Technical Article

Rebound at Pb-Zn Mines Hosted in Carbonate Aquifers: Influence on the Chemistry of Ground Water

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Abstract: Closure of Pb-Zn mines in the Iglesiente district (SW Sardinia, Italy) caused the cessation of pumping in 1997 at Monteponi, and in 1998 at San Giovanni. Consequent flooding of underground workings occurred in the district and also involved Campo Pisano. In June 1998, as the water table rose from 160 to 20 m below sea level, the deep saline water mixed with the shallow ground water at Monteponi and nearby mines. In the same period, an increase in dissolved metals (especially Zn, Cd, and Pb) was observed under near-neutral pH conditions. Following peak concentrations, a marked decrease of Zn, Cd, and Hg occurred. Dissolved Pb showed fluctuating concentrations over the monitoring period (1996-2005). In January 2000, when the water table rose to 20 m above sea level, the salinity of ground water decreased significantly at all of the mines. Stratification caused the more saline water at depth to settle three years after rebound started. Depth profiles carried out in 2005 at Monteponi, San Giovanni, and Campo Pisano showed an increase in conductivity and dissolved metals in ground water at deeper levels, especially at depths below sea level. After eight years of rebound, a marine component was still present at depth in ground water at San Giovanni (about 2%), and to a lesser extent at Monteponi (about 0.4%).

Key Words: Abandoned mines; heavy metals; monitoring; rebound; Sardinia; water chemistry

Introduction

Water quality degradation in areas affected by past mining is an environmental issue recognized worldwide. Water management at abandoned mine sites is especially problematic where no clear 'problem-owner' can be identified. With no responsible party to implement treatment measures, polluted water from abandoned mine workings can flow into the aquatic system causing its degradation (Younger et al. 2005). This situation occurred in Sardinia (Italy) where mining activity lasted for centuries and ended without any specific legal responsibility for post-abandonment pollution. Within this context, the hydrogeochemical investigations carried out in this study may give a significant contribution to the local authorities for taking decisions on restoration actions and on the management of mine waters.

In the Iglesiente district (SW Sardinia), Pb-Zn deposits are hosted in Lower Cambrian limestone and dolostone (Pillola et al. 1998, and references therein). The area, known as the Metalliferous Ring, covers about 150 km^2 (Figure 1). Stratiform and stratabound ore bodies deposits mainly consist of 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 et al. 1999, and references therein). The most abundant metallic minerals are sphalerite and galena, with variable pyrite content. Barite is the prominent ore mineral at some locations. Ore bodies near the surface are generally oxidized, and consist mostly of smithsonite, hydrozincite, and cerussite (Boni et al. 1999). Mined since pre-Roman times, the Pb-Zn deposits were intensively exploited from 1870 to 1995; oxidised deposits were exploited until the 1960's. Thereafter, sulphide deposits were mined, mostly underground. About 40 mines have operated in the area. The cessation of mining operations left large quantities of tailings and mine wastes; these materials release high amounts of sulphate and metals to the aquatic system (Cidu et al. 2005).

The study area has a semi-arid climate, rainfall ranging from 400 to 900 mm per year, with a mean of 50 rainy days; drought periods usually extending from May to September. The mean annual temperature is 17°C (E.A.F. 1998). Evapotranspiration averages about 57%, and runoff 24% (Civita et al. 1983). Surface drainage occurs after heavy rain events, mainly through the Rio San Giorgio, which is the only perennial stream in the Iglesias Valley. The Cambrian carbonate formations host the most important aquifers due to intense fracturing and karstification. Dominant winds in the area blow from the NW and carry sea spray inland.
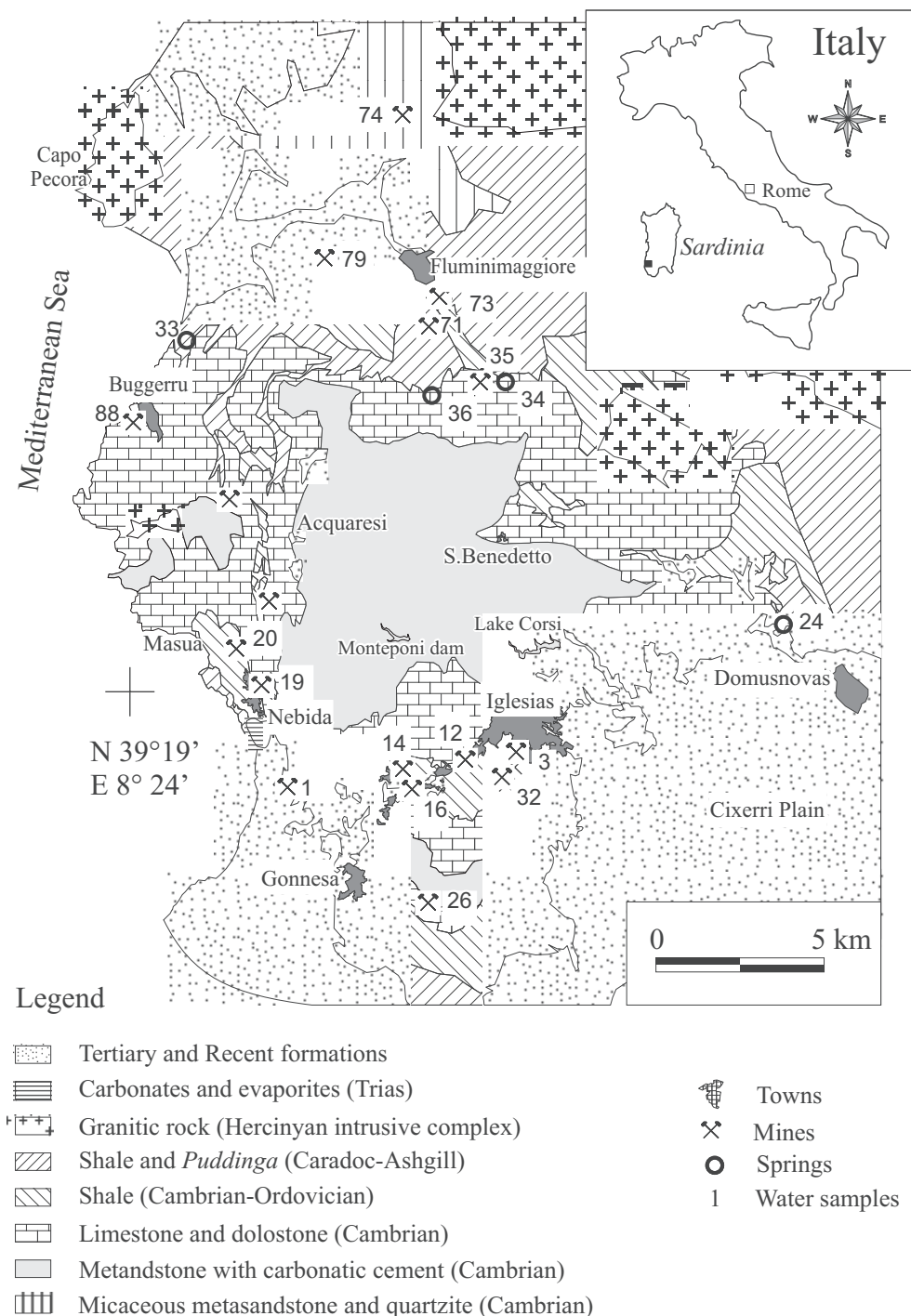
Figure 1. Schematic geology of the Iglesiente district (modified by Carmignani et al. 2001) showing location of the most important mines and the water sampling sites reported in Table 1.

Legend

▦	Tertiary and Recent formations
▤	Carbonates and evaporites (Trias)
✚	Granitic rock (Hercinyan intrusive complex)
▨	Shale and *Puddinga* (Caradoc-Ashgill)
◩	Shale (Cambrian-Ordovician)
▱	Limestone and dolostone (Cambrian)
▤	Metandstone with carbonatic cement (Cambrian)
▥	Micaceous metasandstone and quartzite (Cambrian)

♆	Towns
✕	Mines
◯	Springs
1	Water samples

After closure of mines, most pumping systems ceased operation; thereafter, the underground workings underwent flooding. Drainage out of adits was observed at S'Acquabona, Su Zurfuru, Santa Lucia, Gutturu Pala and Buggerru mines, located in the northern part of the area, near Fluminimaggiore (Figure 1).

