The impact of dismissed mine sites in the Baccatoio Stream catchment (northern Tuscany, Italy) on water contamination by thallium and other potentially toxic elements

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Abstract

The physico-chemical parameters and the concentration of potentially toxic elements (PTE) have been determined in acid mine drainages (AMD) and superficial waters in an area impacted by mining activity in the southern Apuan Alps (northern Tuscany, Italy). The study is particularly focused on the Baccatoio Stream, that receives AMD from Pollone and M. Arsiccio abandoned mines, with regard to the fate of mine-derived elements, including Tl, from the AMD input to the stream mouth. AMDs have an average pH value of 2.2. PTE concentrations exceeding the threshold for Italian Regulation are observed for Al, Fe, Mn, Cu, Zn, As, Ni, Co, Cd, Sb, Pb and Tl, that reaches 475 µg/L. Mine drainages outflow directly into the stream, resulting in a severe contamination of surface water, in particular in proximity of AMD inputs. Downstream of the mining areas, the pH increases and most PTE (especially Fe, Al, As and Pb) are readily scavenged from the stream waters by precipitation and/or adsorption processes. On the contrary, Tl behaves almost conservatively along the stream flow path, undergoing only dilution effects and remaining at the concentration of concern of 5 µg/L near the coastline, sharply decreasing to 0.5 µg/L at the mouth due to seawater intrusion. Since stream waters were locally used for crop irrigation, these observations may have important environmental and public health consequences in such a densely populated area.

Keywords: *Acid Mine Drainage; Thallium; Apuan Alps; Baccatoio Stream catchment*

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Introduction

Weathering of iron sulfide minerals is the primary source of acid mine drainage (AMD) which represents a major environmental problem in many active and abandoned mining sites worldwide. In particular, the biotic/abiotic oxidation of pyrite and other metal-sulfides produces sulfuric acid and releases sulfate and potentially toxic trace metals and metalloids (Chen et al. 2007; Moore and Louma 1990; Nordstrom et al. 2015). Some of the pollutants found in AMD, and particularly Fe and Al, quickly precipitate as the pH increases along the migration path. These precipitates play an important role in the removal of some toxic heavy metals and metalloids (e.g. As or Pb) by adsorption and co-precipitation (Cidu 2011; Cheng et al. 2009). Other elements, such as Cd, Ni and Tl, may be only slightly sorbed on Fe-Al precipitates, and are mainly transported into water as dissolved free ions or complexes (Cidu 2011). In particular, Tl is quite mobile in most aqueous environments, and can easily disperse after oxidation of Tl-bearing minerals (Xiao et al. 2012 and references therein).

Thallium exists in two oxidation states, Tl(I) and Tl(III). Tl(I) is the thermodynamically more stable state in most pH and redox (sub)surface conditions (Lin and Nriagu 1997). It is predicted to exist predominantly as free ion in fresh waters, and to form very few strong complexes, as for example $TlCl^0$ in saline environments (Turner et al. 2010). It has been observed that, compared to other trace elements, Tl(I) has a low affinity for suspended particles, undergoing little removal by Fe-Al oxyhydroxides precipitation or by sorption on organic matter (Law and Turner 2011; Turner et al. 2010). Only under reducing conditions, Tl(I) is removed from waters by co-precipitation with and/or adsorption onto Fe sulfide solids (Laforte et al. 2005). In addition, Tl(I) is believed to be held at exchangeable sites and incorporated into the interlayers of illitic and vermiculitic clays (Jacobson et al. 2005). Tl(I) is oxidized to Tl(III) by Mn oxide phases, the latter being tightly bound to the Mn oxide surface or precipitated on the Mn oxide surface as Tl_2O_3 (Bidoglio et al. 1993; Rehkämper and Nielsen 2004). In strongly oxidizing environments Tl(III) may form and precipitate as $Tl(OH)_3$ and/or Tl_2O_3 (Lin and Nriagu 1997).

In natural environments, Tl generally occurs at very low concentration: the mean abundance of Tl in the upper continental crust is 0.75 mg/kg (Wedepohl 1995), less than 1 mg/kg in soil, 5-10 ng/L in freshwater and 10-15 ng/L in seawater (Fergusson 1990; Flegal and Patterson 1985; Peter and Vìraraghavan 2005). However, Tl may be present at relatively high concentration in some sulfide deposits. For instance, pyrite ores with Tl content up to 2000 mg/kg occur in several ore deposits worldwide (e.g. Emsbo et al. 2003; Large et al. 2009; Scott et al. 2009). Within mineralized areas, Tl is present at high levels also in the aquatic system: concentration levels higher than 30 μg/L have been documented (Casiot et al. 2011; Cidu and Frau, 2009; Petrini et al. 2016), and values as high as 1100 μg/L have been reported in groundwater in the Lanmuchang area (southwestern Guizhou Province, China) (Xiao et al. 2004).

The southern sector of the Apuan Alps in northern Tuscany (Italy) is characterized by the occurrence of a series of Tl-rich baryte-pyrite-iron oxide ore bodies, exploited until the early 1990s. According to D'Orazio et al. (2017), the pyrite ores of the M. Arsiccio mine, one of the main mining sites of the southern Apuan Alps, contain Tl at concentration levels up to ~600 mg/kg. Recent geological studies on this area (D'Orazio et al. 2015; Petrini et al. 2015) highlighted Tl mobilization during pyrite oxidation, in addition to other trace metals and metalloids typical of mine drainages (e.g. Fe, As, Sb, Pb, Zn, Cd). These mine drainages discharge directly into the Baccatoio Stream that crosses the Valdicastello Carducci village in the Pietrasanta Municipality and flows into the Ligurian Sea. The local population used the AMD-affected waters of the Baccatoio Stream to irrigate ornamental and vegetable gardens, so contaminating agricultural soils, which in turn threatens the health of people who consume crops grown on such environments (Vittori Antisari et al. 2016).

