THE FLUMINESE MINING DISTRICT (SW SARDINIA, ITALY): IMPACT OF THE PAST LEAD-ZINC EXPLOITATION ON AQUATIC ENVIRONMENT

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Abstract
A hydrogeochemical survey was carried out in the Fluminese district (SW Sardinia, Italy) to investigate the impact of past mining activities on the aquatic system. Waters in the Fluminese are near-neutral to slightly alkaline. Mine drainages had the highest SO_4 (640 mg/L), Zn (40 mg/L) and Cd (97 µg/L); other metals show a wide range in concentrations depending on dominant mineral assemblages at each mine. Dissolved Pb in mine waters is in the range of 1 to 53 µg/L but Pb > 10 µg/L also occurs in spring and well waters. The metal load discharged daily into the sea under low-flow condition is estimated at about 2160 g for Zn, 21 g for Cd and 30 g for Pb.

Introduction
The Fluminese mining district located in SW Sardinia (Fig. 1) is included in the Sardinian Geomining Park (Parco Geominerario Storico e Ambientale della Sardegna), where environmental reclamation and economic valorisation has been recently planned (R.A.S., 2003). Ore bodies comprise massive sulphides (Sedimentary Exhalative) located in the lower part of the Cambrian sequences, and lower grade sulphides (Mississippi Valley Type) located at the top of carbonate sequences (Boni, 1994). The most abundant metallic minerals are sphalerite and galena, with variable pyrite contents; barite and fluorite are abundant at some locations; ore bodies near the surface are generally oxidized, they consist mostly of smithsonite, hydrozincite and cerussite (Boni, 1994). The Pb-Zn deposits were mined since pre-Roman times; peak exploitation with more than 20 mines in the Fluminese area was reached in the century 1900. A description of host rocks, dominant ores and exploitation period is reported in Table 1. The cessation of mining activity left large quantities of mine wastes dumps and flotation tailings (about 54,000 m^2 and 40,000 m^2 at Su Zurfuru and S. Lucia, respectively).

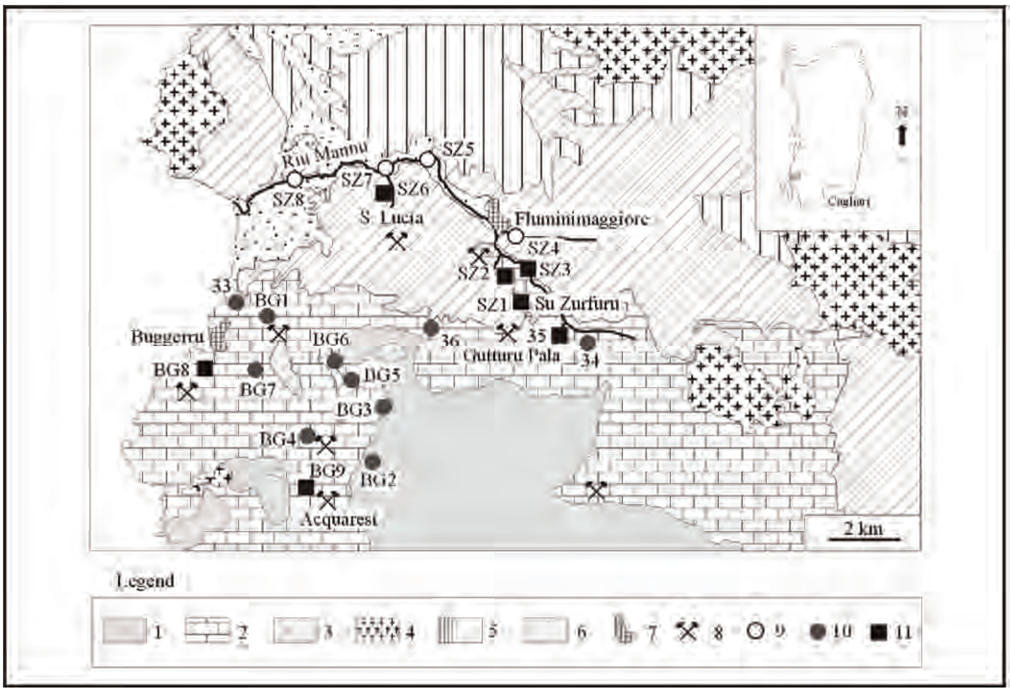

Figure 1. Schematic geology of Fluminese (Barca et al., 2001) with location of water sampling sites. Legend: 1. Lower Cambrian sandstone; 2. Lower Cambrian limestone-dolostone; 3. Upper Cambrian-Ordovician metasiltstone-metasandstone; 4. Hercynian granitic rocks; 5. San Vito Formation; 6. Tertiary-Quaternary sediments; 7. Town; 8. Significant abandoned mines; 9. Stream samples; 10. Spring and well samples; 11. Mine water samples.