Since 1910, the most important drainage system in the Metalliferous Ring was located at the Monteponi mine (Figure 1, # 12); the water was discharged into the sea through the Umberto I drain (Figure 1, # 1). Pumping stations were successively installed at increasing depths to lower the water table to 160 m below sea level (B.S.L.) (Bellè and Cherchi 1996; Bonato et al. 1992). The ground water pumped out of Monteponi was highly saline, dissolved chloride reached 12 g/L in 1996; this has been attributed to contamination by seawater (Civita et al. 1983; Cidu et al. 2001). Concentrations of metals, particularly Pb, Cd, and Hg, were also relatively high. Rebound at the Monteponi mine started in 1997. As flooding progressed at Monteponi, the water table level rose at nearby mines too; this effect extended eastwards to Campo Pisano (#

3) and westwards to San Giovanni (# 16), Nebida, and Masua (see Figure 1).

It is important to point out that the local authorities consider ground water as an important water resource, since there is little water available from reservoirs in the area. Therefore, the research on rebound was aimed at investigating its influence on the quality of ground water in the Metalliferous Ring. The chemical composition of ground water in the most important mines has been monitored since 1996, prior to and during rebound. Previous studies were carried out taking water samples from the water surface in flooded mines. These samples do not represent the water quality existing throughout the entire water column because flooded underground mines are usually hydrochemically stratified (Nuttall and Younger 2004). In order to assess the quality of ground water at increasing depth, a hydrogeochemical survey at the most relevant mines was carried out in 2005. This paper reports the data of the 2005 survey and compares them with those observed during the entire rebound time.

Sampling and Methods

Water sampling started in July 1996 under dewatering conditions, when the water table at Monteponi was 160 m B.S.L. and the pumping rate was 1800 L/s. At Monteponi, the pumping rate was gradually reduced from 1500 L/s in January 1997 to 100 L/s in June 1997; finally, the pumping system was shut down in August, 1997. At San Giovanni, the pumping system was shut down later, in October, 1998.

Water sampling was carried out intensively from January, 1997 to October, 1998 when the water table at Monteponi rose to 7 m B.S.L. (Cidu et al. 2001). As flooding progressed, several mines became inaccessible; sampling at the most representative and accessible sites continued over 1999-2004 (Cidu 2004; Cidu and Fanfani 2002). To acquire hydrogeochemical information on the whole Metalliferous Ring and the nearby area of Fluminimaggiore (Figure 1), additional samples were collected in the period 2002-2004 (Cidu et al. 2005). In 2004, ground water was sampled at different depths in the Monteponi and Campo Pisano mines (Cidu 2005; Nieddu 2004).

In March-April 2005, water samples were collected at the flooded mines still accessible by shafts (samples # 3, 12, 14, 16, 19, 20, 26 and 32) and at the outflow of galleries (samples # 1, 35, 71,73, 79 and 88). The high-flow (i.e. > 10 L/s) springs in the Metalliferous Ring were also sampled; these waters do not apparently circulate in mined zones and supply drinking water in the area. Water samples were then collected at Monteponi # 12, San Giovanni # 16, and Campo Pisano # 3 at depth intervals of 10 m, starting from the water table level (about 43 m above sea level, A.S.L.) down to 56, 66, and 36 m B.S.L., respectively; the pumping systems were not operating during sampling. The location of the sampling sites is shown in Figure 1.

The sampling procedures and analytical protocols reported in Cidu et al. (2001) were used for the entire monitoring period. At each sampling site, temperature, pH, redox potential (Eh), conductivity, and alkalinity were measured; water was filtered (0.4 μm, Nuclepore

Table 1. Flow, temperature, redox potential (Eh), pH, conductivity (Cond) and dissolved chemical components in waters sampled in 2005.

| No.	Name	Flow L/s	T °C	Eh mV	pH	Cond mS/cm	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Cl mg/L	HCO_3 mg/L	SO_4 mg/L	Fe μg/L	Mn μg/L	Ni μg/L	Zn μg/L	Cd μg/L	Pb μg/L	Hg μg/L	As μg/L	Sb μg/L
Springs																						
24	Grotte Domusnovas	>50	14	460	7.6	0.56	76	13	34	1.9	56	260	22	8	4	0.5	200	2.7	9	0.3	0.5	0.10
33	San Salvatore	>20	19	490	7.3	0.90	98	27	70	2.7	116	330	42	13	3	0.6	300	1.4	23	0.6	0.5	0.35
34	Pubusinu	500	15	473	7.5	0.55	79	14	34	2.0	49	230	36	14	3	0.6	290	1.5	18	<0.3	0.2	0.10
36	Su Mannau	100	14	460	7.9	0.64	70	28	46	2.3	73	280	22	8	2	0.3	130	0.4	4	0.4	0.1	0.13
Mine drainages																						
1	Umberto I	0.2	17	480	7.5	1.51	85	56	158	7.9	230	230	230	50	170	0.9	300	6.3	6	0.5	1.0	0.97
35	Gutturu Pala	10	16	475	8.2	0.81	90	33	50	2.2	82	350	47	3	3	0.6	900	1.0	17	<0.3	0.5	0.1
71	Su Zurfuru Pietro	1	18	460	8.0	0.67	70	21	39	3.0	68	214	65	99	260	7.0	2250	12	23	<0.3	1.0	0.54
73	Su Zurfuru	1	17	280	6.9	1.45	140	99	44	5.2	54	104	770	15000	12000	210	100000	270	70	<0.3	2.3	0.26
74	S'Acquabona	2	17	526	6.6	1.18	97	50	66	5.6	103	146	390	300	6000	290	55000	330	5	<0.3	3.4	1.2
79	Santa Lucia	0.3	16	380	6.3	1.43	130	92	50	7.4	60	172	640	2600	18000	260	2000	2.1	1	0.4	1.2	0.06
88	Lucien Buggerru	3	17	500	7.9	0.99	91	18	89	4.0	160	240	84	9	4	0.6	1010	2.2	10	<0.3	<0.3	0.15
Groundwater in flooded mines		Depth m a.s.l.																				
3	Campo Pisano	44	19	470	7.2	1.40	137	73	91	7.7	166	400	220	50	27	1.7	850	1.3	9	0.4	0.6	0.12
12	Monteponi	44	16	470	7.3	1.28	100	57	106	6.4	180	400	71	250	7	1.4	700	1.2	33	0.3	<1	0.24
14	Monte Agruxiau	42	18	477	7.1	1.70	110	64	160	4.0	310	390	75	80	16	1.8	1300	1.7	36	2.3	1.2	0.1
16	San Giovanni	43	16	505	7.3	1.85	130	78	210	8.7	387	400	225	44	13	9.0	3000	8.6	66	0.6	1.5	1.2
19	Nebida	52	18	465	7.4	1.91	116	65	217	7.6	400	280	150	70	10	0.7	1560	3.5	55	<0.3	1.5	0.4
20	Masua	50	15	480	7.5	1.35	115	44	110	8.8	185	270	200	80	11	0.4	1870	8.5	81	<0.3	0.8	0.2
26	Monte Onixeddu	53	17	168	7.5	2.50	70	74	360	6.5	580	410	84	11300	1000	6.5	73	0.2	19	0.8	2.2	0.88
32	Hubert Cabitza	45	18	478	7.3	1.94	160	110	160	7.9	252	390	460	70	10	1.5	800	0.9	26	1.9	0.9	0.1
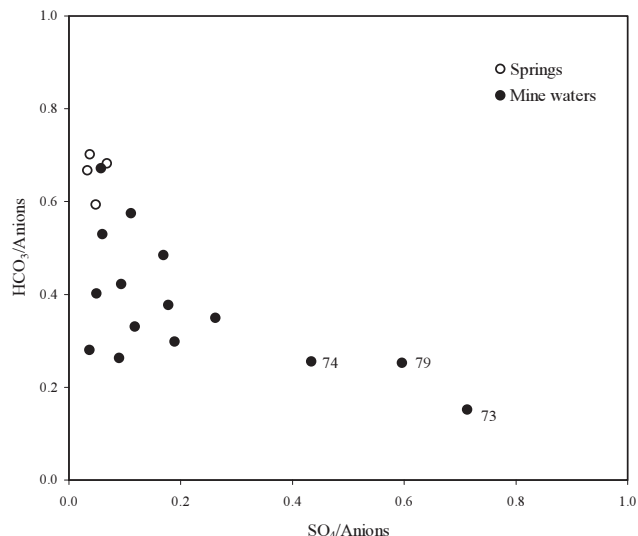
Figure 2. Dissolved HCO₃ versus dissolved SO₄, both normalized to the sum of major anions (i.e. HCO_3, Cl and SO_4).
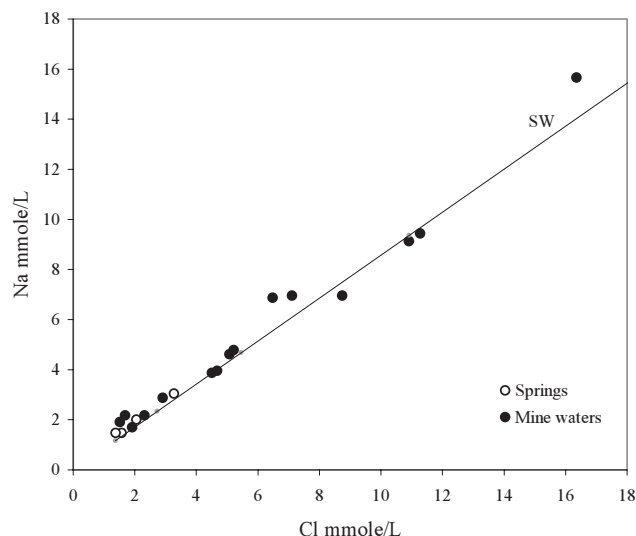