The goal of the present work is to characterize the geochemistry (physico-chemical properties and major and trace elements) of mine drainages and Baccatoio Stream waters impacted by AMD, analyzing the surface water chemical changes that occur along the flow path, with particular attention to the dispersion of Tl in the aquatic environment.

Study area

The study area is located in the Baccatoio Stream basin, extending from the southern sector of the Apuan Alps massif to the coastline (northern Tuscany, Italy) (Figs 1 and 2). In its upper course, the Baccatoio Stream flows through the metamorphic rocks of the Apuan Unit that crop out through the non-metamorphic sedimentary formations belonging to the Tuscan Nappe in the "Sant'Anna tectonic window" (Carmignani et al. 1976; Molli et al. 2000; Fellin et al. 2007; Fig. 1). The Apuan Alps are characterized by several kinds of ore deposits hosted within the metamorphic units (Fig 1; Lattanzi et al. 1994). In particular, in the southern sector the ore bodies are located at the contact between the phyllites of the Paleozoic basement and the Triassic metadolostones (Grezzoni Formation) belonging to the sedimentary cover of the Apuan Unit (Carmignani et al. 1972, 1976). They consist of a series of baryte-pyrite-iron oxide ore bodies aligned along a ~10 km SW-NE discontinuous mineralized area, exploited for iron production and subsequently for baryte, which was used in petroleum well drilling mud, and pyrite, used for the production of sulfuric acid. The baryte-pyrite-iron oxide ore bodies are almost conformable lens showing mineralogical zoning. Pyrite ± baryte typically occur in the lowermost portion of the ore bodies, near the contact or within the phyllitic complex. Upwards, the content of iron oxide ± baryte generally increases near the contact with metadolostones of the Grezzoni Formation (Carmignani et al. 1972, 1976). The fundamental mineral association of these deposits is constituted by baryte, pyrite, hematite, magnetite, with subordinate amounts of Pb-Zn-Sb-Tl-As-Hg sulfide and sulfosalt minerals (Biagioni et al. 2013). The occurrence of Tl mineralization in the southern Apuan Alps is a recent discovery: thallium mineralization consists of Tl-rich pyrite (up to ~1100 mg/kg) and in the occurrence of Tl sulfosalts or Tl-rich varieties of Pb-As-Sb-Cu sulfides and sulfosalts within baryte-pyrite ore bodies (Biagioni et al. 2014a, b; D'Orazio et al. 2017 and reference therein). Two of the main baryte-pyrite-iron oxide mining districts are located in the Baccatoio Stream catchment, named Pollone and M. Arsiccio mining sites (Fig. 1, 2), exploited till the 1990s. Their major drainages discharge directly into the Baccatoio Stream from Ribasso tunnel and S. Erasmo tunnel, respectively. The Baccatoio Stream itself actually originates from an abandoned tunnel of the M. Arsiccio mine (Ribasso Pianello tunnel) and flows into the Ligurian Sea. It also receives tributaries and spring waters downstream of the mining sites (Fig. 2). The catchment area is characterized by high rainfall (more than 2000 mm/a; Giannecchini and D'Amato Avanzi 2012) and most part of the basin is formed of medium-to-high permeability rocks with a high effective infiltration coefficient (up to 75%; Piccini et al. 1999). These conditions favor a pervasive groundwater circulation, the exposition of pyrite ore bodies to oxidation and the consequent release and dispersion of potentially toxic elements in the environment.

Sampling and analytical methods

In the present study a total of 117 water samples were collected, including mine drainages from two tunnels (48 samples) and superficial waters from eight sampling sites along the Baccatoio Stream (69 samples). Surveys were carried out from 2013 to 2016, in both wet and dry seasons.

The sampling sites are shown in Fig. 2. AMD waters were collected from the Ribasso and S. Erasmo tunnels, in the Pollone and M. Arsiccio mining areas, respectively. Superficial waters of the Baccatoio Stream were collected in stations placed in order to assess possible changes in water chemistry upstream and downstream of the mining sites, also taking into account the inflow of tributaries and springs (Fig. 2). In particular, the BS1 station is located very close to an abandoned tunnel in the M. Arsiccio mine (Sant'Olga tunnel). Two sampling points are located downstream of the mine drainages of the S. Erasmo and Ribasso tunnels (BS2 and BS4, respectively). Four sampling stations are located downstream of the main tributaries and springs (BS3, BS5, BS6 and BS7) and one is near the mouth of the Baccatoio Stream next to the coastline (BS8).

The water samples were filtered through 0.45 μm nylon filters into pre-cleaned polyethylene bottles in the field; the filtered samples were acidified on site by adding ultrapure HNO_3 for cations and trace elements analysis. Alkalinity (totally attributed to HCO_3^-) was measured by titration using 0.1 N HCl. Major ions were analyzed by ion chromatography (Thermo Fisher ICS 900) using a conductivity method of detection. For the anions, a Dionex IonPac AS23 analytical column (4 × 250 mm) was used along with the ASRS 500 (4 mm) suppressor. For the cations, a Dionex IonPac CS12A-5μm analytical column (3x 150 mm) was used with the CMMS 300 (2mm) suppressor. In almost every case the relative standard deviation (RSD, calculated on five replicate injections) was less than 5%. Trace element concentrations were obtained by ICP-MS (PerkinElmer-NexION 300X) using ^{103}Rh, ^{187}Re and ^{209}Bi as internal standards to correct for signal fluctuations and matrix effects. The data accuracy has been tested by replicate analyses (n=7) of the certified reference solution IV-STOCK-1643 (Multi-element Solution Standard, Inorganic Ventures). The deviations from the certified values are generally lower than 10% except for Li, Be, Fe and Zn (12-18 %). At the concentration levels of this reference material, the precisions are better than 5% RSD, except for Al and Zn (10-20% RSD). Ultrapure water (Millipore, Milli-Q, 18.2 MΩ/cm) was used for sample dilution and standard preparation.

