

Tallium and Other Heavy Metals Occurences in Acid Mine Drainage, Baccatoio Creek, Apuane Alps, Italy

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Received Date: Sep 01, 2020; **Accepted Date:** Sep 23, 2020; **Published Date:** Sep 25, 2020

Abstract

In this paper we present the geochemical data related to mine Acid Drainage (AMD) contamination along the Baccatoio Creek (Apuan Alps, Tuscany) with focus to some many toxic heavy metals as Cadmium, Mercury, Antimony, Arsenic and Thallium. The formation of AMD and the contaminants associated with it has been described by some as the largest environmental problem facing the world mining industry [1,2]. In the Baccatoio basin, more than 20 kilometers of streams are affected by acid drainage from two abandoned mine sites named Mt. Arsiccio and Valdicastello. These mines were development on some small Ba-Fe deposit which was operated prior to 1989. The main ore bodies are an almost conformable lens characterized by a distinct zoning, with pyrite+baryte at the bottom and iron oxides (magnetite and hematite) + baryte at the top, with various accessory sulfides and sulphosalts bearing heavy metals. The mineralization are hosted into and at the contact between phyllites, related to the paleozoic basement of Apuan Alps, and Triassic dolomitic limestones of the Grezzoni formation. The AMD are generated essentially into underground workings (tunnels) and are scattered along the watercourse from the mine culverts. In the study area the conceptual model related to groundwater, freshwater and stream sediments distribution shows that Tl has a different behavior than other heavy metals present in AMD. Indeed this very high toxic element is missing or present in very low concentrations in sediments while persists in relatively high concentrations in the aqueous matrix. Occurrence of heavy metals in groundwater used for drinking water is confirmed only for Tl.

Introduction

Sediments constitute an integral and dynamic part of stream basins, originating from the weathering of minerals and soils upstream. The mechanical dispersion of particles, either gravity-, wind-, or water-driven, may severely influences environmental quality in the mineral deposits surroundings [3]. In particular, watercourse processes play a fundamental role in the transport and redistribution of heavy metals at the Earth's surface, either in dissolved or suspended forms.

Natural concentrations of heavy metals as a result of the weathering processes of mineral deposits can be quite high in stream sediments close to the deposit, but decrease with increasing distance downstream, due to dissipating energy and dilution of sediments from other unpolluting sources [4].

This is particularly true for streams that cross or flow adjacent to mine sites which are sources of large volumes of AMD from ore bodies and waste materials enriched in ore and gangue minerals. Examples of river systems dramatically impacted by pollution related to mining operations are widespread over the world [5].

It has been known that heavy metals enter into stream by the discharge of Acid Mine Drainage (AMD) and/or by the direct loading of heavy metal containing mine tailings [6]. Even though long after mining has been ceased, heavy metals from mine wastes may enter into the stream via physical erosion and geochemical input [7,8].

Sulfide-bearing mineral deposits formed in reduced conditions out of contact with an oxygenated atmosphere. When sulfides in the

deposits are exposed by natural erosion or by mining to atmospheric oxygen and water, weathering of the sulfides can produce natural or mining-related acid-rock drainage (AMD). Commonly referred to Acid Mine Drainage (AMD), acid drainage from mine waste rock, tailings, and

mine structures such as pits and underground workings is primarily a function of the mineralogy of the rock material and the availability of water and oxygen. Mine activity is many important in AMD production since fine grain material (ore, gangue and tailings) exposes more surface area to oxidation [9]. Mining and other forms of earth moving greatly accelerate the weathering of reactive sulphides because they create conditions that tend to facilitate movement of air and water, expose large volumes of material, increase the surface area of the reactive component, and create the opportunity for colonization by microorganisms that catalyze the oxidation processes in the presence of acidity. Dissolved metals in AMD, in addition to more abundant iron and manganese, may include lead, copper, nichel, zinc, cadmium and other very high toxic metals as Cadmium, Arsenic, Antimony and less frequently Thallium [10]. As a consequence, the potential environmental impact of human activities can be significantly more noticeable than those resulting from natural processes. Therefore the drainage from underground mines may cause significant alteration to the quality of stream sediments and can affect surface and ground water as well preclude their use as drinking water or aquatic habitat.

Thallium is more toxic to humans than mercury, cadmium, lead, copper or zinc. Its chemical behavior resembles the heavy metal lead and the alkali metals (K, Rb, Cs). It occurs almost exclusively in natural

waters as monovalent thallium (Tl+1). The solubility of thallos compounds (e.g., thallos hydroxide) is relatively high so that Tl+1 is readily transported through aqueous routes into the environment [11]. The major sources of thallium are the base metal sulfides and precious metal bearing sulfides. Therefore, it has been shown to be a contaminant constituent in waters emanating from heavy metal sulfide bearing deposits.

Object of this characterization is set an conceptual model about the distribution of AMD contamination aimed at mitigate, through active or passive treatments, the environmental and human impact of ADM.

Are considered active treatment those technologies that require ongoing human operation, maintenance and monitoring, and have or use external sources of energy, infrastructure and engineered systems.

Passive treatment refers to processes that do not require frequent human intervention, operation or maintenance, and that typically employ natural construction materials (e.g., soils, clays, broken rock), natural treatment media (e.g., plant residues such as straw, wood chips, manure, compost), and promote growth of natural vegetation. Passive treatment systems use gravity flow for water movement, and passive energy sources such as solar or wind power. Both active and passive treatment methods potentially combine physical, biological and chemical approaches to treat AMD. The main purpose of both classes of technologies is to raise pH, lower dissolved metal concentrations, and lower sulfate. Active or passive treatment of AMD generally requires long-term maintenance and funding.

Given that to achieve an effective remediation project is necessary to provide a thorough conceptual model of the contamination that allows you to select the best technology available, in this study the pollution of mine deposits of Mt.Arsiccio and Valdicastello were investigated and the contributions of the AMD sources to the pollution load of groundwater, freshwater and stream sediments of Baccatoio Creek were determined.

Geological setting

The Alpi Apuane massif is a metamorphic complex formed by the lowermost tectonic units of the northern Apennines [12]. These units consist of moderate-pressure greenschist facies metamorphic rocks hosting numerous small polymetallic (Fe -Zn-Ag-Hg-Cu-Mn) orebodies intensively exploited since the Middle Ages. Among the ore mineral associations in the Alpi Apuane the barite—pyrite—iron oxide deposits in the southern portion of the massif are of particular interest from an ore genesis and regional geology perspective [13], and have been the subject of several studies [13]. These deposits mainly occurring as stratiform bodies at the transition between the Paleozoic phyllitic basement and the overlying Mesozoic carbonate cover (Figure 1), are almost invariably associated with minor amounts of Pb-Zn-Fe

sulfides and sulfosalts [14]. Careful examination of samples collected in the abandoned barite—pyrite—iron oxide mine of Monte Arsiccio and Valdicastello revealed the widespread occurrence of Tl-Hg-As-Sb sulfosalts [14].

Into the Baccatoio basin the mining activities are located in the highest part of the stream (Figure 2). Immediately downstream of the mining structures referred to the Valdicastello mine lies the town of Valdicastello. The town is located on the first stable alluvial deposits of the stream at the equilibrium section. Downstream of the equilibrium section are prevalent the deposition phenomena. In this section of longitudinal stream profile (the accumulation section) the alluvial deposits are consist of gravels with fine matrix. They have a good continuity and thickness increasing progressively to the mouth in the coastal plain. At the confluence of the coastal plain, the alluvial deposits of the Baccatoio Creek are joined with sediments of the coastal plain by a broad alluvial fan.

Upstream equilibrium sections the alluvial deposits are discontinuous with frequent outcrops of the bedrock. This consists of carbonates (Cv=Calcare Cavernoso) in the vicinity of the watershed passing to the metamorphic formations (Pmg=Pseudomacigno, gr=Grezzoni and P=Phyllites) along the stretch between the mine areas of Monte Arsiccio and Valdicastello.

Large underground workings in the Monte Arsiccio, after have been abandoned, have caused subsidence at the surface, resulting in the development of a wide sink-hole Figure 2, in box of Monte Arsiccio mine) that disturbance the surface and deep water drainages. Downstream of Valdicastello town is located the mining processing plant with settling ponds and waste still containing residues from the ore working (Figure 2).

Material and Methods

A total of 31 samples from the stream sediments of Baccatoio creek were collected. Twenty-nine samples were collected from the Freshwater (FW) and thirty from Groundwater (GW). The groundwater samples include both well water (GWp) that spring waters (GWs). A suite of nine AMD samples was collected from the mine culverts at the Mt.Arsiccio and Valdicastello mines (Figure 3).