Figure 3. Dissolved Na versus Cl. The dilution line of seawater (SW) is shown.
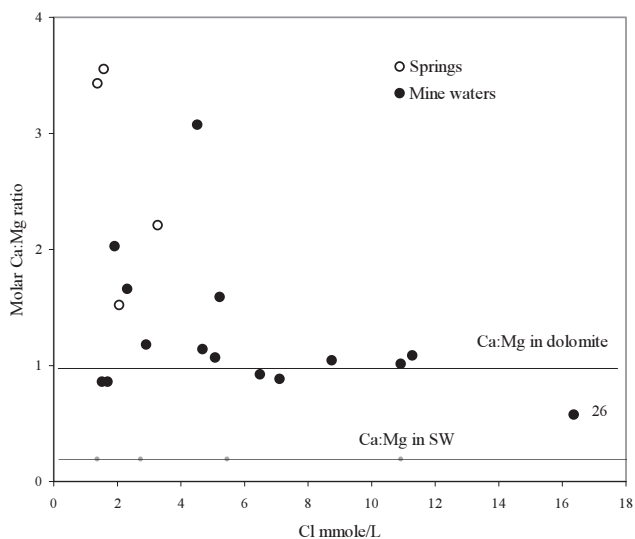

Figure 4. Molar Ca:Mg ratio versus Cl in springs and mine waters. The lines of Ca:Mg ratio in seawater (SW) and dolomite are shown.
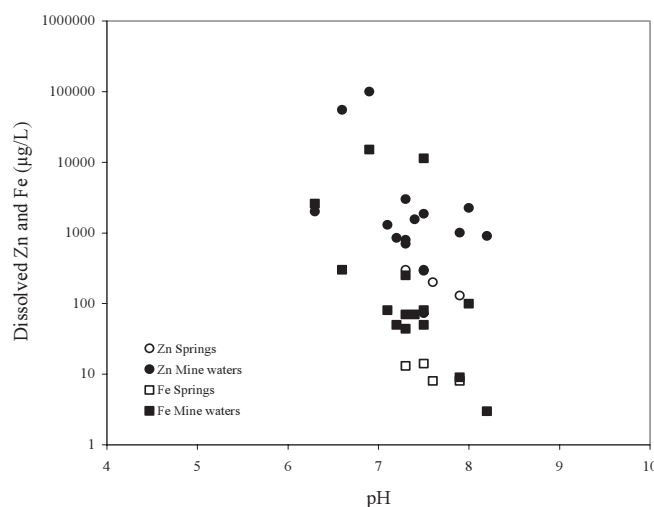

Figure 5. Dissolved Zn and Fe versus pH.

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%, indicating that the analyses were of good quality. Both precision and accuracy were estimated at ≤ 10% by analysing randomly duplicate samples and standard reference solutions (NIST1643c, d, e). The computer program PHREEQC (Version 2) was used for speciation and equilibrium calculations (Parkhurst and Appelo 1999).

Results and Discussion

Hydrogeochemical Features in the Metalliferous Ring

Physical-chemical parameters and the chemical composition of ground water samples collected in 2005 are reported in Table 1. The water samples were near neutral to slightly alkaline in pH (6.3-8.2), reflecting their dominant circulation in carbonate rocks. Most had Eh values > 0.45 V, indicating oxidising conditions, due to the relatively fast ground water circulation through karst features and fractures. Water samples # 26 and 73 had Eh values < 0.30 V, indicating slightly reducing conditions; this might

Table 2. Dissolved Y and REE (La-Lu) in waters sampled in 2005.

| No.	Name	Y ng/L	La ng/L	Ce ng/L	Pr ng/L	Nd ng/L	Sm ng/L	Eu ng/L	Gd ng/L	Tb ng/L	Dy ng/L	Ho ng/L	Er ng/L	Tm ng/L	Yb ng/L	Lu ng/L
Springs																
24	Grotte Domusnovas	46	14	7.2	3.8	16	4.2	10	3.2	0.8	3.8	0.8	2.2	0.3	1.8	0.36
33	San Salvatore	45	22	15	4.5	19	6.2	17	4.4	0.8	3.7	0.9	2.4	0.2	2.2	0.31
34	Pubusinu	79	28	20	6.5	24	6.9	15	5	0.9	5.6	1.5	3	0.6	3	0.47
36	Su Mannau	23	5.1	4.7	1.4	9.1	2.5	7.8	2.2	0.5	1.8	0.4	0.9	0.2	1	0.23
Mine drainages																
1	Umberto I	21	55	99	10	23	3	4.9	4.3	0.6	1.5	0.6	1.5	0.23	1	0.26
35	Gutturu Pala	11	1.1	0.7	0.7	2.3	2	12	1	0.15	0.4	0.15	0.2	<0.1	0.4	<0.1
71	Su Zurfuru Pietro	410	430	360	68	250	46	20	56	7.8	37	6.9	16	1.6	6.8	0.9
73	Su Zurfuru	38400	26000	49000	6200	24000	5200	1150	6600	1030	5200	1040	2400	250	1080	148
74	S'Acquabona	1010	610	480	61	204	51	16	69	10	55	14	37	3	22	2
79	Santa Lucia	840	750	590	67	219	49	12	70	10	56	12	35	3.5	17	2
88	Lucien Buggerru	24	13	17	2.2	6.3	1.8	8.9	1.6	0.5	1.3	0.4	0.8	0.15	0.3	0.18
Groundwater in flooded mines																
3	Campo Pisano	15	5.6	10	2	5.5	1.1	8.1	2	0.3	1.2	0.2	<0.5	0.15	0.4	0.1
12	Monteponi	18	13	19	3	9.5	1.2	10	3.1	0.6	2.6	0.5	0.7	0.4	0.9	0.18
14	Monte Agruxiau	20	10	18	2.7	10	4.2	14	2.9	0.4	2.2	0.6	0.7	0.1	0.3	0.15
16	San Giovanni	31	8	11	1.8	9.5	2.8	5.8	1.5	0.4	2.5	0.5	1.3	0.2	1.1	0.2
19	Nebida	71	62	140	18	71	16	5.5	16	2.3	11	2.5	5	0.7	4	0.8
20	Masua	17	5.7	11	1.8	6	3	4.8	1.2	0.4	1.3	0.37	0.4	0.05	0.4	0.2
26	Monte Onixeddu	32	30	64	8.6	29	6.9	9.8	6.6	1.1	5.2	0.9	2	0.3	1.2	0.31
32	Hubert Cabitza	19	8.2	14	2.2	8.6	3	4.1	2	0.5	1.2	0.42	0.5	0.07	0.5	0.2

reflect a slower underground circulation since these samples were located close to the contact between the meta-sandstones and shales, respectively, and carbonate rocks. Conductivity was < 1 mS/cm in the springs and usually >1 mS/cm in the mine waters.

Figure 2 shows the dissolved HCO_3 versus SO_4; both HCO_3 and SO_4 molar concentrations were normalized to the sum of the major anions (i.e. HCO_3, SO_4, Cl). The spring waters and some mine waters had a dominant bicarbonate composition due to their circulation in carbonate rocks. Three mine drainages had a dominant sulphate composition, associated with the oxidation of sulphide minerals.

As conductivity values increase, the contribution of Cl to salinity increases (Table 1). Figure 3 shows dissolved Na versus Cl. A good correlation between Na and Cl was observed. The waters were close to the line with the Na: Cl ratio observed in seawater, indicating a prevalent marine source of Na and Cl. In the less saline waters, Na and Cl may derive from the infiltrating rain water and the dissolution of sea spray.

Figure 4 shows molar Ca: Mg versus Cl concentrations in the studied waters. The springs had higher levels of dissolved Ca than Mg due to their dominant circulation in limestone formations. Sample # 26 had the highest concentration of Cl. Enrichment in Mg occurred in the mine water; the mine waters that aligned at a molar Ca: Mg ratio = 1 were those with a prevalent circulation in dolomite formations.