Results

Acid mine drainages

Representative physico-chemical parameters and concentrations of major and trace elements of AMD from the Ribasso tunnel (Pollone mining site) and S. Erasmo tunnel (M. Arsiccio mining site) are given in Table 1. The pH ranges from 1.5 to 5.8 in the M. Arsiccio AMD and from 1.6 to 2.5 in the Pollone AMD. S. Erasmo drainages show a greater variability also for EC (313-8970 μS/cm) and Fe concentration (2.08-2240 mg/L) than the Ribasso tunnel ones (2780-6270 μS/cm and 338-1300 mg/L, respectively). In particular, the highest value of pH and the lowest EC and Fe concentration values were observed in the S. Erasmo drainage collected soon after the 08/02/2016 heavy rainfall (more than 60 mm in few hours), likely indicating dilution effects resulting from rapid and direct infiltration of meteoric waters. The higher variability of M. Arsiccio mine waters compared to Pollone is hence likely related to the larger effect of seasonal variability in the former.

The extremely high concentrations of SO_4^{2-} vary from an average value of 4.9 g/L in the Pollone mine drainages (4.0-5.8 g/L) to 5.9 g/L in the M. Arsiccio mine drainages (3.8-7.9 g/L); the Cl^- concentrations are relative low, with average values of 19.6 mg/L and 12.2 mg/L, respectively. The dominant dissolved metals and metalloids in the M. Arsiccio mine waters, in order of average abundance, are Fe (1190 mg/L) > Al (12 mg/L) > Mn (3.31 mg/L) > As (1.42 mg/L) > Zn (1.1 mg/L) > Sr (951 μg/L) > Tl (475 μg/L) > Ni (246 μg/L). For the Pollone mine, they are: Fe (748 mg/L) > Zn (59 mg/L) > Al (20 mg/L) > As (3.31 mg/L) > Cu (1.91 mg/L) > Mn (1.74 mg/L) > Ni (427 μg/L) > Sb (364 μg/L).

The average concentrations of Fe, Al, Mn, As, Ni, Co, Cd, Sb, Tl and Pb exceed their respective maximum contaminant levels for groundwater imposed by Italian Regulation (Decreto Legislativo no. 152/2006; Table 1); in the case of the Pollone mine, Cu and Zn also exceed the normative values.

Baccatoio Stream water

Variations of the physico-chemical and geochemical parameters of the waters along the Baccatoio Stream are summarized in Table 2 and plotted in Figs. 3 and 4.

The pH ranges from 2.7 in BS1 (where the stream originates from an abandoned mine working at the M. Arsiccio mining site) to 8.2 in BS6. The EC varies from 392 (BS3) to 2330 μS/cm (BS1). pH and EC show a negative correlation (Fig. 3) related to the pH-dependent precipitation of iron-bearing phases and adsorption processes (Edraki et al. 2005; Nordstrom 2011). In general, the EC decreases downstream, except for the sharp increase at station BS8, close to the mouth, reflecting the marine ingression in the surface waters. The seawater ingression is also supported by the highest average values of K^+ (20.0 mg/L), Na^+ (273 mg/L) and Cl^- (492 mg/L) of the samples taken from the BS8 station. The Baccatoio Stream waters show a dominant Ca(Mg)-SO_4 composition in the upper course of the stream (BS1 and BS2 sampling stations). Along the Baccatoio watercourse, the stream waters are shifted towards a graduate increase in the HCO_3^- content, due to the mix with uncontaminated tributaries and groundwater draining carbonatic rocks. From BS5 to BS7 stations, the stream waters show a dominant Ca-HCO_3(SO_4) composition. Trace element data show that the average concentrations of Al, Mn, Fe, Ni, As, Sb, Tl and Pb exceed their respective environmental quality standards (EQS) as reported in the Italian Regulation for surface and groundwater (Decreto Legislativo no. 152/2006), in many stations (Table 2; Fig. 4). In particular, the sampling sites BS1, BS2 and BS4 are the most impacted, as expected since they are the nearest sites downstream of the S. Erasmo and Ribasso discharges. Moreover, the surface water samples collected at these sites show a great variability in water chemistry (Table 2), mainly due to seasonal variations related to rainfalls. The metals and metalloids concentrations significantly attenuate along the watercourse (Fig. 4). Only Tl is invariably above the threshold of 2 μg/L, except at the mouth of the stream, with average concentrations ranging from 90 μg/L 200 m downstream of the S. Erasmo tunnel water input (BS2) to 3.8 μg/L in the BS6 sampling point, just outside the Valdicastello village.

Discussion

The data collected allow us to make a first evaluation of the environmental impact of the mine drainages on the water quality in the Baccatoio Stream catchment.

The low pH, high EC, and high Fe and SO_4^{2-} concentrations of mine drainages (SO_4^{2-} up to 5800 mg/L in the Ribasso AMD and 7940 mg/L in the S. Erasmo AMD, Table 1) can be attributed to the oxidation of pyrite and other sulfide minerals.

The differences in the chemistry of the two mine drainages are shown in the Ficklin diagram (Fig. 5). According to Plumlee et al. (1999), the differences in the sum of Zn, Cu, Cd, Pb, Co and Ni concentrations for different mine waters allow us to distinguish the geological characteristics of the deposits from which they drain. Both the AMD studied can be classified as high acid-high metal type, though the Pollone mine drainages show a much higher metal content likely due to the occurrence of a larger proportion of polymetallic sulfides other than pyrite, e.g. sphalerite and galena (Carmignani et al. 1972; Costagliola et al. 1998). In fact, while in the M. Arsiccio mine almost 99.3% of the total metals and metalloids in AMD is Fe (98.3%) and Al (1.0%), in the Pollone mine waters Fe (89.4%), Zn (7.1%), Al (2.4%) and As (0.4%) altogether represent 99.3% of the total metals and metalloids. It is likely that Al originates from the dissolution of aluminosilicate minerals occurring within the ore bodies or within the host rocks. By contrast, M. Arsiccio mine drainages disperse in the environment the highest levels of Tl (Table 1). This is due to the Tl-rich nature of the pyrite ore of this mine, where macroscopic Tl-sulfosalts have also been found (D'Orazio et al. 2017 and references therein).