Table 1. Description of relevant abandoned mines located in the Fluminese area.

Mine name	*host rocks*	Dominant ore	Exploitation decade	Mine closure
S. Lucia	*slate-conglomerate-limestone*	Ox-Zn	1880-1940	1942
		PbS	1945-1960	1968
		Ba-F	1970-1980	1981
Su Zurfuru	*slate-conglomerate-limestone*	F-(Ag)PbS-Ba	1890-1960	1968
		Py-ZnS-PbS	1970-1980	1987
Gutturu Pala	*dolostone-limestone-breccia*	Py-Zn>>PbS	1880-1990	1992
Nanni Frau	*quartzite-dolomitic breccia*	Ba-PbS	1880-1980	1989
Su Sollu	*slate-conglomerate-limestone*	Ba (30-60%)	1870-1980	1989
Candiazzus	*dolostone*	ZnS>>Py(+PbS)	1880-1970	1977
Planusartu	*Chert-rich limestone-dolostone*	ZnS-Py(PbS)	1870-1960	1962
Malfidano	*dolomite-limestone*	PbS-ZnS-Py	1870-1980	1980
Acquaresi-Masua	*dolomite-limestone*	ZnS>PbS	1880-1990	1998

Ba = barite; F = fluorite; Ox-Zn = oxidized Zn minerals; Py =pyrite and pyrrotite; PbS = galena; (Ag)PbS = Ag-rich galena; ZnS = sphalerite.

The study area has a semi-arid climate with drought periods usually extending from May to September. Rainfall ranges from 400 to 900 mm per year with a mean of 50 rainy days and the mean annual temperature is 17°C (E.A.F., 1998). Elevation is in the range of 0 to about 600 m a.s.l.. Dominant winds in the area blow from NW and carry sea spray inland. Surface drainage occurs after rain events mainly through the Rio Mannu, which is the largest stream in the Fluminese. The Cambrian carbonate formations (Pillola et al., 1998) host the most important aquifers due to intense fracturing and karst processes. Groundwater is considered by local authorities a significant water resource, due to the low availability of water from reservoirs in this area. After closure of mines, most pumping systems ceased operation, thereafter the underground workings underwent flooding and drainages out of mine galleries were observed at several sites. This study was aimed to investigate the impact of past mining on the aquatic system in the Fluminese area; preliminary results are reported here.

Methods

Water sampling was carried out in June 2006 under low-flow condition. Sampling sites are shown in Figure 1. Water samples comprise the high-flow springs (No. 33, 34 and 36) used to supply drinking water in the area, the main stream Rio Mannu, as well as low-flow surface and ground water. Mine water samples were taken at the outflow of galleries (Gutturu Pala, Su Zurfuru, S. Lucia, Lucien Buggerru) or nearby the mine (Acquaresi). Mine drainages at Su Zurfuru flow into a pond, then into the Rio Mannu stream; drainage at Lucien is discharged directly into the sea while drainages at other sites flow into streamlets. Temperature, pH, redox potential (Eh), conductivity and alkalinity were measured on site; water was filtered (0.4 µm, Nuclepore 111130), and acidified for metal analyses. Anions were determined by ionic chromatography, and cations by ICP-OES and ICP-MS. Amounts of chemical components refer to the aqueous fraction below 0.4 µm, and are reported as dissolved concentrations. The ionic balance was always less than ± 5%. Both precision and accuracy were estimated at ≤10% by analysing randomly duplicate samples and standard reference solutions (NIST1643c, d, e). The computer program PHREEQC was used for equilibrium calculations (Parkhurst and Appelo, 1999).