With reference to the guidelines established by the World Health Organization (WHO 2006) for drinking water, data reported in Table 1 show that dissolved As and Sb were relatively low in all samples, which is consistent with the dominant mineral ores in this mining district. Concentrations were always below the limits of 10 and 20 µg/L for As and Sb, respectively. 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 samples # 33 and 34 (Table 1).
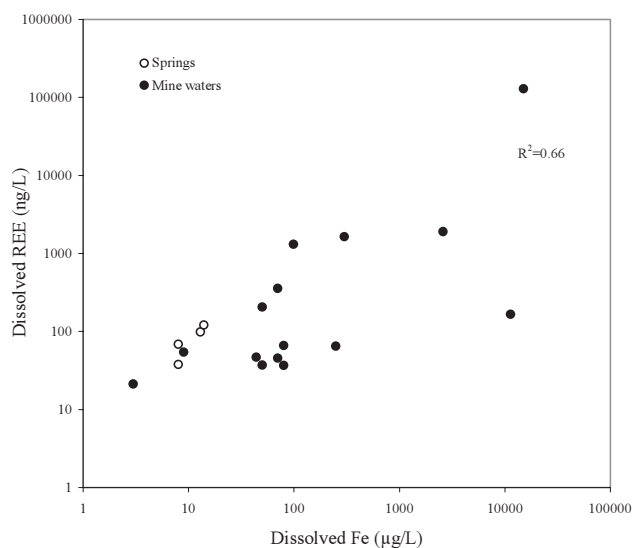
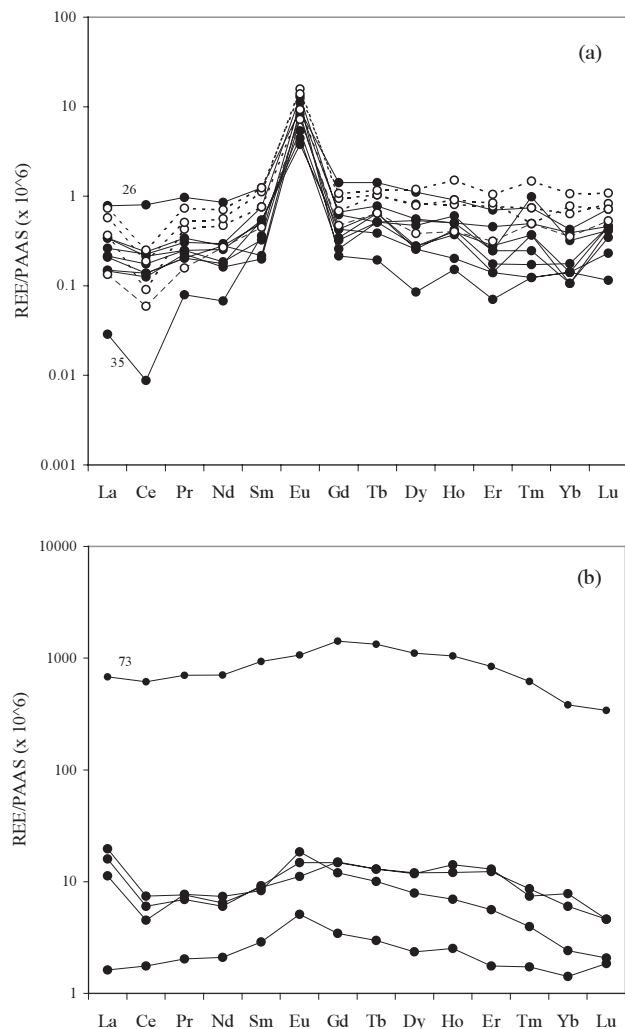**Figure 6.** Dissolved rare earth elements (REE: ∑La-Lu) versus Fe.

Figure 7. Patterns of dissolved REE normalized to Post Archaean average Australian Shale (PAAS) in springs (open circles) and mine waters (black circles).

The mine waters had a wide range of metal concentrations depending on the dominant mineral assemblage at each mine. Concentrations of metals were most extreme in mine drainages and were generally associated with high sulphate (Table 1). The highest concentrations of dissolved metals were observed for Zn (100 mg/L), Mn (18 mg/L), Fe (15 mg/L), Cd (330 µg/L) and Ni (290 µg/L). Figure 5 shows that dissolved Zn and Fe tend to decrease at increasing pH; other metals (e.g. Mn, Ni, Cd) also showed a similar trend. The conditions observed in this study are within the range reported for non-acidic mine drainage in other locations in Sardinia (e.g. Cidu and Fanfani 2002) and elsewhere (e.g. Plumlee 1999).

In waters circulating in the Metalliferous Ring, oxidation of sphalerite is presumably responsible for the relatively high concentrations of dissolved Zn, together with Cd and Tl, which can substitute for Zn in sphalerite. The 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 were not found in the Metalliferous Ring. The highest concentrations of Fe were observed at slightly reducing conditions and near-neutral pH, i.e. samples # 73, 79, and 26 (see Table 1). In these samples, dissolved Fe occurred in part as soluble Fe^{2+} species (< 10%), but most of the Fe was probably present as colloidal particles, < 0.4 µm. These fine particles can host other metals, such as Zn, Ni, and Cd. Galena oxidation is presumably responsible for the high concentrations of dissolved Pb, together with the Ag, which occurs in Ag-rich galena. The weathering of oxidized ore minerals, such as smithsonite, hydrozincite, and cerussite, might also have contributed to the dissolved metals observed in the mine waters.

Table 2 reports the concentrations of dissolved Y and the rare earth elements (REE, i.e. elements from La to Lu) in the studied waters. Dissolved Th was < 2 ng/L in many samples; detectable Th was always < 12 ng/L; considering its low occurrence, Th was not reported in Table 2. Dissolved Y and REE showed low concentrations in the springs and in ground water sampled at flooded mines, while they were found at high concentrations in some waters flowing out of mine adits. Figure 6 shows that concentrations of dissolved REE ($\sum$La-Lu) generally increase as dissolved Fe increases.