As already stated, the acidic waters flow directly from the mine tunnels into the adjacent Baccatoio Stream. The superficial waters taken from the sampling sites downstream of the mine water inputs are classified as high acid-low metal (BS1 and BS2) and near neutral-high metal (BS4) waters. The surface waters collected in remaining sampling sites are near neutral-low metal waters (BS3, BS5, BS6, BS7, BS8). These observations are consistent with a decrease in the concentration of SO_4^{2-} and metals and metalloids along the Baccatoio watercourse, with simultaneous increase in pH. To evaluate the contribution of dilution/precipitation effects on the changes of the Baccatoio water chemistry along its watercourse, the average concentrations of BS2 and BS3 can be compared, since an abrupt increase in pH and decrease in dissolved metals and metalloids is observed (Figs. 3, 4). Such variations are caused by the inflow of near-neutral spring waters (flow rate in the range 12 - 200 L/s; Fig 6) into the Baccatoio Stream (Fig. 2). In particular, downstream of the spring inflow, the concentrations of Fe, Al, Pb and As significantly decrease, suggesting the combining effects of dilution due to the spring water and the removal by precipitation of Fe-Al oxyhydroxides, which in turn favours adsorption and removal of other dissolved species (Cidu 2011; Nordstrom 2011). The precipitation of Fe-bearing solid phases is confirmed by the widespread encrustations observed on the Baccatoio Stream bed (Fig. 6). A decrease in the Tl concentration is also observed, even if this element remains at concentration of concern suggesting a higher mobility with respect to Pb and As in this environment. A linear positive correlation is observed between SO_4^{2-} and Tl concentration in stations from BS3 to BS7 (not shown, R^2=0.97): considering SO_4^{2-} as conservative in this pH range (Edraki et al. 2005; Nordstrom 2011), it is suggested that the decrease of Tl concentration in this section of the stream mostly results from dilution, and that sorption is not a significant process for immobilization of this element. In summary, the data obtained by this study indicate that the Baccatoio Stream catchment is a favorable area for the natural release of Tl and other toxic metals and metalloids into the aquatic system. Drainages from mines appear to be the main source of contamination. The input of unpolluted tributaries and groundwater in the stream mitigates the contamination for all elements through dilution and precipitation of solid phases. Due to its quite high mobility and its low affinity for the precipitates, Tl may disperse easily in most aqueous environments (Xiao et al. 2012), representing an environmental and human health hazard.

Conclusions

Geochemical surveys carried out over three years allowed us to make a first evaluation of the environmental impact of AMD on the Baccatoio Stream waters, which are used for irrigation by the local population.

The data suggest that the oxidation of pyrite and other sulfides is occurring, generating acidity and metal-rich discharges. The highest dissolved base-metal (Zn, Cu, Cd, Pb, Co, Ni) values are found in the Pollone mine waters, reflecting a large abundance of base-metal sulfides, such as sphalerite and galena, in the ore bodies they drain. In contrast, the M. Arsiccio mine drainages disperse into the environment the highest levels of Tl, because of the Tl-rich nature of the pyrite ores occurring in this mine. The Baccatoio Stream is highly impacted by AMD since it receives the acidic high metal-content mine waters. However, most of the pollutants decrease in concentrations along the Baccatoio watercourse up to fit the standard quality levels set by the Italian Regulation. Indeed, the uncontaminated tributaries and groundwater mix with polluted surface waters, thus lowering the concentration of most toxic elements by dilution, as well as by precipitation of Fe-Al oxyhydroxides and adsorption or co-precipitation of some elements (in particular As and Pb). Thallium migrates along the Baccatoio Stream maintaining concentrations above 2 µg/L (maximum contaminant level for groundwater set by Italian Regulation). The use of the Baccatoio Stream as irrigation source for ornamental and vegetable gardens may cause a Tl-contamination in agricultural soils, creating the conditions for environmental and human health hazards. In addition, the highly polluted character of the catchment requires the careful monitoring of water quality of natural springs currently used as drinking water supply.

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Figure captions

Fig. 1 Simplified geological map of the southern Apuan Alps, Tuscany, with locations of the baryte – pyrite – iron oxides deposits (modified after D'Orazio et al. 2017). The solid white line encloses the "Sant'Anna tectonic window"

Fig. 2 Sketch map of the study area showing the sampling sites along the course of the Baccatoio Stream

Fig. 3 Variations of average pH and EC along the Baccatoio Stream watercourse. The inflow from the S. Erasmo and Ribasso AMDs and from the Molini di Sant'Anna spring is indicated

Fig. 4 Variations of average metals and metalloids concentrations along the Baccatoio Stream watercourse. The environmental quality standards (EQS) according to the Italian Regulation for surface and groundwater (Decreto Legislativo no. 152/2006) are superimposed. Arrowed symbols indicate concentrations below the detection limits

Fig. 5 Ficklin diagram (Plumlee et al. 1999) for mine drainages (red solid circles) and Baccatoio Stream waters (black solid square)

Fig. 6 Baccatoio Stream at the point where uncontaminated water from the Molini di Sant'Anna spring (left side) mixes with the AMD-contaminated water of the stream (right side)