The stream sediments were collected in the channel bed and depositional bars in Baccatoio creek and some its tributaries, using manual instrumentation. Except in the upstream section, where sediments are of small thickness or missing, in all other stations, championships were superficial and deep layers of bed sediments. In field, sample separation of the fractions <2 mm has been carried out. Ambient water was used for the wet-sieving of the sediment to minimize the loss of particulate bound trace metals to the dissolved

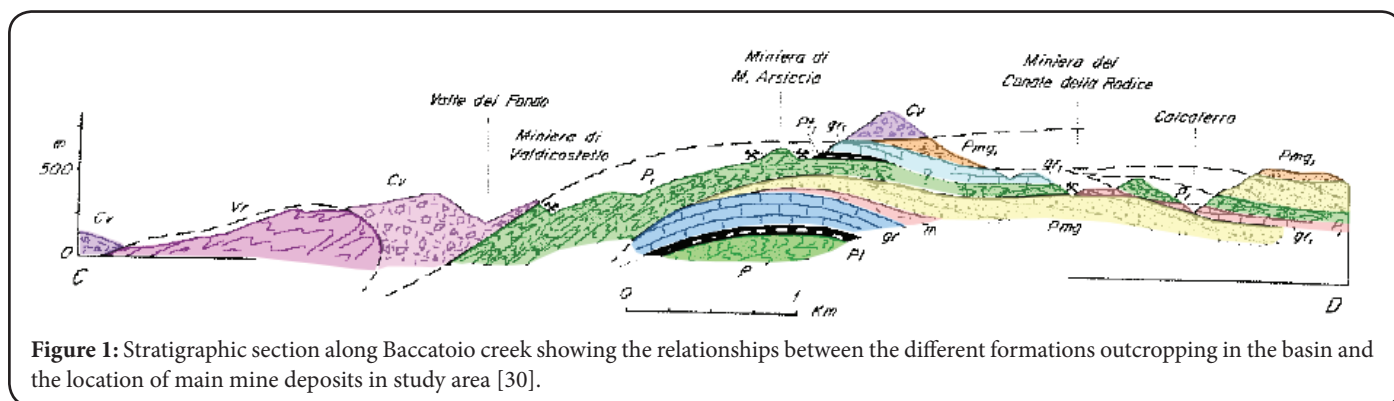


Figure 1: Stratigraphic section along Baccatoio creek showing the relationships between the different formations outcropping in the basin and the location of main mine deposits in study area [30].

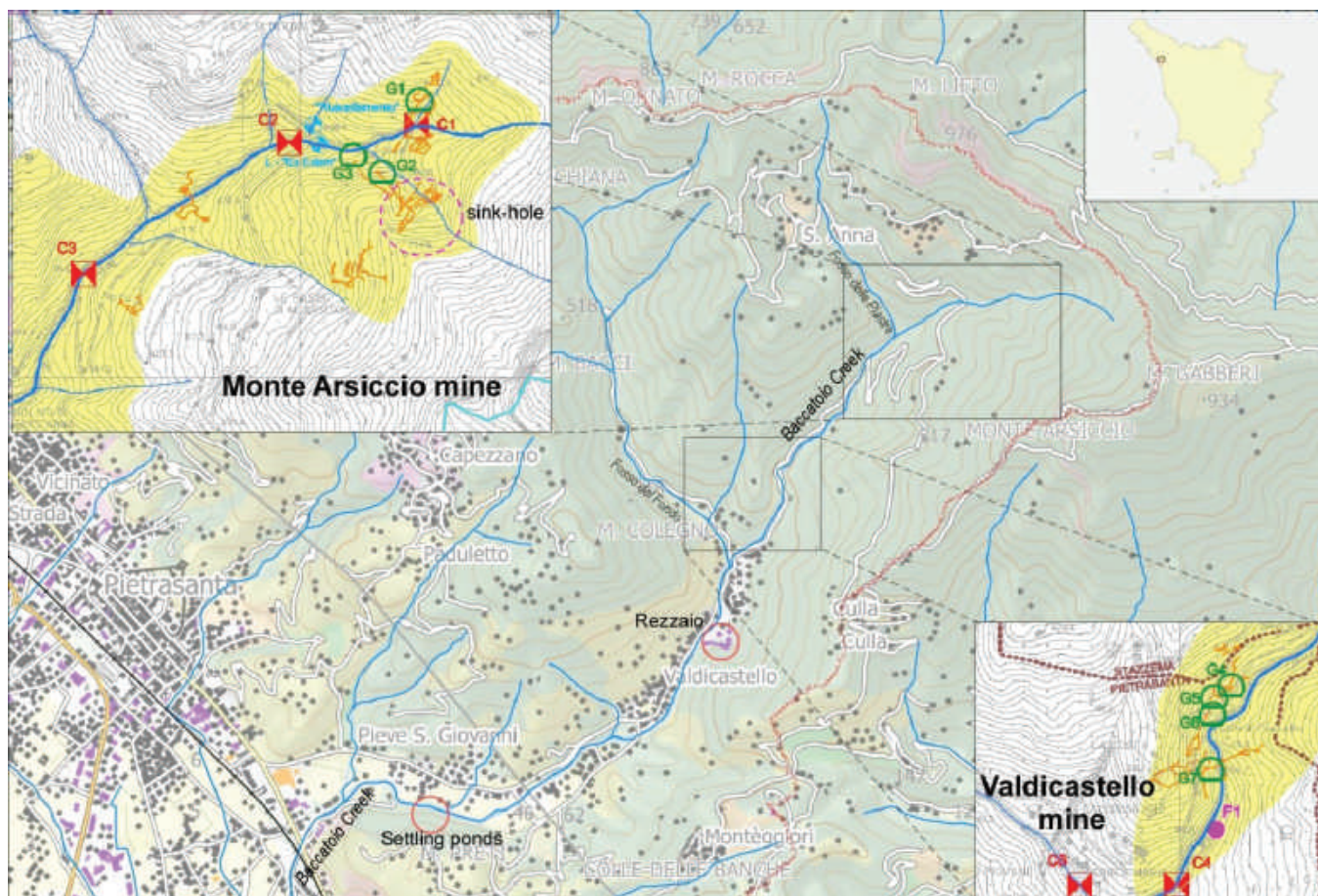


Figure 2: Location of Mt.Arsiccio and Valdicastello mines into the Baccatoio basin. The red dashed line indicates the boundary of the basin. In the boxes are reported the entrances of mine tunnels (green) and the proximal sediment and water samples. In yellow the mine pertinent areas with the main underground mine works.

phase. The sieved fractions were recovered in containers of 500 ml in PE to be analyzed.

All stream samples were dried at 30 °C for 24h. About 20 g of sample was pulverized and sieved of 200 µm mesh. The final product is a 10-g vial of representative powder suitable for acid dissolution.

The technique of the pseudo-total digestion has been used [15]. Therefore about 0,3 g of powdered sample was digested by a closed-digestion procedure in inverse aqua regia (9 ml HNO₃ 65% and 3 ml HCl 37%). A microwave system was used to accomplish sediment digestion. A blank was prepared with the same amount of acids for each digestion program. After cooling, the resulting obtained solutions were diluted to 50 ml in volumetric flasks with MilliQ water (18,2 MR cm). After acid digestion of samples, metal concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The analyses were performed by the laboratory of the ARPAT, Department of Pisa. Some sediment samples were analyzed in duplicates. The accuracy of the analytical procedures has been checked by analysing a multistandard NIST traceable certificate. Thallium was not initially determined. Its concentrations have been retrieved from the database of the instrument until later. This did not permit the determination of its concentrations below 5 mg/kg.

AMD were sampled near the entrances of mine tunnels where are present spilling of mine water. Freshwater were collected into the Baccatoio Creeks and some its affluents. Springs samples were collected

proximity to the rock emergences or to the nearest distribution points. Well samples were collected at the wellhead. Only a few wells had to be purged before sampling, as most are pumped continuously. The pH and E.C. were measured in the field using portable instruments. Water samples were filtered through 0.45 µm membrane filters. Samples for the determination of dissolved metals were collected in polyethylene bottles (pre-rinsed with HCl 1N) and acidified through the addition of superpure HNO₃ 1:1. Samples collected for the determination of dissolved anions were stored in polyethylene bottles without further treatment. The following laboratory analyses were completed: 1) anions were determined using ion-chromatography; 2) trace metals were determined by ICP-OES and ICP-MS. Some spring water analysis were performed by Earth Science Department by ICP-MS instrument.

Results and Discussion

Acid mine drainage

Table 1 shows physical-chemical data for AMD. G1, G2 and G3 samples come from Monte Arsiccio culverts while G5, G6 and G7 come from Valdicastello mine. G8 sample was sampled at an old culvert belonging to a Argentera mine located near S.Anna town in a hydrogeological context different from the two mining sites in object. This sample can represent the blank because the mining activity in the Argentera mine complex is many ancient and the mine water haven't acid characteristic. The metals concentration is very low and the pH,

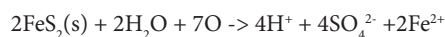
Table 1: Metals and major anions concentration (µg/L) in the AMD of Monte Arsiccio and Valdicastello mines

Code	x	y	Date	pH	Cond. µS/cm	Sb µg/l	As µg/l	Ba µg/l	Cd µg/l	Cr µg/l	Fe µg/l	Hg µg/l	Ni µg/l	Pb µg/l	Cu µg/l	Zn µg/l	Tl µg/l	C Chlor. Nit rat. Solph. Fluor. mg/l mg/l mg/l mg/l				
AMD	G1	1603264	4869610	02/08/11	2,7	3213	5,3	1,279	10,9	5,5	32,5	782,200	3,2	415,3	154,7	14,7	597	154,0	12,4	<0,5	3,490	<25
AMD	G2	1603190	4869454	02/08/11	3,2	1204	0,7	6,5	13	30,8	3,6	15,130	0,4	115,4	11,8	42	5,516	26,0	15,2	<0,5	833,2	19,068
AMD	G3	1603110	4869493	02/08/11	2,3	3618	28,4	479,9	5,6	8,1	24,2	486,600	2,2	324,9	65,3	141,5	1,424	nd	11,1	<0,5	3,739	<25
AMD	G5	1602088	4868736	21/12/11	2,5	3024	5,9	302,8	248,0	50,7	14,3	265,300	<0,1	455,5	4,1	583,1	13,640	nd	25,2	2,4	2,914	36,312
AMD	G6	1602070	4868706	03/08/11	5,13	746	0,8	0,3	23,3	0,1	<0,1	36,5	<0,1	23,4	0,2	<0,1	209,3	2,78	25,1	<0,5	325,6	<25
AMD	G7	1602066	4868567	21/12/11	1,20	19260	1506	23,920	502,1	1,038	157,6	3,46E+06	65	2,171	1,795	20,160	165,000	nd	28,8	7,2	29,292	<25
AMD	G8	1601160	4870061	27/10/14	7,32	309	8,06	1,59	55,41	0,02	571,02	0,03	6	0,15	0,37	18,77	1,09	nd	nd	nd	nd	nd

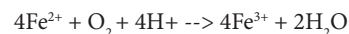
basic parameter for distinguishing AMD from groundwater, is similar to hydrogeochemical context related to the basin water. All AMD samples coming from Monte Arsiccio and Valdicastello mines have particularly high values of heavy metals with concentration differences related to the different percentage of dilution with groundwater circulation. The sample that has the highest values is also the sample with the lowest pH. It was sampled into the lower culvert of Valdicastello mine and it is absolutely the sample with the largest load of contaminants. Graphs in Figure 6 and 7 show a comparison between AMD concentrations and other water samples.