Figure 7 shows the patterns of REE dissolved in the water, each REE being normalized to the corresponding concentration in the Post-Achaean average Australian Shale (indicated as PAAS, McLennan 1989). Many waters, comprising all springs and most of the ground water in flooded mines, showed REE patterns characterized by a strong positive Eu anomaly (Figure 7a). The Eu anomaly might be due to dissolution of Eu-enriched minerals, such as calcite (Lee et al. 2003) and sulphide minerals (Leybourne et al. 2000), which is consistent with the dominant carbonate rocks and mineral ores. The springs and mine drainage # 35 had a pronounced negative Ce anomaly (Figure 7a). Taking into account that these waters are in contact with the atmosphere (i.e. under oxidizing conditions), the Ce anomaly was likely due to oxidation of Ce^{+3} to Ce^{+4}, and its subsequent precipitation as CeO. The Ce anomaly was less pronounced in ground water from flooded mines, and it was absent in water sample # 26, which had a low Eh value (see Table 1). Mine drainage water samples showed REE patterns with less marked anomalies (Figure 7b). Water sample # 73 (drainage from the Su Zurfuru mine) had the highest REE concentrations, which were associated with high concentrations of Fe and other metals (see Tables 1 and 2); this water
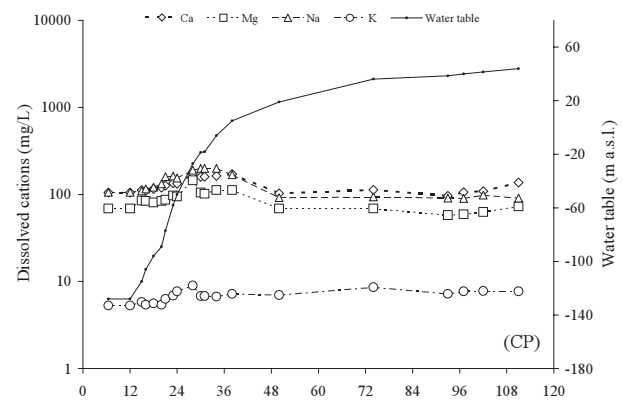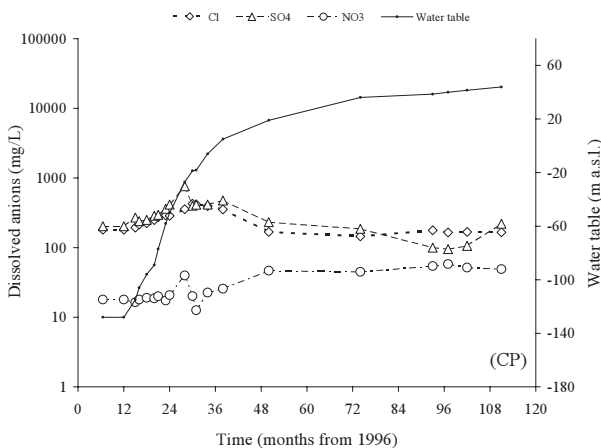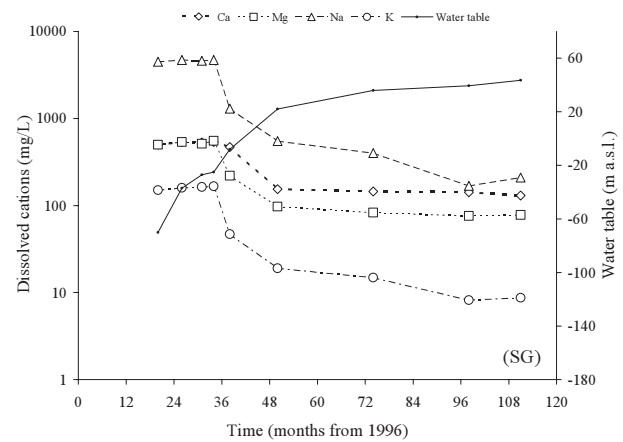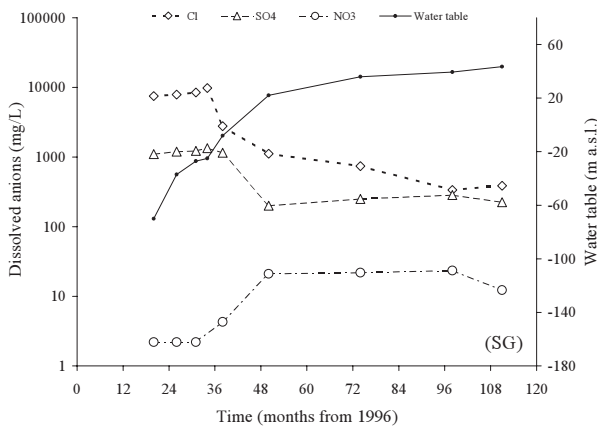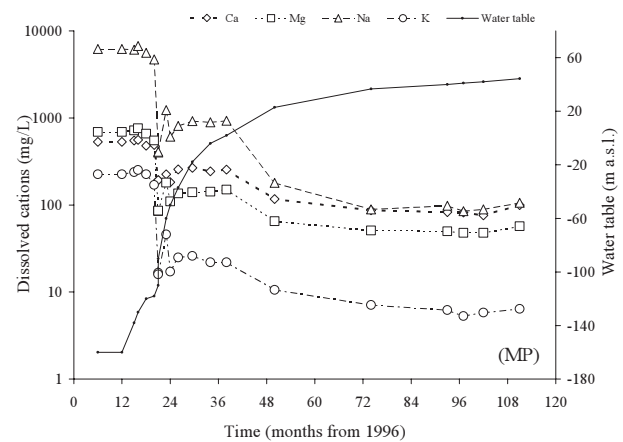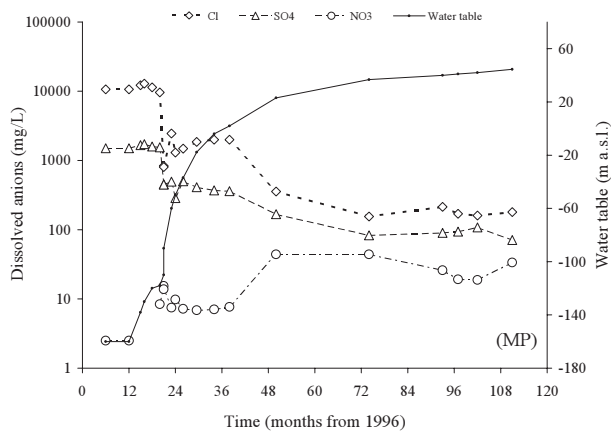
Figure 8. Temporal variations of dissolved anions in groundwater at Monteponi (MP), San Giovanni (SG) and Campo Pisano (CP) (rebound starting at month 12; last sampling was carried out in March 2005).

showed a REE pattern with a weak convexity centred on the intermediate REE (Figure 7b). This pattern has been explained by adsorption onto very fine particles (e.g. Elderfield et al. 1990); since this process involves all the REE, a nearly flat pattern was observed.

Temporal Variations in Dissolved Chemical Components

In this study, three sites were selected to show the chemical variations occurred in ground water during

Figure 9. Temporal variations of dissolved cations in groundwater at Monteponi (MP), San Giovanni (SG) and Campo Pisano (CP) (rebound starting at month 12; last sampling was carried out in March 2005).

rebound: Monteponi and San Giovanni represent the central part of the aquifer, while Campo Pisano represents the peripheral part of the aquifer. It is useful to remember that the deeper pumping system in the Monteponi mine was located at 200 m B.S.L.; it collapsed during the first stages of rebound. A new pumping system was installed in 2003, when it was used for a few months to extract small quantities of water (< 100 L/s). This pumping system did not operate in 2004 and 2005. The pumping system in the
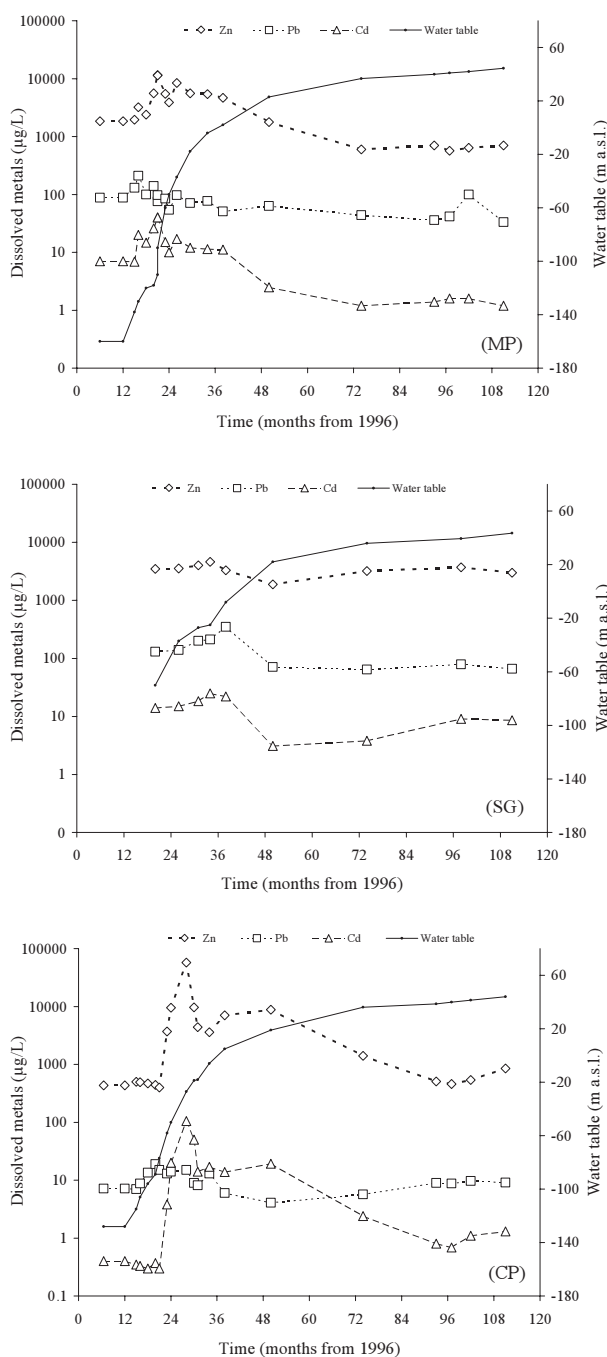
Figure 10. Temporal variations of dissolved metals in groundwater at Monteponi (MP), San Giovanni (SG) and Campo Pisano (CP) (rebound starting at month 12; last sampling was carried out in March 2005).

San Giovanni mine was permanently shut down in October, 1998. The pumping system in the Campo Pisano mine was active from 1996 to 2005; 50 to 100 L/s were extracted daily for several hours, depending on demand. This water has been used mostly by industry, and occasionally for domestic purposes.

The temporal variations reported below refer to the ground water sampled at the water table level. Variations relative to the major anions and cations in

ground water at the Monteponi, San Giovanni, and Campo Pisano mines are shown in Figures 8 and 9; the level of the water table at each mine is also shown in these plots. Data from prior to 2005 were taken from Cidu et al. (2001, 2005). Since alkalinity showed small variations at all sites, it was not included in these plots. Before the beginning of rebound in December, 1996, the highest seawater contribution occurred at the Monteponi (12 g/L Cl, Figure 8a) and San Giovanni (8 g/L Cl, Figure 8b) mines. Ground water at the Campo Pisano mine showed a negligible seawater contribution (0.2 g/L Cl, Figure 8c). During the first year of rebound (January to December, 1997) the water table rose to 50 m B.S.L. in the Monteponi and Campo Pisano mines. Small variations in the chemical composition were observed in ground water at Monteponi. In contrast, Cl, SO_4, Na, Mg, and K in the Campo Pisano water increased significantly in June, 1997 (Figures 8c and 9c), due to mixing of the shallow ground water with saline water from below. Following the progress of flooding, in December, 1999, an increase in NO_3 concentrations was observed at all sites (Figure 8); the highest concentrations of dissolved NO_3 (up to 58 mg/L) occurred at Campo Pisano (Figure 8c). Dissolved NO_3 in mine waters might be related to past exploitation processes, such as the use of wood and explosives in mining workings (Cidu et al. 2005). As the water table level continued to rise up to 20 m A.S.L. in 2000, the concentrations of Cl, SO_4, Na, Mg, and K decreased significantly in ground water at all sites, while NO_3 remained relatively high (Figure 8).