Figure 1-revised

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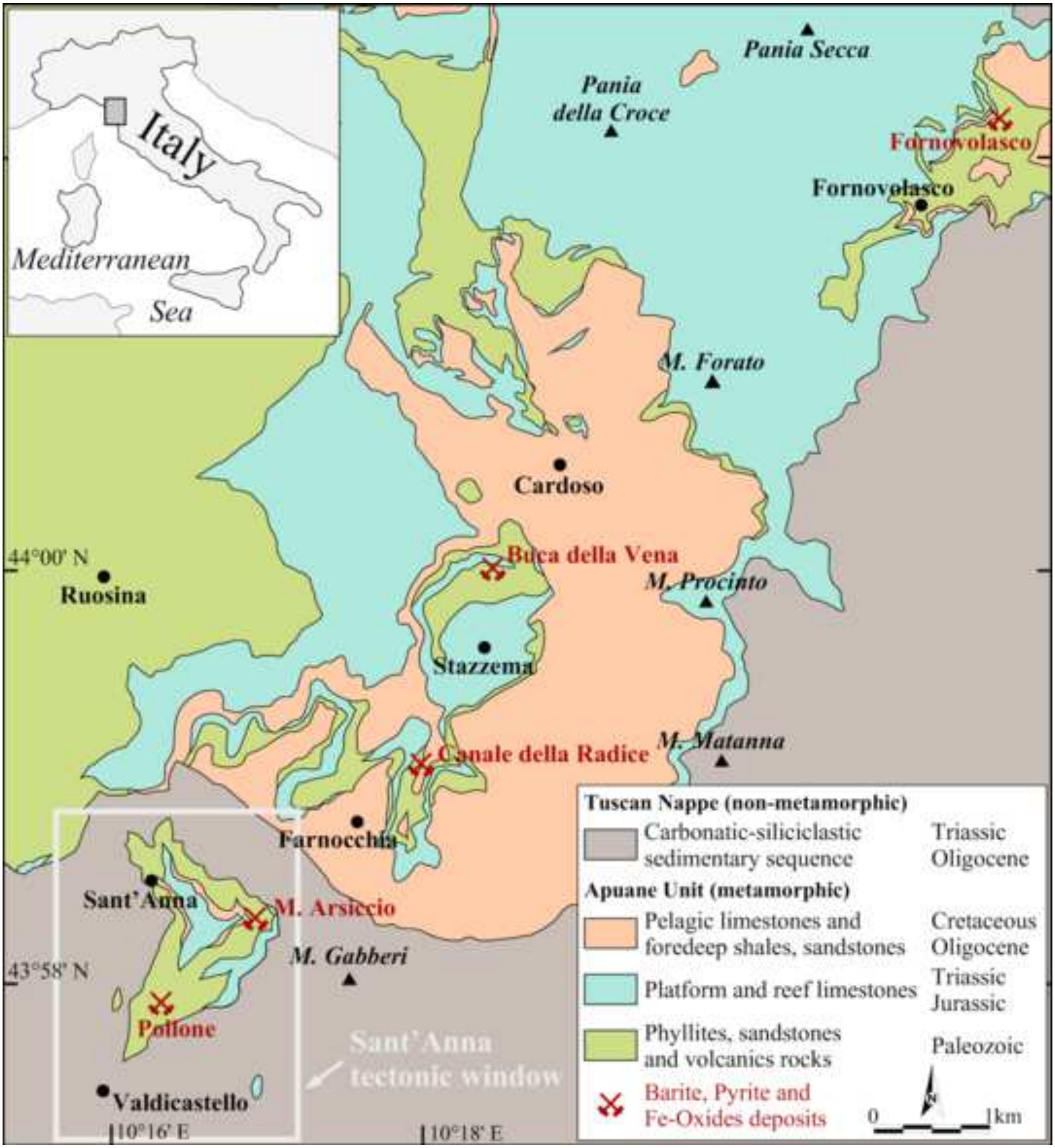

Figure 2-revised

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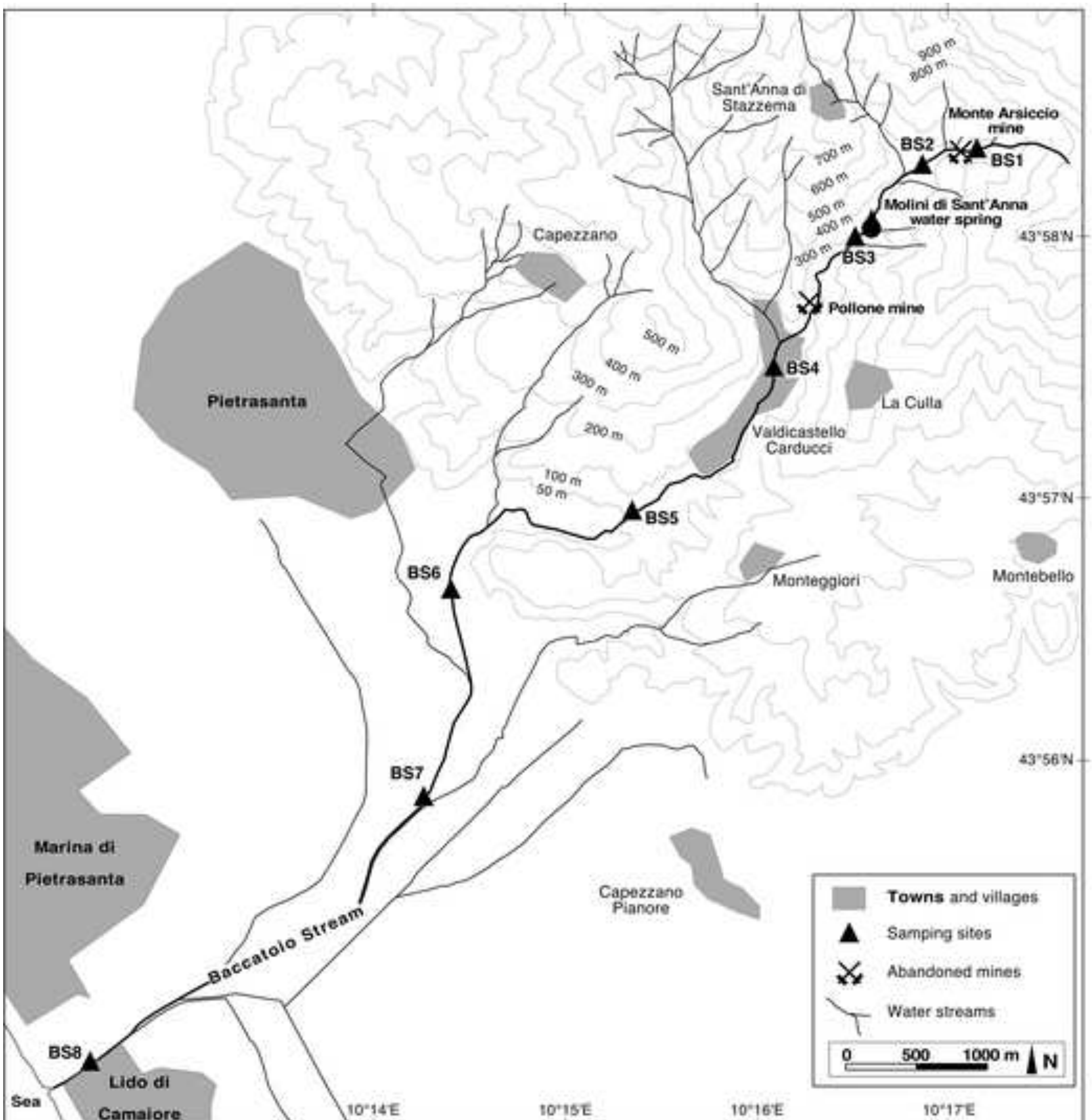

