Al–Cu colloids; 14% serp, 20% shales) to 16% at site 24 (6% Fe–Cu and 10% Al–Cu colloids; 16% serp, 68 shale). Although the values are merely rough approximations of the colloids carried by the Gromolo sediments, the high contents of colloidal phases in the sediments of the middle course of Gromolo River and also the conspicuous content at site 24, some kilometres downstream of the barrier and less than 3 km from the coast, are alarming for the environment.

Preliminary results (Dinelli et al., 1998) indicated that the heavy metals are strongly bonded to these type of colloidal precipitates, so that easy remobilisation should not be expected. However, if the natural control of metal dispersion is interrupted, e.g. by pH decrease, part of the metals carried by colloids can dissolve and, in addition to Cu and Zn, also large amounts of Al might be released to solution. Anyway, as reported by Schemel et al. (2000), also the physical properties of colloidal phases can affect habitats and organisms in the riverine systems, and when colloids are floated to the sea by violent discharges, as in the case of Libiola, also the coastal environment can be involved. Further studies on this subject are on the way to be completed.

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