Figure 10 shows the behaviour of Zn, Pb, and Cd in the mine waters over the monitoring period. In 1997, during the first year of flooding, dissolved concentrations of Zn and Cd increased at Monteponi, while they did not show marked variations at Campo Pisano; dissolved Pb increased significantly both at Monteponi and Campo Pisano.

In 1998, a dramatic increase in dissolved Zn and Cd was observed at Campo Pisano (Figure 10, CP); as reported in Cidu et al. (2001), high concentrations of Fe and a marked increase in suspended matter were also observed in 1998. Peak concentrations of Zn and Cd occurred in April, 1998, when the water table rose to 27 m B.S.L. This corresponded with the Campo Pisano well being flooded, and consequent sampling from the flooded underground galleries. The observed increase in Zn, Cd, and Fe was consistent with records of the underground workings at 25 m B.S.L. in the Campo Pisano mine; exploitation of sphalerite and pyrite at the -25 level extended over a large area, about 10,000 m^2 (Società di Monteponi 1951).

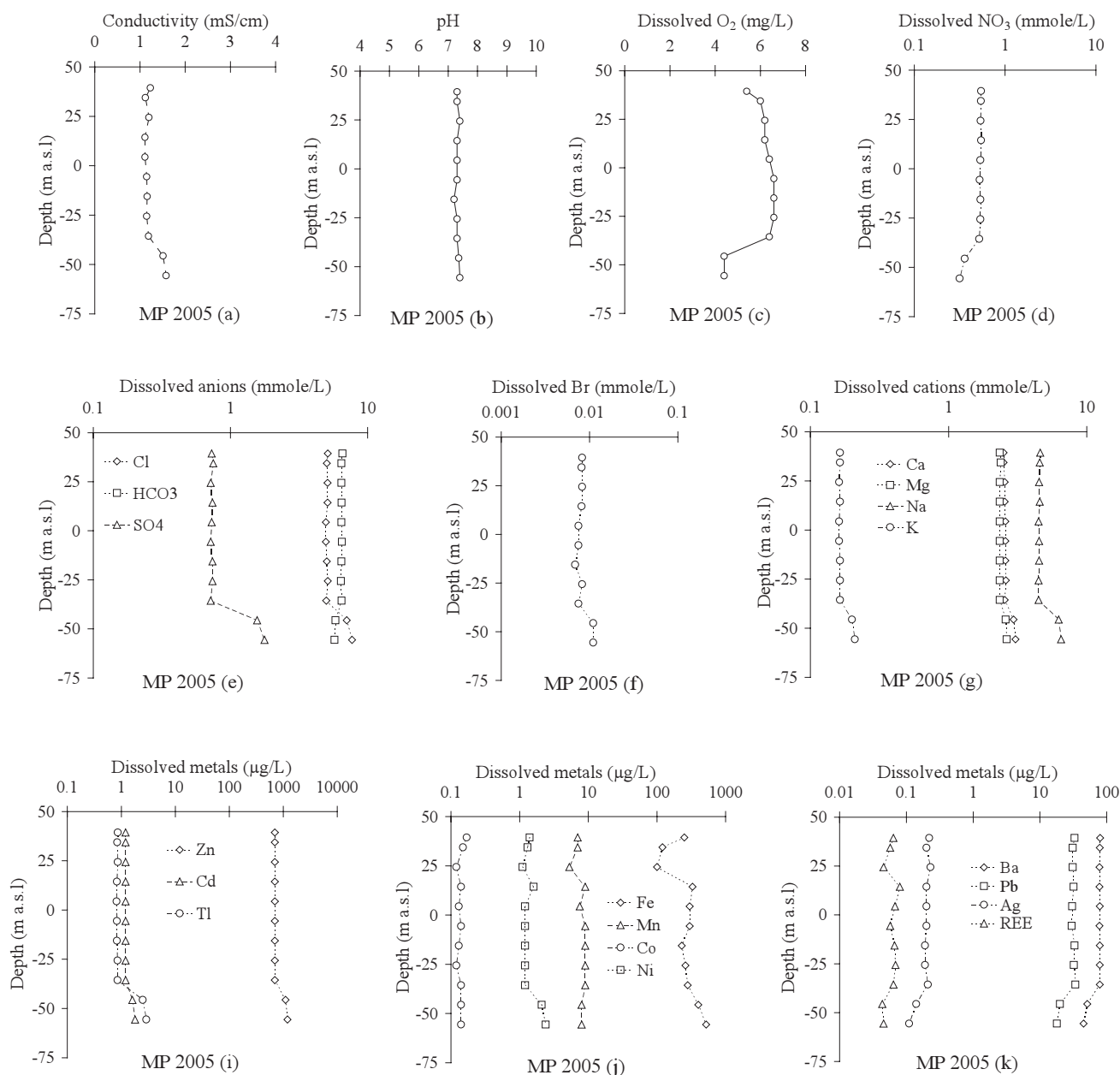Dissolved Pb in ground water at Monteponi and San Giovanni was higher than in ground water at Campo

Figure 11. Variations observed in groundwater at the Monteponi mine from the water table level downwards.

Pisano, which is consistent with the low occurrence of galena in the Campo Pisano mine. In all waters, the most abundant species of dissolved Pb was $PbCO_3^0$ (80-95%); this ion pair is stable in solution and might explain the relatively high Pb observed in the studied waters at non-acidic conditions. Lead speciation in the studied waters did not change significantly due to flooded or dewatered conditions, or at low or high salinity. Dissolved Zn, like Pb, was present mainly as the $ZnCO_3^0$ aqueous species under dewatered conditions and during the first year of flooding, but free ions became increasingly important (Zn^{+2} up to 55%) as the flooding progressed. In the chloride-rich waters ($Cl > 0.1$ M), under dewatered conditions and at the first stage of flooding, the $CdCl^+$ and $CdCl_2^0$ species represented about 80% of the total cadmium, while at

Cl concentrations < 0.01 M and low salinity, cadmium was mostly present as Cd^{2+}, since the $CdCO_3^0$ species is only prevalent at pH > 8.

Concentrations of Hg before rebound were 50 µg/L, 42 µg/L, and 2 µg/L, respectively at Monteponi, San Giovanni, and Campo Pisano. The $HgCl_n^{2-n}$ complexes dominated the speciation of mercury; the $Hg(OH)_2^0$ species was only important at Cl concentration < 0.005 M and pH > 8. Indeed, the increase in mercury concentrations at Campo Pisano (up to 10 µg/L Hg) was closely associated with an increase in chloride, while a decrease in mercury concentrations at Monteponi, San Giovanni, and also at other mines, was closely associated with a decrease in chloride (Cidu et al. 2005).

	MP12	MP12 Water at 56 m below sea level			
	44 m A.S.L.	Observed	Calculated (0.44% SW)	Difference	
	mmole/L	mmole/L	mmole/L	mmole/L	%
Ca	2.50	3.05	2.55	0.50	20
Mg	2.35	2.61	2.58	0.03	1
Na	4.50	6.52	6.56	-0.04	-0.6
K	0.16	0.21	0.205	0.005	2
Cl	5.00	7.39	7.39	-	-
Br	0.008	0.011	0.0117	-0.0007	-5
SO$_4$	0.73	1.67	0.85	0.82	96
	SG16	SG16 Water at 66.5 m below sea level			
	39 m A.S.L.	Observed	Calculated (2.18% SW)	Difference	
	mmole/L	mmole/L	mmole/L	mmole/L	%
Ca	3.20	6.00	2.73	3.28	120
Mg	3.21	4.32	3.51	0.81	23
Na	9.13	14.35	14.73	-0.38	-2.6
K	0.22	0.36	0.38	-0.02	-6.0
Cl	10.91	16.81	16.90	-	-
Br	0.017	0.026	0.0263	-0.0003	-1.1
SO$_4$	2.34	6.15	1.35	4.80	357

Table 3. Composition of groundwater at the water table level and comparison between observed and calculated dissolved components in the deep groundwater at Monteponi (MP12) and San Giovanni (SG16).