Figure 3-revised

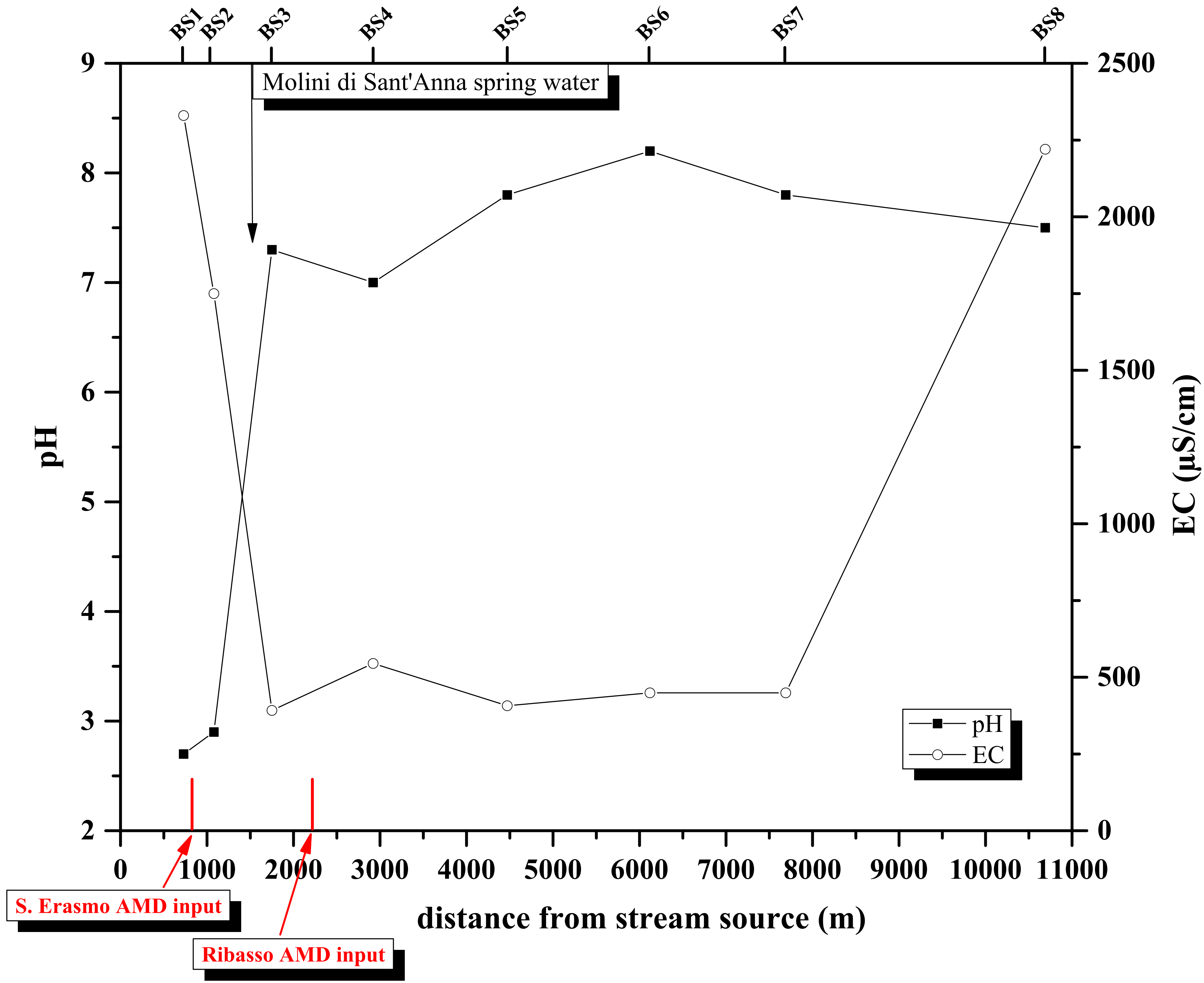

Figure 4-revised

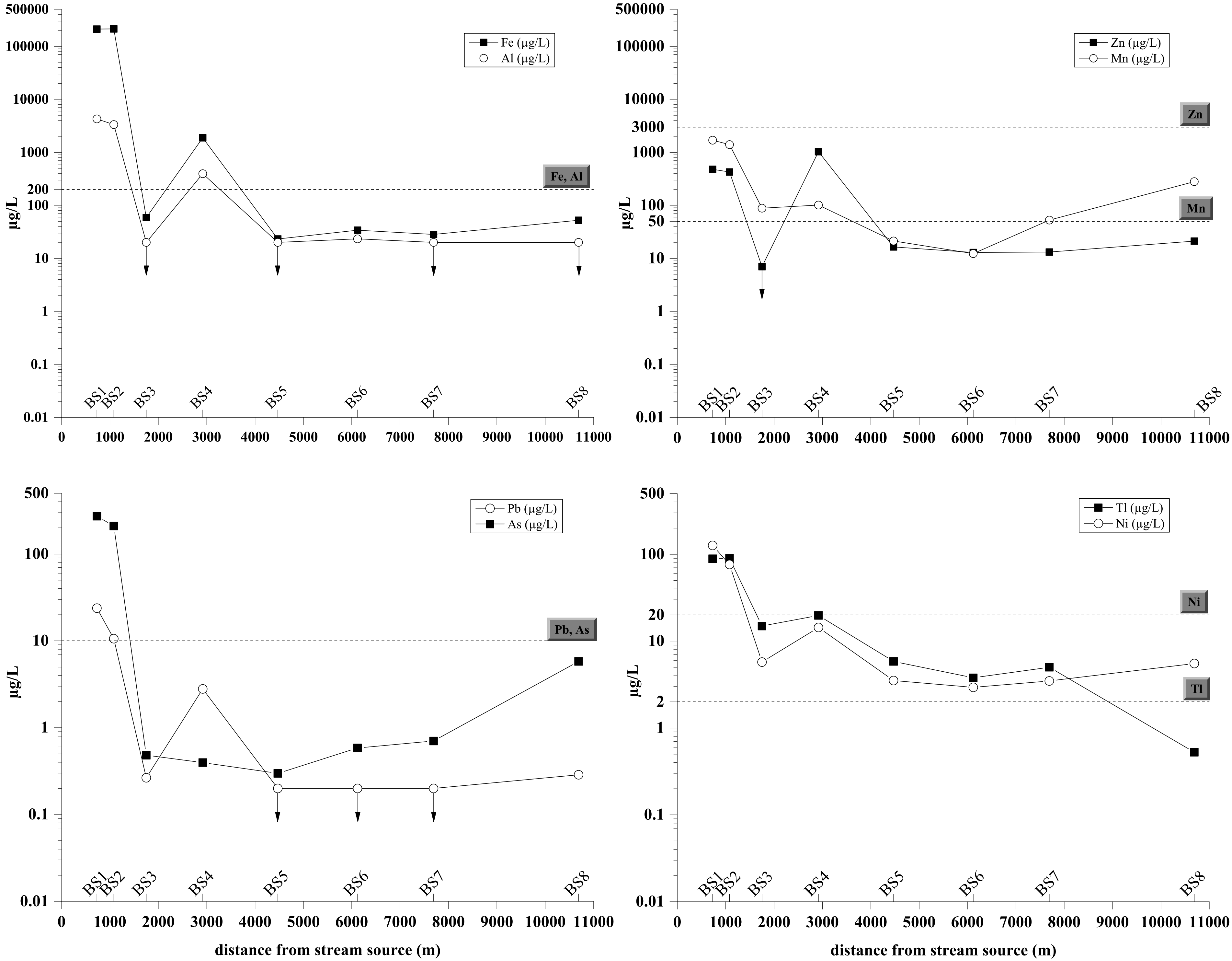

Figure 5-revised

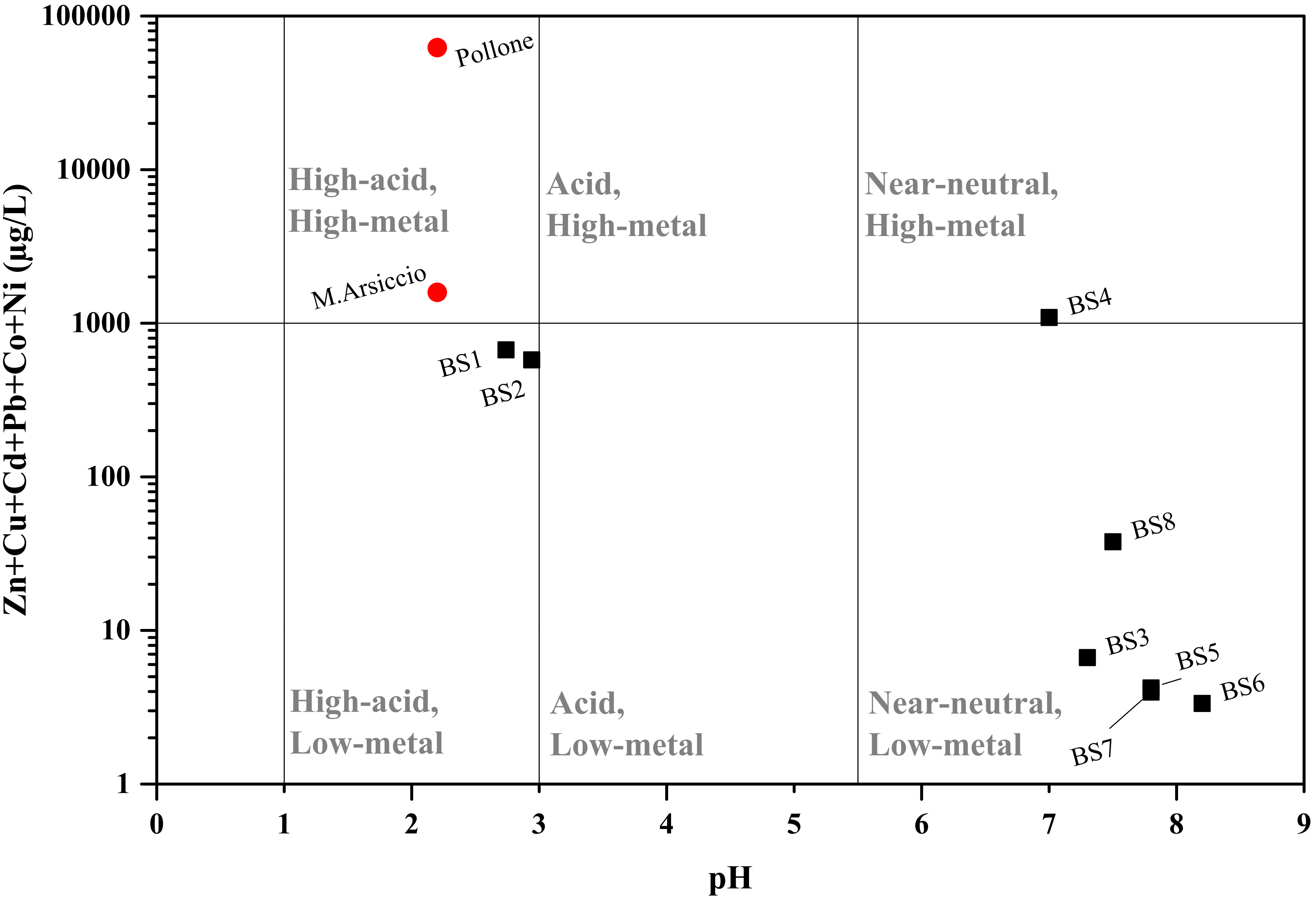

Figure 6-revised

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Table 1 Average value and variation interval (min-max) for temperature (T), pH, electrical conductivity (EC) and concentration of major ions and trace elements in mine drainage waters. n: number of samples; min: minimum value; max: maximum value. The gray background highlights the values that exceed the limits set by the Italian Regulation for groundwater (Al 200, Fe 200, Zn 3000, Mn 50, Cu 1000, As 10, Ni 20, Cr 50; Co 50, Cd 5, Sb 5, Tl 2, Pb 10, all values in µg/L; SO_4 250, in mg/L)

	Pollone mine – Ribasso tunnel				**M. Arsiccio mine** – S. Erasmo tunnel			
	n	min	max	**average**	n	min	max	**average**
T (°C)	14	10.6	17.2	**12.4**	14	8.9	15.6	**11.3**
pH	29	1.6	2.5	**2.2**	18	1.5	5.8	**2.2**
EC (µS/cm)	29	2780	6270	**4240**	19	313	8970	**5520**
Na (mg/L)	5	9.3	13.7	**11.5**	6	5.3	10.1	**7.8**
K (mg/L)	5	1.8	4.7	**2.9**	6	2.12	7.3	**3.6**
Ca (mg/L)	5	113	154	**134**	6	184	321	**251**