Sulfide-bearing mineral deposits formed in reduced conditions out of contact with an oxygenated atmosphere. When sulfides in the ore deposits are exposed by natural erosion or by mining to atmospheric oxygen and water, weathering of the sulfides can produce natural or mining-related acid-rock drainage (AMD). Acid is generated at mine sites when metal sulfide minerals are oxidized. Metal sulfide minerals are present in the host rock associated with most types of metal mining activity. Prior to mining, oxidation of these minerals and the formation of sulfuric acid is a function of natural weathering processes. The oxidation of undisturbed ore bodies followed by release of acid and mobilization of metals is slow. Extraction and beneficiation operations associated with mining activity increase the rate of these same chemical reactions by exposing large volumes of sulfide rock material with increased surface area to air and water.

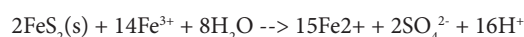
The oxidation of sulfide minerals consists of several reactions. Each sulfide mineral has a different oxidation rate. For example, marcasite and pyrite will oxidize quickly while crystalline pyrite will oxidize slowly. For discussion purposes, the oxidation of pyrite (FeS₂) can be examined [16].



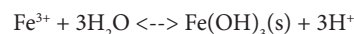
In this step, S₂ is oxidized to form hydrogen ions and sulfate, the dissociation products of sulfuric acid in solution. Soluble Fe²⁺ is also free to react further. Oxidation of the ferrous ion to ferric ion occurs more slowly at lower pH values:



At pH levels between 3.5 and 4.5, iron oxidation is catalyzed by a variety of Metallogenium, a filamentous bacterium. Below a pH of 3.5 the same reaction is catalyzed by the iron bacterium Thiobacillus ferrooxidans also exists other bacteria capable of catalyzing the reaction. If the ferric ion is formed in contact with pyrite the following reaction can occur, dissolving the pyrite:



This reaction generates more acid. The dissolution of pyrite by ferric iron (Fe³⁺), in conjunction with the oxidation of the ferrous ion, constitutes a cycle of dissolution of pyrite. Ferric iron precipitates as hydrated iron oxide as indicated in the following reaction:



Fe(OH)₃ precipitates and is identifiable as the deposit of amorphous, yellow, orange, or red deposits on stream bottoms (“yellow boy”).

In Baccatoio creek is evident the presence of this sequence of reactions as coloring of the bed of the stream and as the presence of bacterial colonies within the mining tunnels [17]. Figure 4 shows a portion of the bed of the stream characterized by the typical red color and two entrances of mining tunnels.

Stream sediments

Table 2 shows chemical results regarding the stream sediments. In are reported the distribution of the main contaminant along the Baccatoio

Table 2: Metals and major anions concentration (mg/mg) in the stream sediment of Baccatoio Creek and its some tributaries. Start to C6 sample the thickness of alluvial bed allowed the sampling depth too.

C1	1603251	4869558	2-ago-11	0-0,10	538.9	3620.0	1873.0	1.1	12.2	280800	7.9	51.5	267.1	25.8	151.2	<5
C2	1603016	4869521	2-ago-11	0-0,10	627.3	1068.0	2073.0	0.4	7.7	183300	22.8	6.9	85.3	17.9	111.0	<5
C3	1602329	4868923	3-ago-11	0-0,10	37.6	266.1	1774.0	6.1	16.3	287900	1.0	118.2	88.8	101.6	970.5	<5
C4	1601990	4868327	3-ago-11	0-0,10	197.0	1862.0	464.0	1.1	13.0	279800	3.2	12.2	80.8	60.3	254.3	<5
C5	1601299	4868788	3-ago-11	0-0,10	225.4	53.0	80.3	0.8	8.7	10982	0.1	13.0	9183.8	15.6	79.6	<5
C6/1	1601777	4868338	3-ago-11	0-0,10	15.7	39.0	746.8	1.7	19.4	19780	0.1	32.6	788.8	35.9	201.1	<5
C6/2	1601777	4868338	23-set-11	0.6	8.4	21.0	517.9	0.1	12.2	14098	0.1	15.5	317.3	20.0	97.2	<5
C7/1	1601655	4867788	4-ago-11	0-0,10	117.5	1063.0	1203.0	10.2	21.0	271000	1.2	46.9	151.2	291.2	2111.0	<5
C7/1 bis	1601677	4867827	23-set-11	0.2	96.5	327.4	1692.9	8.8	13.4	102093	3.2	48.0	375.6	138.5	1657.9	<5
C7/2	1601655	4867788	23-set-11	1.0	1262.9	330.6	5723.0	1.1	14.5	97855	80.1	21.7	299.0	11.3	360.8	<5
C8/1	1601422	4867369	3-ago-11	0-0,10	92.5	152.6	4765.0	4.7	19.9	67740	3.7	33.2	201.6	68.1	896.4	<5
C8/2	1601422	4867369	23-set-11	0.8	74.6	137.1	1652.9	2.9	13.6	45530	3.6	27.3	299.3	54.4	684.1	<5
C9/1	1600768	4867003	23-set-11	0.2	71.7	147.6	2546.7	3.3	12.4	56094	4.4	38.2	157.3	54.4	799.5	<5
C9/2	1600768	4867003	23-set-11	0.45	98.3	236.9	5250.2	5.8	13.0	56231	5.4	35.8	260.1	75.4	1223.8	<5
C10/1	1600351	4866960	23-set-11	0.2	89.7	134.1	4044.9	3.5	12.0	57636	9.9	27.5	225.8	53.2	913.1	<5
C10/2	1600351	4866960	23-set-11	0.6	245.5	184.2	1825.0	2.5	12.8	66596	17.5	26.8	359.8	38.7	702.4	<5
C11/1	1599607	4866553	23-set-11	0.2	92.8	155.9	3976.3	4.1	13.9	52841	16.1	34.3	207.6	69.1	1015.8	<5
C11/2	1599607	4866553	23-set-11	1.0	10.7	29.9	733.3	0.4	10.6	21769	0.3	26.6	159.4	28.2	173.4	<5
C12/1	1599744	4865834	23-set-11	0.2	53.3	103.9	755.3	0.9	9.9	27272	1.2	19.6	101.1	27.1	362.4	<5
C12/2	1599744	4865834	23-set-11	0.6	35.9	52.0	3390.2	0.6	14.7	25269	1.5	19.1	80.5	23.4	250.9	<5
C13/1	1599085	4864738	23-set-11	0.2	99.7	119.3	4826.3	4.0	21.4	50223	6.6	35.3	257.3	111.7	819.4	<5
C13/2	1599085	4864738	23-set-11	1.0	141.4	137.7	3496.6	4.6	22.8	53114	11.5	39.2	407.9	79.9	995.3	<5
C14/1	1597596	4863692	23-set-11	0.2	21.6	29.8	5368.4	2.5	25.4	14228	1.0	25.6	252.2	44.6	498.8	<5
C14/2	1597596	4863692	23-set-11	1.2	19.6	35.7	337.9	4.9	17.3	11260	0.1	14.5	410.6	32.4	535.2	<5
C15/1	1597087	4863275	23-set-11	0.2	11.6	12.5	2786.0	0.1	53.4	12297	0.1	41.3	53.2	22.2	73.8	<5
C15/2	1597087	4863275	23-set-11	0.9	10.1	8.1	2271.4	0.1	51.5	11532	0.1	37.0	39.2	20.6	68.2	<5
C16	1602564	4869836	2-ago-11	0-0,10	11.4	201.2	169.9	1.9	26.4	22520	0.3	41.6	73.3	39.1	277.7	<5
C17	1602283	4870021	2-ago-11	0-0,10	7.1	19.2	680.7	0.6	34.5	13220	0.1	28.5	54.2	22.9	108.3	<5
C18	1602305	4870330	2-ago-11	0-0,10	6.1	61.8	116.8	0.5	18.9	20100	0.1	22.0	44.8	31.8	83.7	<5
C19	1601205	4869438	21-dic-11	0-0,50	12.0	44.9	548.7	1.4	9.9	17050	0.1	13.9	198.1	18.5	152.2	<5
G6	1602070	4868706	3-ago-11	0-0,10	58.4	209.7	527.2	18.0	14.8	377700	0.3	48.7	415.2	220.0	4390.0	<5

watercourse (Figure 5a and 5b). As evident in the samples represent the whole watercourse of the Baccatoio Creek and its main tributaries, Fosso del Fondo e Fosso delle Piastre (Figure 2). The sampling stations have been located evenly along the watercourse. The sample G6 is the sediment of a pool of AMD in close proximity to one of the culvert of Valdicastello mine. All samples show very high concentration in heavy metals with values that rise quickly in proximity to the inputs of AMD in surface water. Among the most toxic heavy metals only thallium is absent.