Results and Discussion

Physical-chemical parameters and the major ions dissolved in the Fluminese water samples collected in 2006 are reported in Table 2. Waters are circumneutral to slightly alkaline (pH: 6.3-8.2); this reflects their dominant circulation in carbonate rocks. Eh values are mostly in the range of 400-500 mV, indicating oxidising conditions, due to the relatively fast groundwater circulation through karst features and fractures. Conductivity in mine waters (up to 1.43 mS/cm) is generally higher than in springs and streams.

Water samples show different chemical composition (Fig. 2). Most waters have dominant Ca-Mg-bicarbonate composition due to their circulation in carbonate rocks. Waters having a dominant circulation in dolostone exhibit a molar Ca:Mg ratio close to 1. BG1, BG5 and BG6 groundwater samples have prevalent Na-Cl composition with relatively low conductivity (see Table 2); their composition reflects the influence of sea spray and the low salinity indicates a shallow circulation. The more saline SZ3 and SZ6 mine water samples show a dominant Ca-Mg-SO_4 composition likely derived from the oxidation of sulphide minerals or dissolution of sulphate minerals. These samples also show the highest F concentrations, which is consistent with the large occurrence of fluorite at Su Zurfuru and S. Lucia (see Table 1).

Table 2. Flow, redox potential (Eh), pH, conductivity (Cond) and major ions in the Fluminese waters.

No.	Name	Flow	T	Eh	pH	Cond	Ca	Mg	Na	Cl	HCO_3	SO_4	F
		L/s	°C	mV		mS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Streams													
SZ4	Rio Bau Porcu	2	20	450	8.1	0.56	41	15	46	72	131	56	0.50
SZ5	Rio Mannu	80	20	460	7.8	0.64	64	18	46	62	213	46	0.33
SZ7	Rio Mannu	60	23	450	8.1	0.64	64	19	42	64	215	48	0.33
SZ8	Rio Mannu	100	21	460	7.8	0.64	60	19	45	70	185	52	0.44
Springs and wells													
33	San Salvatore	>20	21	nd	7.3	0.74	79	28	54	92	360	27	0.06
34	Pubusinu	>50	16	nd	7.5	0.52	66	14	31	47	250	31	0.15
36	Su Mannau	>10	15	nd	7.7	0.73	65	30	45	74	330	20	0.06
BG1	Sa Tanca	-	15	480	7.5	0.42	28	6.8	38	62	113	13	0.19
BG2	Terra Arrubia	<0.05	15	490	7.5	0.76	71	18	57	92	290	24	0.12
BG3	Grugua farm	0.4	17	500	7.6	0.60	50	17	43	71	213	19	0.07
BG4	Pira Roma	-	14	490	6.8	0.57	47	11	45	86	140	34	0.07
BG5	M.te Segarino	<0.05	14	390	6.4	0.50	20	14	51	87	84	37	0.08
BG6	M.te Nieddu	0.2	17	490	7.0	0.69	24	22	76	96	198	35	0.26
BG7	Carcinadas	<0.05	22	490	7.4	0.92	82	28	72	112	308	41	0.06
Mine waters													
35	Gutturu Pala	2	16	nd	8.2	0.76	79	28	41	71	310	34	0.08
SZ1	Pietro	0.5	16	480	7.9	0.66	68	25	42	78	214	73	1.06
SZ2	Su Zurfuru	0.3	16	500	7.6	0.70	71	26	42	77	208	73	0.96
SZ3	Su Zurfuru	1	18	270	7.2	1.22	115	69	42	65	126	540	2.40
SZ6	S. Lucia	0.3	16	380	6.3	1.43	130	92	50	60	172	640	3.45
BG8	Lucien	3	17	500	7.9	1.01	91	18	89	160	240	84	0.15
BG9	Acquaresi	0.2	14	530	7.7	0.71	78	21	43	82	308	17	0.10

nd = not determined; - = well (water table at 2 to 3 m below ground level)