Mg (mg/L)	5	21.9	29.2	**26.5**	6	96	151	**127**
Cl (mg/L)	2	15.5	23.6	**19.6**	2	9.7	14.7	**12.2**
SO_4 (mg/L)	2	4010	5800	**4900**	2	3790	7940	**5870**
Al (mg/L)	13	6.9	36	**20**	13	0.21	22	**12**
Mn (mg/L)	13	1.11	2.50	**1.74**	13	0.19	5.4	**3.31**
Fe (mg/L)	13	338	1300	**748**	13	2.08	2240	**1190**
Cu (mg/L)	13	1.03	3.7	**1.91**	13	0.01	0.28	**0.16**
Zn (mg/L)	13	45	89	**59**	13	0.14	1.6	**1.1**
As (mg/L)	13	1.12	6.8	**3.31**	13	0.14*	2.66	**1.42**
Li (µg/L)	13	12.5	30.1	**18.5**	13	0.81	27.3	**14.2**
Be (µg/L)	12	1.02	3.25	**1.87**	13	0.09	1.88	**0.86**
V (µg/L)	13	8.9	45	**25.4**	13	0.03	120	**55**
Cr (µg/L)	13	17.5	62	**37**	13	0.20	43	**20.7**
Co (µg/L)	12	131	222	**172**	13	1.76	94	**57**
Ni (µg/L)	13	276	1060	**427**	13	13.1	370	**246**
Sr (µg/L)	13	68	406	**285**	13	88	1450	**951**
Mo (µg/L)	12	3.4	9.4	**5.4**	13	0.20	19.2	**10.3**
Ag (µg/L)	12	0.43	1.93	**0.95**	13	< 0.02	0.73	**0.17**
Cd (µg/L)	13	88	419	**284**	13	1.29	12.0	**7.6**
Sn (µg/L)	12	< 0.04	0.58	**0.14**	12	0.06	0.62	**0.29**
Sb (µg/L)	13	111	639	**364**	13	0.16	200	**105**
Ba (µg/L)	12	5.0	11.7	**9.8**	13	5.0	54	**29.5**
Tl (µg/L)	13	107	1000	**266**	13	7.3	856	**475**