Summarizing, compared to the first stages of flooding when peak concentrations of metals were observed, and with reference to ground water at the water table level, a significant decrease in Zn, Cd, Pb, and Hg was observed in all mine waters in April, 2005, i.e. after eight years of rebound. Relatively high levels of Pb (10-81 µg/L) were still present in ground water at most mines; also, in water samples # 32 and 14, Hg was 1.9 and 2.3 µg/L, respectively, in April, 2005 (see Table 1).

Stratification Processes

In addition to temporal variations, the chemical composition of ground water at each mine showed variations from the water table level downwards. Results from 2004 at Monteponi and Campo Pisano showed an increase in conductivity and metals in ground water at increasing depth (Cidu 2005; Nieddu 2004). Results from 2005 are reported here.

Figure 11 shows the variations observed in ground water at the Monteponi mine at increasing depth from the water table level (44.4 m A.S.L) to 100 m below. At 46 m B.S.L., conductivity was higher (Figure 11a), pH was nearly constant (Figure 11b), and dissolved O$_2$ (Figure 11c) and NO$_3$ (Figure 11d) decreased. The decrease in dissolved NO$_3$ is consistent with the decrease in dissolved O$_2$, and with the temporal variations observed in ground water at Monteponi, showing lower concentrations of NO$_3$ at deeper levels (see Figure 8). Alkalinity, reported as the dominant

HCO$_3$ species, showed small variations (Figure 11e), which is consistent with calculations showing the ground water always at equilibrium or supersaturated with respect to calcite and dolomite.

As conductivity increased, an increase in dissolved SO$_4$ and Cl (Figure 11e), Br (Figure 11f), Na, K, Mg, and Ca (Figure 11g) was observed. Such an increase might indicate that a marine-derived component was still present in the deep ground water at Monteponi. The amount of the marine component was estimated using the mass balance equation, assuming that the seawater contribution was negligible in ground water at the water table level, that the increase in Cl observed at depth was totally derived from seawater (SW), and that dissolved Cl should behave as a conservative ion in mixing processes:

$$x\text{Cl}_{SW} + (1-x)\text{Cl}_{nMIX} = \text{Cl}_{MIX}$$

where subscripts nMIX and MIX refer to dissolved Cl in the initial non-mixed solution and in the mixed solution, respectively. An estimate of 0.44% seawater was obtained. This value was used to calculate the composition of ground water mixed with seawater. Results are shown in Table 3. Very small differences between calculated and observed concentrations occurred for Mg, Na, K, and Br, indicating that their increase was consistent with a marine-derived component. In contrast, a marked excess of SO$_4$ was observed, indicating additional sources for this
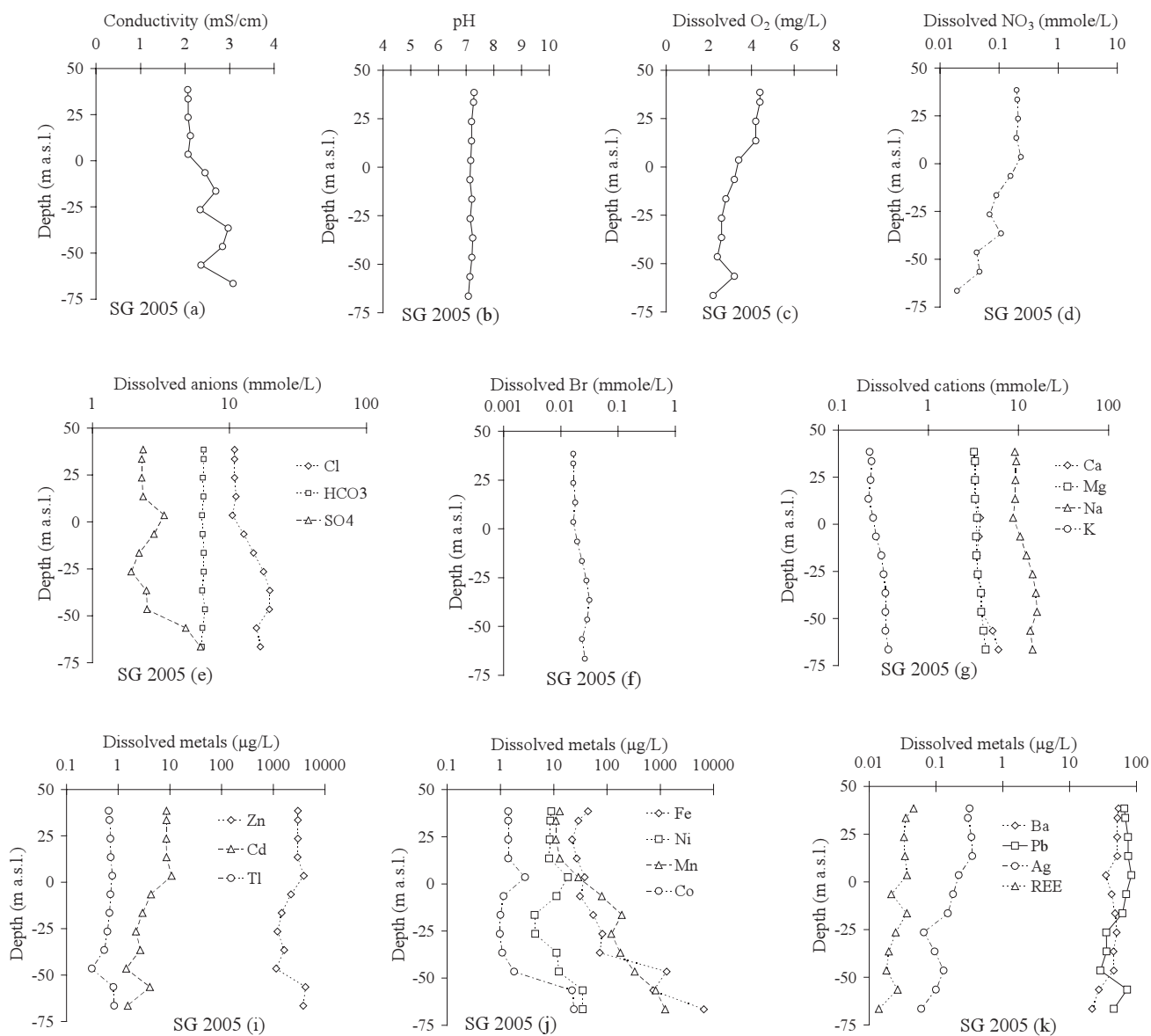
Figure 12. Variations observed in groundwater at the San Giovanni mine from the water table level downwards.

component. Part of the SO_4 may derive from the oxidation of sulphide minerals, such as sphalerite and pyrite, which would be consistent with the observed increase in dissolved Zn, Cd, Tl, Fe, and Ni (Figure 11i and j).

The excess of Ca (20%, Table 3) indicated that mixing was unable to explain the increase in Ca observed in Figure 11g, but this might be explained by its speciation. Calcium was mostly present as Ca^{2+} species (> 93%) at low SO_4 concentrations; Ca^{2+} was less abundant when SO_4 increased, while the aqueous ion pair $CaSO_4^0$ increased significantly.

The marked increase in SO_4 was coupled with a significant decrease in dissolved Ba, Pb, and Ag (Figure 11k). Ground water all along the profile was supersaturated with respect to barite; this implies that

at increasing SO_4, dissolved Ba should decrease to maintain equilibrium. In contrast, ground water was strongly undersaturated with respect to anglesite (saturation index -3.7), so that the decrease in Pb was unlikely related to chemical equilibrium, while sorption processes could explain the decrease in Pb. Among other metals, the concentrations of dissolved Mn, Co, and REE were always low.