Sulfide oxidation produces acidification of waters resulting in high dissolved metal concentrations and possible migration and precipitation into river sediments. Also if suspended fine-grained minerals and colloids may play a significant role in metal mobility this is most commonly connect to pH change and ion precipitation in association with iron and manganese ox-hydroxides [9,18-23]. In Figure 4 (left picture) the development of the typically red watercourse confirms the presence of plentiful contaminated sediments. The photo represents the watercourse immediately downstream of the Valdicastello mine where is most relevant the AMD contribution by this mining area.

In the following figures are the measured concentrations about the main heavy metal detected with color highlighting different concentrations. Green color shows the concentrations lower the threshold values of contamination imposed by the Italian law (column

A and B, tab.1, Annex 5 from Legislative Decree No. 152/2006.). In yellow are shows the values exceed the threshold concentrations related to residential and recreation sites and in red/purple the values exceed the threshold concentrations of industrial sites. Regarding barium the threshold value is referred to resolution from Istituto Superiore di Sanità (2007) [24].

Many samples show concentration higher, also of an order of magnitude, than the highest industrial threshold limit. Among the most toxic metals arsenic and antimony have a particularly wide distribution downstream with particularly high values (Figure 5a).

Mercury presents high values only near to Monte Arsiccio mine and much further downstream close to Rezzaio where are located the mining processing plant. In fact in this plant was also processing ore from the mines of Levigliani where was extracted cinnabar [25]. As observed to AMD analysis the contribution of this metal from mines object of this study is relatively low. Despite that the concentrations in sediments although localized remain particularly high (values of up to 80 mg/Kg).

Arsenic has high values even in the sub-basin of the Fosso delle Piastre where are not present releases of AMD In fact Figure 3. The high values of arsenic, antimony and lead in the sediments of the Fosso del Fondo are to be attributed to the presence of a trapshooting field.

Table 3: Metals and major anions concentration in ground water of the Baccatoio basin.

pH					Cond.	Sb	As	Ba	Cd	Cr	Fe	Hg	Ni	Pb	Cu	Zn	Tl	C chlor. N it rat. Solph.			
	Code	x	y	Date	µS/cm	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	
GWs	F1	1602431	4868969	21/09/11	6.85	514	<0,1	0.1	60.3	<0,1	0.1	<1,0	<0,1	5.8	0.2	<0,1	<0,1	14.1	11.3	1.5	124
GWs	F1a	1602431	4868969	27/10/14	7.38	416	0.35	0.55	61	0.14	0.04	1337	0.56	7.4	<0,1	0.29	10.6	17.3	nd	nd	nd
GWs	F1b	1602431	4868969	3/12/14	7.6	375	0.4	0.14	48	0.05	0.03	13.2	0.49	3.8	<0,1	0.29	5.2	5.4	nd	nd	nd
GWs	F2	1601778	4868022	03/08/11	8.4	414	7.8	1.0	31.7	<0,1	0.2	3.7	<0,1	0.8	2.9	0.1	0.6	<0,05	15.6	1.2	49.8
GWs	F2a	1601400	4867522	9/7/14	7.56	418	0.05	0.19	16.88	<0.01	0.4	21.2	0.13	2.69	<0,1	0.94	2.41	<0.01	20.08	7.90	16.55
GWs	F3	1601369	4867328	03/08/11	8.2	577	1.1	0.6	35.1	0.2	0.3	20.5	<0,1	1.2	0.3	0.2	31.8	0.25	15.8	3.7	105.2
GWs	F3a	1601502	4867468	27/10/14	7.28	453	1.58	0.31	37.92	0.31	0.19	23.56	0.1	3.12	<0,1	0.77	45.69	1.03	nd	nd	nd
GWs	F3b	1601481	4867430	9/7/14	7.44	521	1.4	0.27	34.6	0.52	0.27	30.75	0.17	4.18	<0,1	0.83	87.89	1.31	16.30	3.76	84.04
GWs	F4	1602565	4869559	02/08/11	7.43	377	0.3	0.4	16.4	<0,1	0.3	37.5	<0,1	0.9	0.5	0.2	16.3	<0,05	11.1	2.7	7.5
GWs	F6	1602773	4868773	02/08/11	7.5	412	0.5	2.1	386.2	<0,1	0.2	1.5	<0,1	0.8	0.3	<0,1	0.7	<0,05	15.5	<0,5	16.0
GWs	F6a	1602773	4868773	9/7/14	7.54	416	0.36	2.11	296.9	<0.01	0.09	17.27	0.11	2.1	<0,1	0.29	1.98	<0.01	14.58	<0,125	14.88
GWs	F8	1601527	4866949	21/09/11	7.1	513	<0,1	0.4	<0,1	<0,1	0.7	3.6	<0,1	1.1	0.3	0.3	<0,1	nd	24.5	32.4	31.8
GWs	F8a	1601527	4866949	9/7/14	7.53	506	0.04	0.24	16.82	<0.01	0.38	23.47	0.22	3.17	<0,1	0.71	13.08	<0.01	19.37	30.92	23.57
GWs	F22	1602144	4869820	3/12/14	7.46	350	0.15	0.21	53.06	0.01	0.17	17.4	0.04	2.43	<0,1	0.49	1.85	<0.01	nd	nd	nd
GWs	F23	1603012	4869747	7/5/14	7.41	406	0.14	0.12	10.11	<0.01	0.05	22.19	0.24	3.03	<0,1	3.73	21.59	<0.01	nd	nd	nd
GWs	F24	1602784	4869910	7/5/14	7.53	403	0.13	0.12	10.35	<0.01	0.05	23.45	0.14	3.23	<0,1	2.13	8.72	<0.01	nd	nd	nd
GWs	F25	1602302	4870316	27/10/14	7.95	307	0.1	0.1	18.94	0.03	0.08	15.28	0.04	2.11	<0,1	0.43	0.62	<0.01	8.1	1.18	3.63
GWs	F26	1601817	4869734	27/10/14	7.3	342	0.13	0.2	4.9	0.04	0.04	58.02	0.66	3	<0,1	0.34	3.24	0.013	5.24	0.14	3.17
GWs	F27	1601952	4870252	7/5/14	7.5	350	0.13	0.1	107.7	<0.01	0.07	15.2	0.08	1.98	<0,1	0.23	0.65	<0.01	nd	nd	nd
GWs	F28	1602306	4869431	9/7/14	7.52	486	0.12	0.33	4.22	<0.01	0.03	32.84	0.11	4.1	<0,1	0.45	2.3	<0.01	14.57	<0,125	8.00
GWs	F29	1602397	4869075	9/7/14	7.58	410	4.59	0.61	28.89	0.02	0.12	23.61	0.16	2.87	4.58	0.66	3.1	<0.01	16.27	<0,125	9.42
GWs	F30	1602420	4869115	3/12/14	7.64	371	0.99	3.29	109.6	0.06	0.07	108.26	0.14	2.27	0.19	0.55	8.07	0.03	nd	nd	nd
GWs	F31	1601613	4868414	27/10/14	7.47	431	0.18	0.28	7.69	<0.01	0.14	22.27	0.04	2.95	0.24	0.55	4.02	0.02	nd	nd	nd
GWp	F10	1599511	4866682	30/01/12	7.2	540	0.8	1.6	117.8	<0,1	0.5	67.7	<0,1	1.1	0.3	3.3	104.1	nd	19.1	10.2	62.7
GWp	F11	1599567	4866177	30/01/12	7.32	523	0.5	0.3	73	0.4	0.2	18.1	<0,1	9.4	0.2	76.2	2233	nd	15	6.5	83.4
GWp	F12	1598897	4864843	30/01/12	7.63	1660	<0,1	8.7	23.3	<0,1	1	12,940	<0,1	5.7	0.1	<0,1	307.7	nd	114.1	<0,5	512
GWp	F18	1601061	4867212	30/01/12	6.8	539	0.1	0.8	97.5	<0,1	0.2	20.4	<0,1	0.7	<0,1	2.3	13	nd	21.2	8.2	106.7
GWp	F19	1600780	4866943	30/01/12	7.15	504	0.2	0.6	170.5	<0,1	0.2	28.5	<0,1	1	0.1	7	8.1	nd	24.6	9.8	47.7
GWp	F20	1600892	4867010	30/01/12	6.95	291	<0,1	0.8	410.4	0.6	<0,1	2,556	<0,1	2	1.2	<0,1	8.2	nd	10.4	<0,5	<2,5
GWp	F21	1599481	4866195	30/01/12	7.26	572	0.3	0.8	79.1	<0,1	0.4	13.3	<0,1	0.7	<0,1	<0,1	3.4	nd	19.4	10.3	95.6