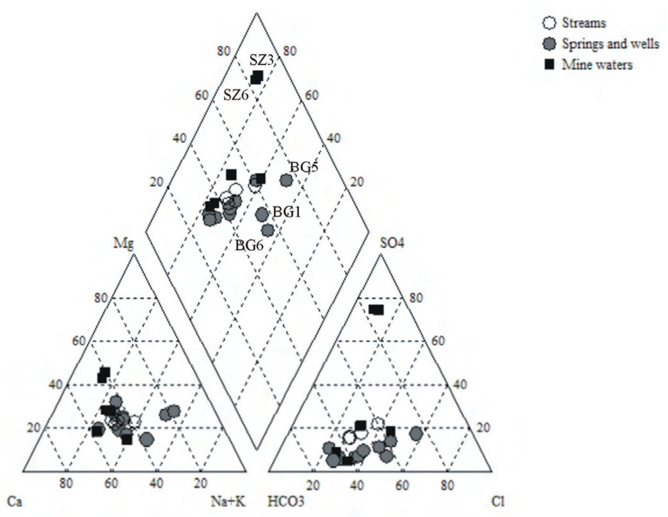

Figure 2. Piper diagram showing the main chemical composition of waters in the Fluminese area.

With reference to the guidelines established by the World Health Organization for drinking water (WHO, 2006), dissolved As and Sb (not reported here) were relatively low in all samples (i.e. always below the limits of 10 and 20 μg/L for As and Sb, respectively), which is consistent with the low occurrence of As and Sb minerals in this mining district. The spring waters had concentrations of dissolved Cd and Hg below the limits (3 and 1 μg/L for Cd and Hg, respectively). Dissolved Pb in spring waters was above the 10 μg/L limit in the samples No. 33 and 34 (Table 3) that are used for domestic purposes; Pb concentrations similar to those found in 2006 were already observed in previous surveys carried out in 2002 and 2004 (Cidu et al., 2005).

The mine waters had a wide range of metal concentrations (Table 3) depending on the dominant mineral assemblage at each mine; at some localities the amount of dissolved metals exceed the Italian limits for the discharge of industrial effluents into surface water. Concentrations of Zn, Cd, Fe, Mn, Ni and Co tend to increase as pH decreases. The highest concentrations of these metals were observed in mine drainages at Su Zurfuru (SZ3) and S. Lucia (SZ6) and were associated with high sulphate (Table 2). Oxidation of sphalerite is responsible for high concentrations of dissolved Zn, together with Cd that can substitute for Zn in sphalerite. High concentrations of dissolved Pb mostly derive from galena oxidation. The weathering of oxidized ore minerals might also contribute to the dissolved metals observed in the mine waters. High concentrations of dissolved Fe and Ni may derive either from pyrite or sphalerite oxidation. Any acidity produced by oxidation of pyrite, and other Fe-bearing sulphide minerals, was neutralized by the high acid-neutralizing capacity of the carbonate minerals. In fact, acid waters in the Metalliferous Ring comprising the Fluminese and Iglesiente areas were not found (Cidu et al., 2005). The highest concentrations of Fe in the Fluminese waters were observed under slight reducing conditions and near-neutral pH (samples SZ3 and SZ6, Table 2). In these samples dissolved Fe occurred in part as soluble Fe^{2+} species (<10%), but most of Fe might be associated to particles of size <0.4 μm. These fine particles may host other metals, such as Zn, Ni and Cd.

Table 3. Total dissolved solids (TDS) and selected metals dissolved in waters from the Fluminese area.

No.	TDS g/L	Zn μg/L	Cd μg/L	Pb μg/L	Fe μg/L	Mn μg/L	Ni μg/L	Co μg/L
Streams								
SZ4	0.31	140	1.5	1.7	41	5.4	1.9	0.1
SZ5	0.36	450	2.7	9.0	70	40	2.6	0.5
SZ7	0.36	300	3.0	6.7	48	24	1.9	0.3
SZ8	0.35	220	2.4	3.2	48	20	1.3	0.2
Springs and wells								
33	0.46	460	1.0	33	9	1.0	0.6	0.1
34	0.32	330	1.6	20	12	1.9	0.6	0.1
36	0.40	200	0.6	2	8	4.4	0.38	0.1
BG1	0.21	125	0.4	80	700	200	1.6	0.6
BG2	0.40	70	1.1	0.7	4.5	8.2	0.5	0.1
BG3	0.31	85	0.7	0.9	7	1.3	0.4	0.1
BG4	0.29	315	2.8	7.2	21	9.9	0.8	0.2
BG5	0.26	740	2.5	11	2900	180	14.0	4.2
BG6	0.36	170	0.3	1.4	350	1800	6.7	3.0
BG7	0.49	17	0.1	6.3	10	13	0.5	0.1
Mine waters								
35	0.41	880	1.0	14	7	5.3	0.55	0.1
SZ1	0.41	2100	15	26	5	165	7	1.4
SZ2	0.41	2700	16	53	120	240	8.8	2.0
SZ3	0.97	40000	97	32	12000	6500	130	72
SZ6	1.11	2000	2.1	1.1	2600	18000	260	120
BG8	0.58	1010	2.2	9.9	9	4.4	0.6	0.1
BG9	0.40	1600	1.1	7.1	48	1.4	0.7	0.1
Guidelines[a]		2000	20	200	2000	2000	2000	-

[a]= Italian limit for the discharge of industrial effluents into surface water.