Figure 12 shows the behaviour of dissolved components in ground water at the San Giovanni mine from the water table level (43.5 m A.S.L.) to 110 m below. The water table in the San Giovanni mine was found at a depth similar to that in Monteponi, but ground water at San Giovanni showed higher salinity (see Table 1). Nevertheless, variation trends in ground water at San Giovanni were similar to those observed at Monteponi. At 6.5 m B.S.L., conductivity showed an
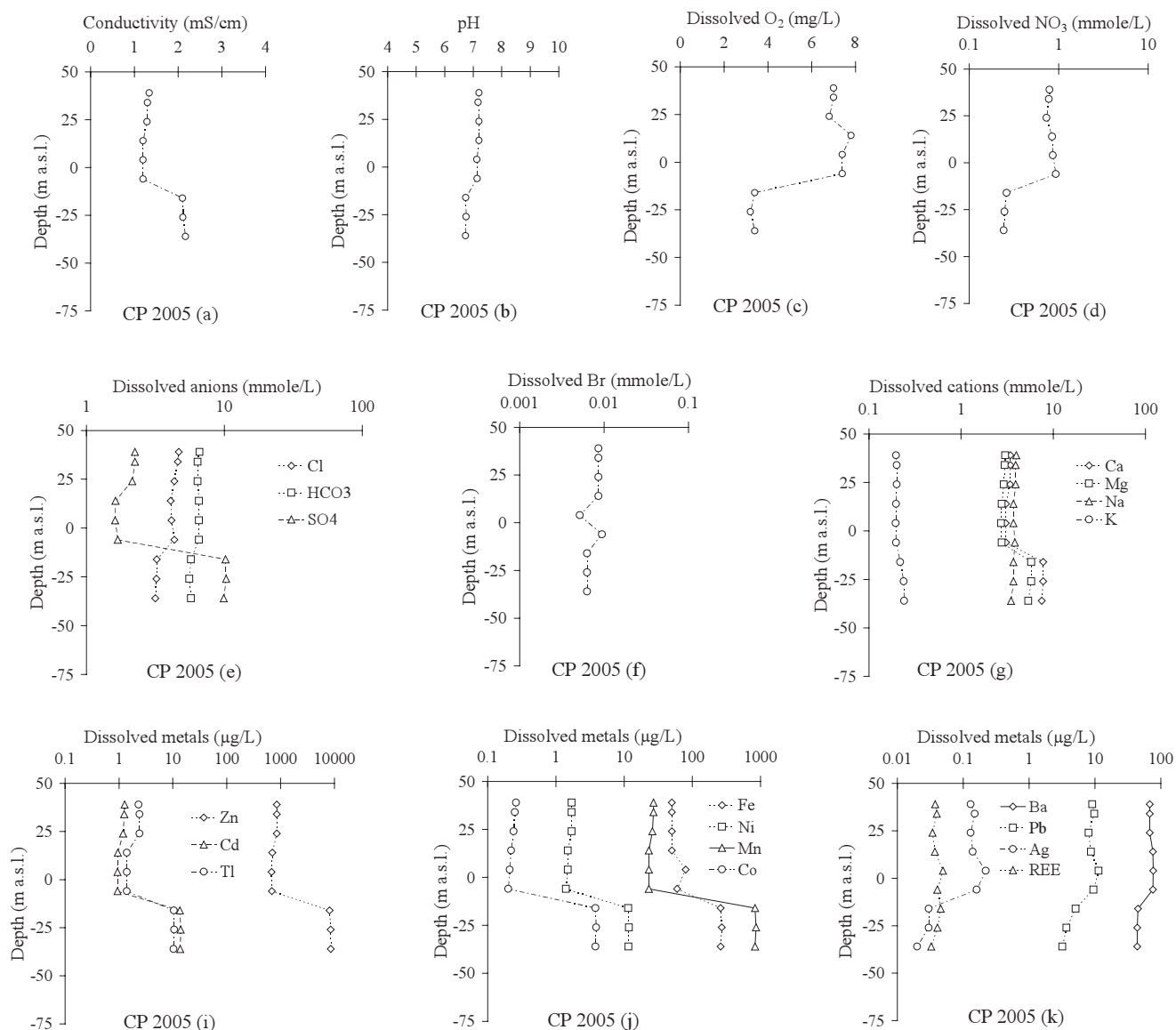
Figure 13. Variations observed in groundwater at the Campo Pisano mine from the water table level downwards.

increasing trend (Figure 12a), pH was nearly constant (Figure 12b), dissolved O_2 (Figure 12c) and NO_3 (Figure 12d) decreased, and alkalinity showed low variations (Figure 12e). As conductivity increased, an increase in dissolved SO_4 and Cl (Figure 12e), Br (Figure 12f), Na, K, Mg, and Ca (Figure 12g) was observed. The marked increase in SO_4 at 56 m B.S.L. was coupled with a significant increase in Zn, Cd, Tl, Fe, Mn, Co, and Ni (Figure 12 i and j). The concentrations of dissolved Ba, Pb, Ag, and REE in ground water at deeper levels showed decreasing trends (Figure 12k). Geochemical processes affecting the ground water at San Giovanni appear to be like those occurring at Monteponi. Considering the similar geology, hydrology, and ore features, the assumptions made above for Monteponi could be also valid for San Giovanni. On this basis, using the same amount of ClnMIX for the initial non-mixed solution, the marine-derived component in ground water at San Giovanni was calculated, resulting in 2.18% seawater. This value was used to calculate the composition of ground water mixed with seawater. Results are shown in Table 3. The increase in conductivity in ground water at San Giovanni occurred at a level less deep than that at Monteponi. Considering that rebound at San Giovanni started 22 months later than Monteponi, a more saline water and a lower degree of stratification were expected.

Figure 13 shows the behaviour of dissolved components in ground water at the Campo Pisano mine at increasing depth from the water table level (43 m A.S.L.) to 80 m below. Profiles showed small changes in ground water from the water table level to 50 m downwards. At 16 m B.S.L. an increase in conductivity was observed (Figure 13a), pH (Figure 13b) and

alkalinity (Figure 13e) were slightly lower, and a marked decrease in dissolved O_2 (Figure 13c) and NO_3 (Figure 13d) occurred. Dissolved Cl (Figure 13e), Br (Figure 13f), Na, and K (Figure 13g) showed small variations. It appears that the marine component in ground water at Campo Pisano was absent, or negligible. The increase in conductivity was due to a marked increase in dissolved SO_4 (Figure 13e), and higher Ca and Mg (Figure 13g). Meanwhile, dissolved Ba, Pb, and Ag (Figure 13k) decreased significantly, as was observed at Monteponi and San Giovanni.

The high SO_4 in ground water at Campo Pisano was associated with a dramatic increase in dissolved Zn, Cd, Tl, Mn, Fe, Ni, and Co (Figure 13i and j). The dramatic increase in SO_4, Zn, and related metals was likely due to the oxidation of sphalerite and pyrite, which was consistent with the dominant ore at Campo Pisano, i.e. ZnS > Zn-oxidized minerals > PbS ($+FeS_2$) hosted in early diagenetic dolomite (Boni et al 1999). The acidity produced by the oxidation of pyrite favoured the dissolution of carbonate minerals, which might explain the observed increase in Ca and Mg. Taking into account the decrease in pH, it can be argued that the acidity produced was not completely buffered.

Conclusions

This study showed that salinisation occurred in shallow mine waters during rebound. At Monteponi and San Giovanni, the increase in salinity was due to the rise of deep saline water. At Campo Pisano, the increase in salinity was due to mixing between shallow ground water and deep saline water. The peak in salinity was observed at Campo Pisano in October, 1998, i.e. 22 months after the rebound started. Increasing amounts of Zn, Cd, and Pb were also observed as flooding progressed. This increase was likely due to the interaction of water with the ore minerals and with the mine waste accumulated in the pits during the long period of exploitation. Salinity decreased after three years of rebound when stratification caused the saline water to settle at depth. In 2005, i.e. 8 years after rebound started, the more saline water was found in the San Giovanni mine, where rebound started later. A small percentage of marine-derived contributions (0.4%) was still present at 45 m B.S.L. in the Monteponi mine, but was not recognized in the Campo Pisano mine at the investigated depth.

In the survey carried out in February, 2004, at Monte - poni, the increase in salinity was observed at a depth corresponding to 8 m B.S.L., while in March, 2005, it occurred at a deeper level, 45 m B.S.L.; this was consistent with the longer time of rebound and absence of extraction. Results from the survey carried out in 2004 at Campo Pisano were very similar to those observed in March 2005, but in June, 2004, the increase in sulphate and metals occurred at a depth corresponding to 27 m B.S.L., while in 2005, the increase was observed at a higher level, i.e. 6 m B.S.L. This could be due to the continuous pumping at Campo Pisano that did not favour stratification. Notwithstanding the peculiarities observed in ground water at each mine, deterioration of water quality was observed at deeper levels. This needs to be carefully considered when planning the quantity of water to be extracted from the flooded mines. Detailed information on the management of water at abandoned flooded mines is reported in Wolkersdorfer (2006).

The extended exploitation of metal ores in the Iglesiente district makes it difficult to distinguish waters circulating in mining areas from waters not affected by past mining. Nevertheless, the dissolved Zn, Cd, Pb, and Hg observed in the spring waters probably approximate the pre-mining background conditions in this area. The decreasing trend in dissolved Zn, Cd, Pb, and Hg observed in all mine waters might indicate that the concentrations of these metals will approach the values observed in water sampled outside of the mined areas. If this trend continues, ground water in flooded mines could be regarded as an important water resource, especially for industrial uses. The hydrogeochemical approach appeared to be a valuable tool for the understanding of processes occurring during rebound; monitoring of the water quality in the flooded mines should continue to pinpoint eventual variations related to extraction. Detailed knowledge of the composition of the host rocks, ore minerals, and mine wastes would be necessary in order to better understand the water-rock interaction processes and the geochemical behaviour of each metal.

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