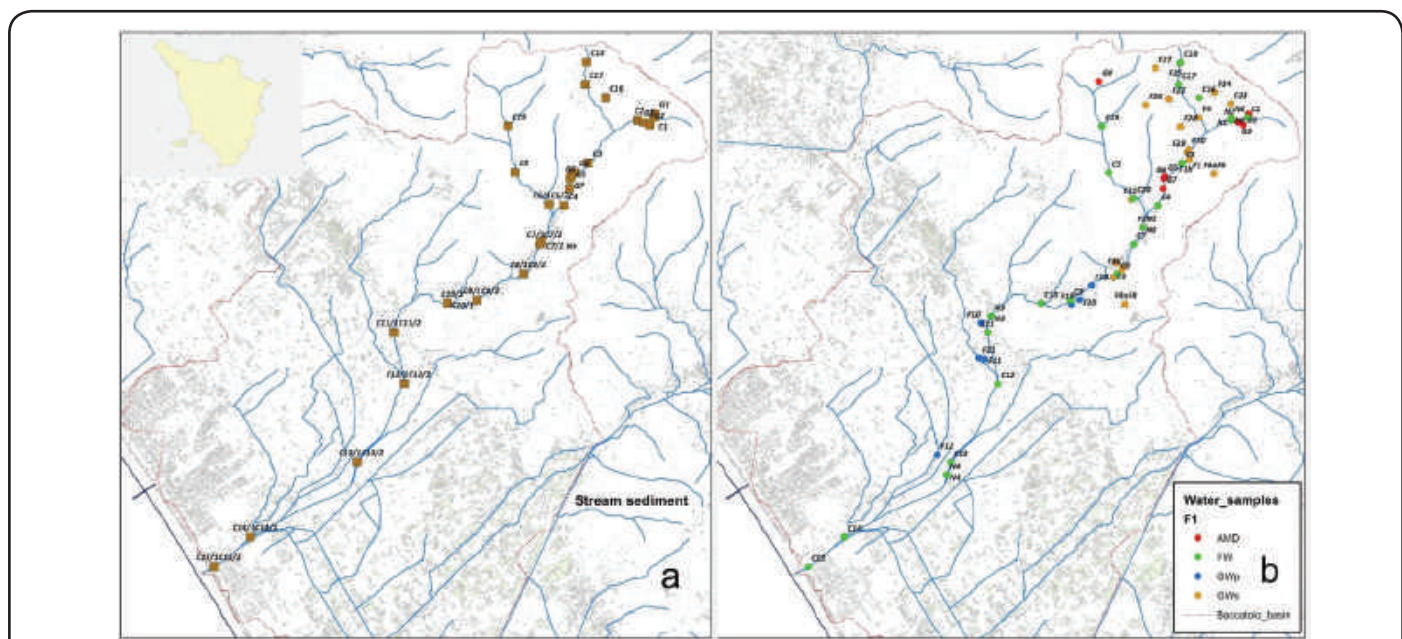


Figure 3: Ubication of sampling stations a) Stream sediments b) Water distinct in groundwater, from wells and spring, AMD and freshwater.

Table 4: Metals and major anions concentration in fresh water of the Baccatoio basin

	Code	x	y	Date	pH	Cond. µS/cm	Sb µg/l	As µg/l	Ba µg/l	Cd µg/l	Cr µg/l	Fe µg/l	Hg µg/l	Ni µg/l	Pb µg/l	Cu µg/l	Zn µg/l	Tl µg/l	C hlor. mg/l	Nit rat . mg/l	Solph. mg/l
FW	C1	1603251	4869558	21/12/11	8.78	696	0.4	14.6	45.5	<0,1	<0,1	<1	<0,1	0.4	<0,1	<0,1	<0,1	nd	13.6	1.1	45.8
FW	C2	1603016	4869521	02/08/11	3.2	4	4.3	604.3	7.4	5.7	22.4	470,000	2.1	300.6	74.0	64.0	837.6	nd	12.7	<0,5	2,894
FW	N1	1603016	4869521	29/05/13	3.1	1324	3.8	40	11	1.2	2.3	50787	0.277	46	11	13	177	53	nd	nd	nd
FW	N1	1603016	4869521	17/09/13	3.2	1867	nd	4	nd	3.7	2	nd	<0,01	140	23	nd	540	88	nd	nd	nd
FW	C3	1602329	4868923	03/08/11	7.9	862	1.8	0.9	32.3	0.1	0.1	16.4	<0,1	2.5	0.1	0.2	7.5	nd	15.4	<0,5	689.2
FW	C4	1601990	4868327	03/08/11	5.79	727	0.5	1.3	107.0	29.1	0.1	70.0	0.4	59.3	7.8	181.5	4,533	nd	15.9	<0,5	420.4
FW	C5	1601299	4868788	03/08/11	7.6	394	18.1	1.1	46.6	<0,1	0.2	<0,1	<0,1	0.8	23.8	0.2	2.2	nd	16.6	1.3	10.9
FW	C7	1601655	4867788	03/08/11	3.8	1124	0.3	2.3	69.0	73.6	2.9	1270.0	0.6	123.6	62.5	920.7	12,640	nd	17.9	<0,5	696.8
FW	N2	1601778	4868023	29/05/13	8	379	6.2	72	59	3.1	1.2	17153	0.083	8.7	4.9	45	508	9.1	nd	nd	nd
FW	N2	1601778	4868023	17/09/13	7.3	628	nd	124	nd	12.3	2	nd	0.034	25	9	nd	2300	17	nd	nd	nd
FW	C8	1601422	4867369	03/08/11	5.0	497	2.0	0.7	57.8	0.2	0.3	11.5	<0,1	1.6	0.2	2.8	31.0	nd	16.1	3.7	89.8
FW	C9	1600768	4867003	15/11/11	7.3	553	1.8	0.5	40.9	0.4	0.2	<1	<1	1.9	<0,1	0.9	65.6	nd	17.0	4.3	101.2
FW	C10	1600351	4866960	21/09/11	nd	nd	1.6	1.1	314.8	<0,1	0.2	4.2	<0,1	1.3	0.2	0.6	<0,1	nd	18.5	6.1	74.3
FW	C11	1599607	4866553	21/12/11	7.6	486	17.0	0.3	41.1	0.3	<0,1	<1	<0,1	2.2	<0,1	<0,1	14.2	nd	17.8	4.6	125.2
FW	N3	1599651	4866778	29/05/13	8.4	413	3.7	33	54	1.3	<1	12751	0.079	5.3	2.9	18	208	5.5	nd	nd	nd
FW	N3	1599651	4866778	17/09/13	8.5	560	nd	12	nd	0.8	<1	nd	0.02	3	<2	nd	240	5	nd	nd	nd
FW	C12	1599744	4865834	21/12/11	7.6	483	2.0	0.3	42.9	0.3	<0,1	4.3	<0,1	2.2	<0,1	<0,1	13.8	nd	17.2	4.5	122.6
FW	C13	1599085	4864738	23/09/11	6.9	913	10.4	13.1	238.7	<0,1	0.2	126.7	<0,1	7.2	0.3	1.0	<0,1	nd	92.6	<0,5	165.1
FW	C14	1597596	4863692	23/09/11	7.2	2637	2.5	12.6	<0,1	<0,1	0.7	31.4	<0,1	4.3	1.7	0.5	11.2	nd	694.8	<0,5	165.1
FW	N4	1599032	4864559	29/05/13	8.1	501	5.2	53	89	2.8	1	21643	0.164	8.5	11	44	456	4.6	nd	nd	nd
FW	N4	1599032	4864559	17/09/13	7.8	588	nd	11	nd	0.5	<1	nd	<0,01	4	14	nd	92	4	nd	nd	nd
FW	C15	1597087	4863275	23/09/11	7.1	5265	2.5	11.3	<0,1	<0,1	1.2	70.3	<0,1	4.0	0.9	0.5	1.8	nd	1,703	3.4	263.2
FW	C16	1602564	4869836	21/12/11	8.86	92	<0,1	47.5	<0,1	0.2	<0,1	<1	<0,1	0.4	<0,1	<0,1	28.1	nd	13.9	<0,5	12.5
FW	C17	1602283	4870021	21/12/11	7.85	317	<0,1	3.1	54.6	<0,1	<0,1	<1	<0,1	0.2	<0,1	<0,1	<0,1	nd	13.4	3.1	10.8
FW	C18	1602305	4870330	15/11/11	7.4	359	0.1	3.6	13.5	<0,1	<0,1	<0,1	<0,1	1.2	<0,1	7.9	4.3	nd	9.8	5.1	9.8
FW	C19	1601205	4869438	21/12/11	7.59	388	0.3	1.1	53.8	<0,1	<0,1	12.8	<0,1	0.3	0.3	<0,1	4.5	nd	16.6	1.3	9.3
FW	N0	1603021	4869556	29/05/13	8.1	175	0.7	3.5	60	0.17	<1	11	0.921	1.1	<1	<1	15	<0,05	nd	nd	nd
FW	N0	1603021	4869556	17/09/13	8.6	291	nd	4	nd	<0,4	<1	nd	nd	<2	<2	nd	21	<1	nd	nd	nd
FW	N5	1604691	4871036	29/05/13	8.3	236	<0,5	<1	51	<0,05	<1	131	0.084	<1	<1	<1	1.3	1	nd	nd	nd
FW	N5	1604691	4871036	17/09/13	8.5	282	nd	<1	nd	<0,4	<1	nd	0.087	<2	<2	nd	<10	1	nd	nd	nd
FW	C20	1601650	4868428	9/7/14	7.61	408	4.47	0.66	28.19	0.01	0.14	21.66	0.12	2.8	4.49	0.43	3.53	<0,01	16.12	<0,125	10.18