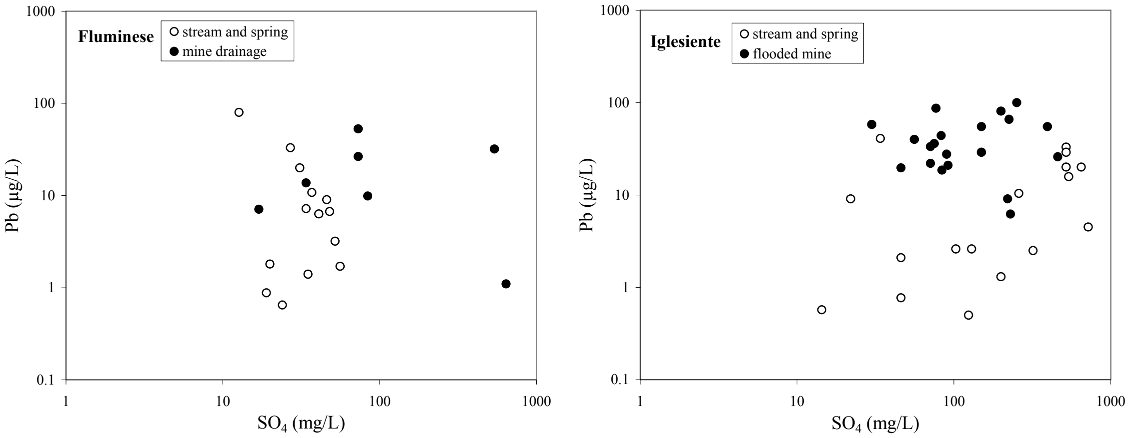

Figure 3. Concentrations of Pb versus SO_4 in waters from Fluminese and Iglesiente mining districts.

Figure 3 shows concentrations of dissolved Pb versus SO_4 in water samples from the Fluminese (this study) and from the Iglesiente (Cidu et al., 2005) mining district, located in the southern part of the Metalliferous Ring. Dissolved Pb is generally higher in groundwater in flooded mines of Iglesiente than in mine drainages of Fluminese, which is consistent with the occurrence of larger Pb deposits in the Iglesiente. Figure 3 shows that relatively high Pb may occur in water with relatively low SO_4 (e.g. sample BG1, Tables 2 and 3); this suggests that Pb might derive from cerussite dissolution. Notwithstanding that Pb is generally higher in mine waters, Pb > 10 µg/L can be also found in ground and surface waters from both districts. The most abundant Pb species in water samples circulating in the Metalliferous ring is $PbCO_{3(aq.)}$; this aqueous species is stable under the observed pH conditions (Stumm and Morgan, 1996) and persists at long distance from Pb sources.

Conclusions

This study shows that mine drainages transport high metals to the aquatic system. Estimates of the metal load transferred into the sea, mostly by the Rio Mannu stream and to a lesser extent by the Lucien drainage, are 2160 g Zn/day; 21 g Cd /day and 30 g Pb /day in 2006 under low-flow condition. Moreover, the detriment of water quality might be more severe during the rainy season, since runoff might transport large amounts of metals leached by the tailings and mine wastes spread in the area. Indeed, a survey carried out in March 2005 showed that the metal load transported by the Rio Mannu into the sea was at least one order of magnitude higher under high-flow (about 1000 L/s) condition than observed in 2006 under low-flow (100 L/s) condition. Although Italian regulations do not include specific standards for mining residues, remediation actions are necessary to reduce pollution in waters draining areas affected by past mining in the Fluminese.

Acknowledgements

This work was supported by the University of Cagliari (60% Cidu). Thanks to G. Contis for IC analyses.

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