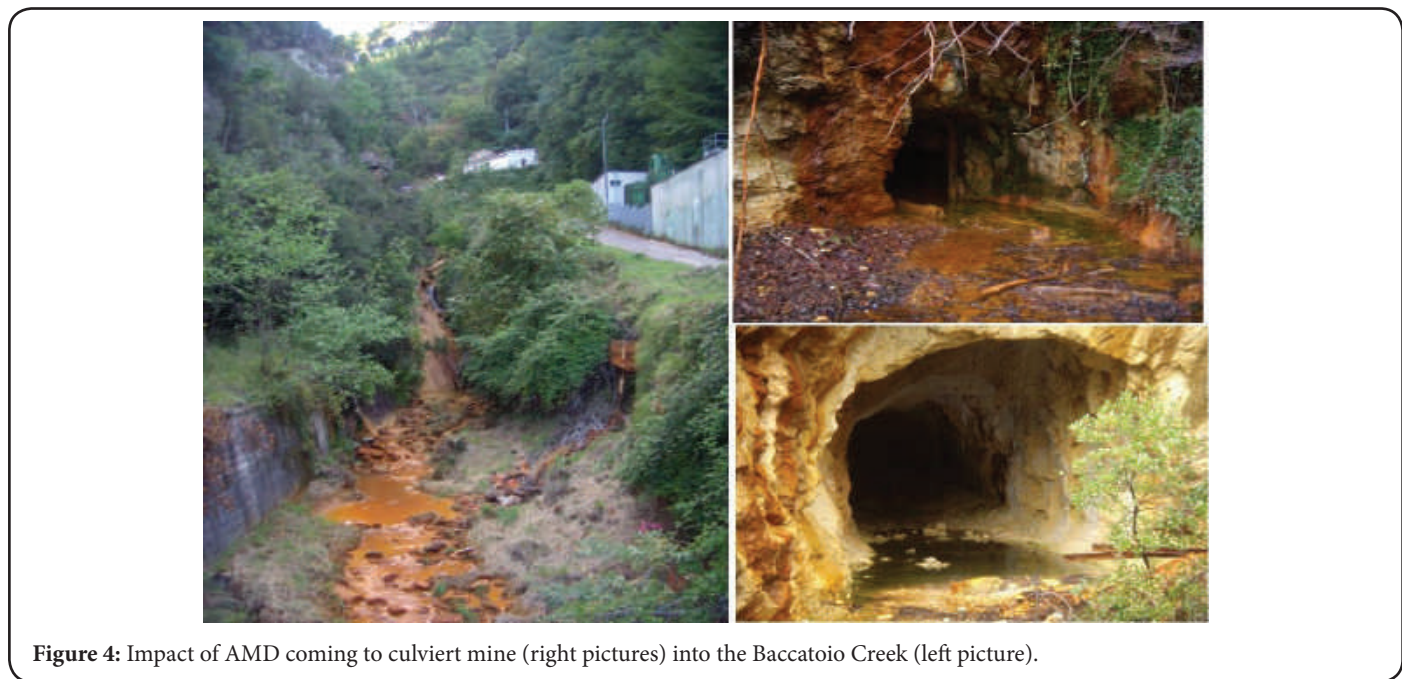


Figure 4: Impact of AMD coming to culviert mine (right pictures) into the Baccatoio Creek (left picture).

Particularly regarding the Pb the contribution of this metal from mine areas is very low. Also Cu and Ni are very low according to their missing into the mineral deposits.

Barium is not considered a toxic element and is surprisingly abundant in the Earth's crust, being the 14s most abundant element. So the red color in are referred to concentrations in excess of 3400 mg/Kg Figure 5a. This concentration doesn't represent values connected with threshold or sanitary effect but only its crust abundance.

In all sediment samples except for copper and nichel, concentrations remain high even in the stations positioned very far from the mining areas. Unlike surface waters are not contaminated or contaminated only in the vicinity of the mining areas Figure 8a. This is in agreement with the presence of weak phenomena of desorbing by the sediments.

The potential for acid generation is offset by the ability of a material to neutralize acid. Acid neutralization is imparted by various minerals including calcium- and magnesium-bearing carbonates, oxides and

hydroxides of calcium, magnesium, and aluminum, some silicate minerals, and some phosphates [26]. In general, dissolution rates (and hence neutralization) are considerably faster for carbonate minerals than for other neutralizing minerals. So in study area the extensive outcrops of carbonatic rocks promotes faster rise in the pH resulting in fast precipitation of the soluble metals. Then these latter can be dragged downstream by the water flow. The precipitation phenomena is concentrated close to the main arrivals of AMD in the Baccatoio watercourse.

Groundwater and freshwater

Tables 3 (GW) and 4 (FW) report the physical-chemical data for water samples. In Figure 8a and 8b are reported the distribution of the main contaminant along the Baccatoio watercourse.

From hydrogeological point of view can be distinguished two main types of springs into the Baccatoio basin. The first group has a relatively shallow circulation into the carbonate formations forming the main

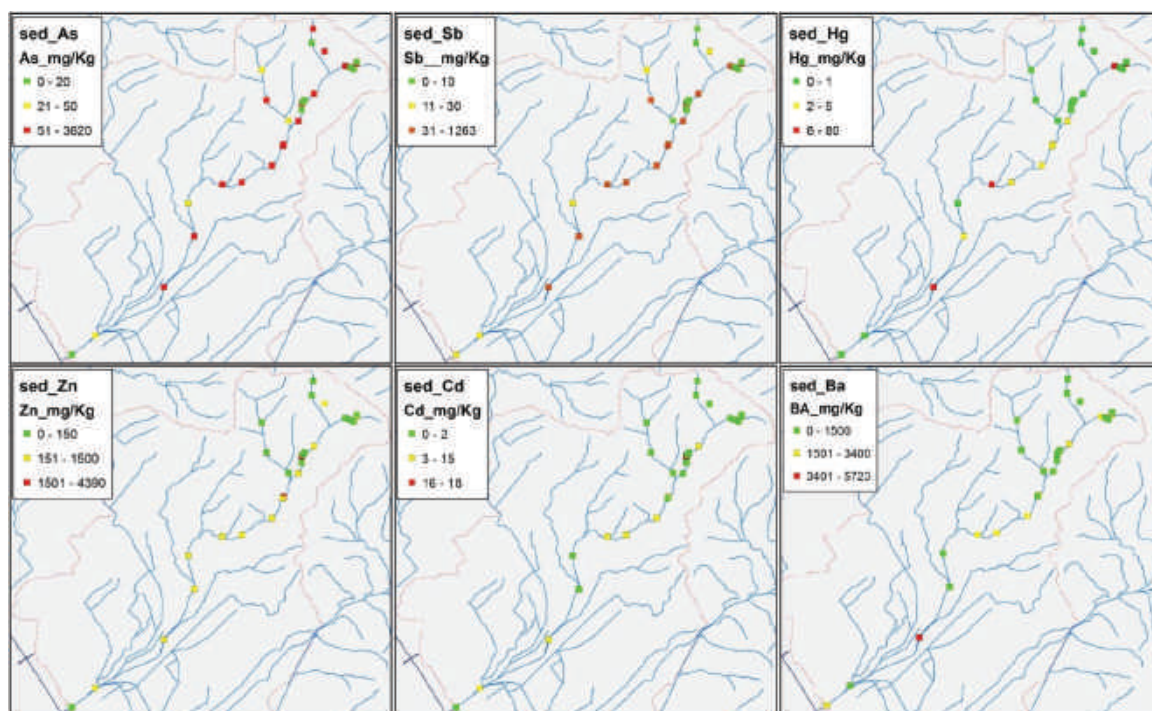


Figure 5a: Distribution of As, Sb, Hg, Zn, Cd and Ba in stream sediments along Baccatoio creek.

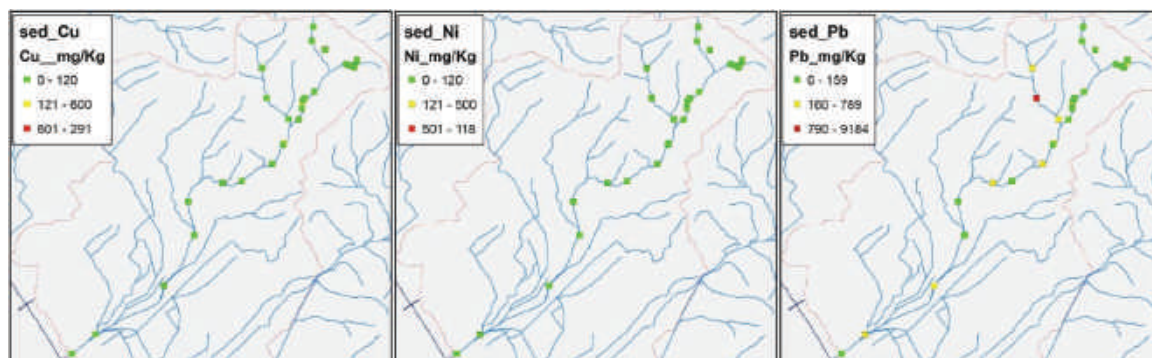


Figure 5b: Distribution of Cu, Ni and Pb in stream sediments along Baccatoio creek.

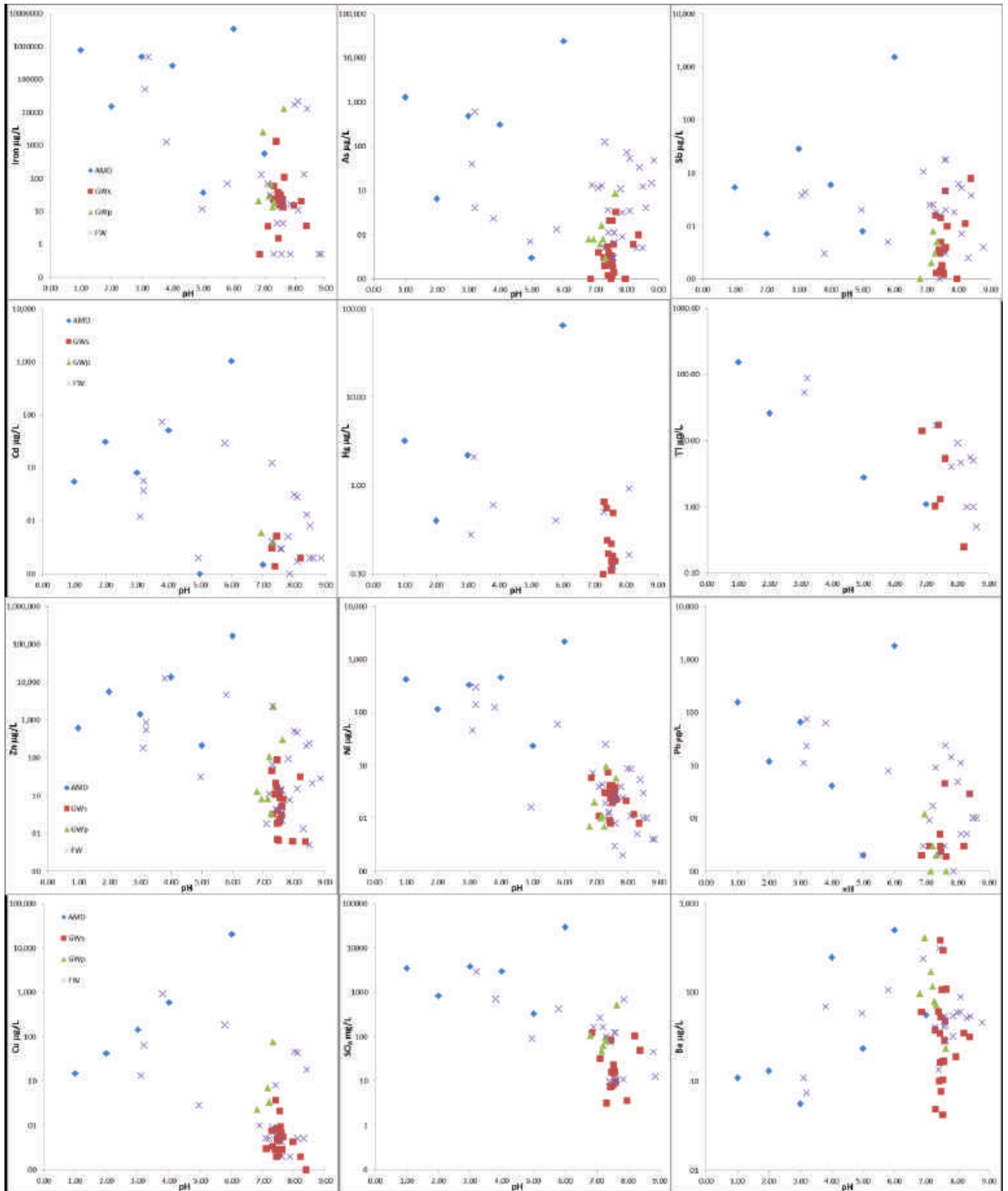


Figure 6: Plots of dissolved species concentrations of groundwater (GWs from spring and GWp from wells), Freshwater (FW) and AMD as a function of pH.

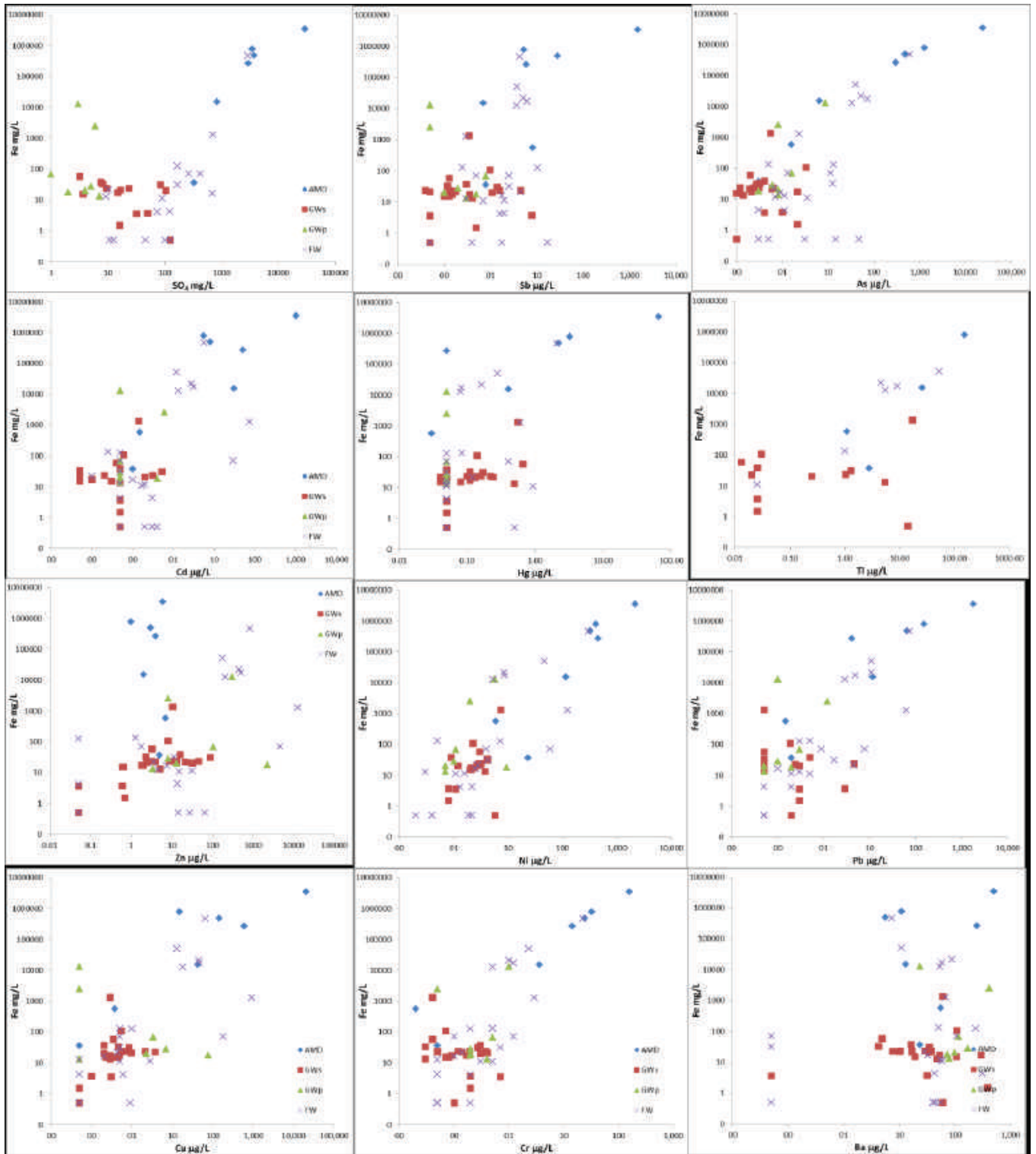


Figure 7: Plots of dissolved species concentrations of groundwater (GWs from spring and GWp from wells), Freshwater (FW) and AMD as a function of Fe concentration.

reliefs of watershed basin. This group includes all the sampled springs except F29, F30, F4 and F1. This latter is characterized by a high flow and intercepted since many years for drinking use. The F1, F1a and F1b represent three samples taken from the same spring in different times. This spring could represent a deeper circulation into the Phillytes and its location, downstream respect to mine area of Monte Arsiccio, justified its Tl content. All other springs and most water wells don't show significant heavy metal values.

The missing of the other heavy metals in this spring, particularly As and Sb, can be due to the slowly circulation into the rock that favors the reactions of oxidation with precipitation of all the heavy metals except thallium. F29, F30 and F4 have deeper circulation too but it is confined into the Grezzoni formation underlying the Phillytes formation. Tl is absent and only low concentrations of As and Sb and other heavy metals are observed in F29 and F30 springs.

All sampling wells were set to alluvial plain in the mountain section of the watercourse. These are shallow

wells which draw water from groundwater flowing into riverbed aquifer. Downstream of mountain section

the sampling wells draw water from coastal multilayer aquifer. The wells nearest to the mine areas don't show high metal concentrations confirming that the ADM contamination is confined to the Baccatoio watercourse. The high metal values in F12 well, located into the coastal plain, is probably connected to local contamination as shown by the values of conductivity and sulphates.

Analyzing chemical fate and transport at mine sites is a complex task due to the interactions between the hydrologic cycle, pollutant cycle, and sedimentation (watershed) cycle [27].

Because the contamination by heavy metals is confined in the watercourse shows that the main diffusion phenomenon is represented by the combination of precipitation and transport in the solid phase (stream sediments). In Figure 6 are plotted the pH values vs. heavy metals concentration.

The graphs show very clearly the link between the precipitation of dissolved metals in AMD with the sudden rise in pH that is when AMD will introduce in the river network. In Figure 4 is evidence of the impact of the mining AMD Valdicastello on Baccatoio creek which here takes the characteristic red color of the metals in precipitation as oxides and hydroxides.

In Figure 7 the main heavy metals concentrations in water are plotted vs. iron concentration, that represent the main metal in the mine deposits. All heavy metals, including thallium, show a linear trend with more high concentration in presence of Fe high values. This is in agreement with the precipitation phenomena connected to change of pH. Only the barium does not have this linear trend. In is also evident as the spring with the higher values of thallium (samples F1 and F1a) has very different iron concentrations (1337 mg/L against <1 mg/L respectively) Figure 7. This great difference between concentrations of iron in equal concentrations of thallium may be due to a shallow mixing of groundwater.

In the Baccatoio valley human populations living near and downstream of heavy metals deposits and Tl-As-Sb-Hg-Cd bearing ore deposits are susceptible to contamination because of their high toxicity and high uptake rate by crops. The dispersion of heavy metals associated with the primary mineralization has been traced through physical and chemical weathering and production of AMD, producing

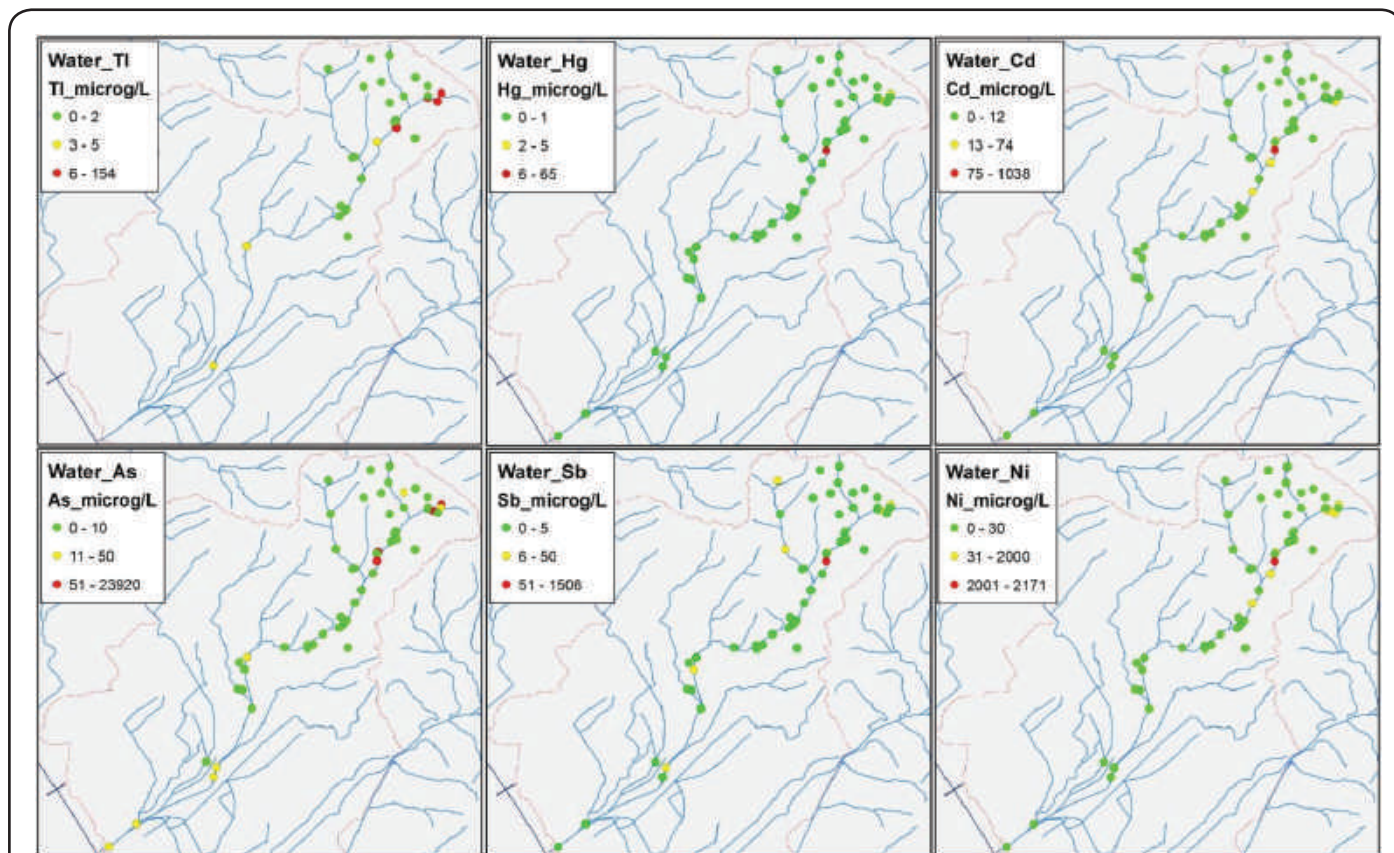


Figure 8a: Distribution of Tl, Hg, Cd, As, Sb and Ni in water samples.

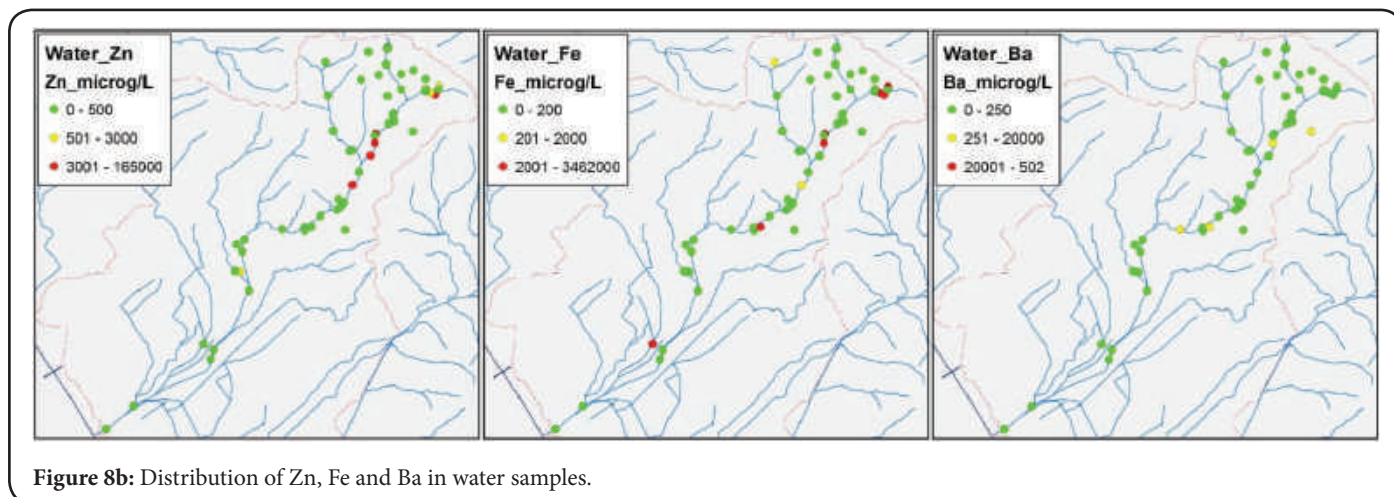


Figure 8b: Distribution of Zn, Fe and Ba in water samples.

secondary dispersion into stream sediments, groundwater and surface water. The effect of mining activity on the stream water chemistry was attenuated in a relatively short distance from the source along the watercourse but the signature in the sediment showed a longer lasting effect than in the stream water.

Major and trace metals in AMD coming from Monte Arsiccio and Valdicastello culverts are sourced from the oxidizing sulphides and dissolving acid-consuming minerals as indicated by the very high content of sulfates that range from 800s to 30,000s mg/L. In the AMD, Fe is the principal major dissolved metals, with contents that range from 800s to 3,500s mg/L. Trace metals such as As, Sb, Cu, Pb, Zn, Cd, and Ni can achieve elevated concentrations in AMD, reaching values over 100s mg/L. AMD also contain high levels of Tl up to 154 mg/L. The data highlight the mining activities increase exponentially the natural processes, readily dispersing heavy metals into the surface environment through the AMD. Into the study area the presence of extensive outcrops of carbonatic rocks promotes in AMD faster rise in the pH resulting in precipitation of the soluble metals into the watercourse. Heavy metals are then mobilized through the flow of water and redistributed downstream. Stream sediments have been shown a very high contamination by heavy metals but not by thallium. The waters were slightly contaminated. Only in one sample of the investigated spring was measured thallium concentration higher than the threshold value. All other ground water and fresh water aren't contaminated.

Investigating on heavy metals mobility is particularly important in the case of thallium which is a highly toxic substance potentially dangerous to humans and environment and has a strong tendency to remain as ion in solution in the water leaching [28]. The groundwater and freshwater chemical data illustrate Tl contamination related to a Tl-rich deposit due to the impact of mining. In the study area the conceptual model related to groundwater, freshwater and stream sediments distribution shows that Tl has a different behavior than other heavy metals present in AMD. This metals was found in a spring for drinking use and it is present in freshwater far to mine areas. Other metals are instead closely associated with sediments and are subject to only transport in suspension [29-31].

These studies of water and stream sediments quality that results from mining and mineral processing activities in the Baccatoio basin has therefore become a high priority in order to mitigate the environmental effects of deleterious drainage waters and to implement remediation activities. Containment of previous contamination essentially into the watercourse and the location of active contamination sources close

of AMD input in the creek suggests the possibility of implementing remediation diversified:

- Reduce the amount of AMD with targeted passive treatments in tunnels mining exploiting the enabling capacity of bacterial.
- Intercept and promote through passive treatments to raise pH after the contact between AMD and freshwater;
- Restrict access to the watercourse and the uses freshwater.

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