Pb (µg/L)	13	191	388	**279**	13	< 0.2	36	**18.0**
Th (µg/L)	12	62	174	**99**	13	0.16	50	**29.9**
U (µg/L)	12	37	112	**66**	13	0.29	37	**24.4**

Table 2 Average value and variation interval (min-max) for temperature (T), pH, electrical conductivity (EC) and concentration of major ions (a) and trace elements (b) in the Baccatoio Stream waters. n: number of samples; min: minimum value; max: maximum value; av: average value; nd: not determined

(a)

		T (°C)	pH	EC μS/cm	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	Cl mg/L	SO_4 mg/L	HCO_3 mg/L
BS1 (n=4)	min	8.9	2.5	1540	7.3	0.68	227	92	11.2	1420	nd
	max	11.9	2.9	2800	8.8	0.85	290	111	12.8	1600	nd
	av	**10.8**	**2.7**	**2330**	**7.9**	**0.77**	**259**	**102**	**12.0**	**1507**	**nd**
BS2 (n=13)	min	8.1	2.4	401	4.3	0.91	80	24.9	7.5	589	nd
	max	17.9	6.0	3570	9.5	2.69	269	122	23.9	2580	nd
	av	**10.5**	**2.9**	**1750**	**7.4**	**1.62**	**159**	**65**	**11.7**	**1400**	**nd**
BS3 (n=5)	min	12.2	6.9	324	5.9	0.57	57	12.5	10.1	143	30
	max	13.0	7.8	460	8.9	5.5	86	23.4	19.4	158	171
	av	**12.5**	**7.3**	**392**	**7.2**	**2.08**	**69**	**16.4**	**12.8**	**150**	**97**
BS4 (n=11	min	10.4	3.2	286	5.6	0.53	50	6.3	7.7	40	nd
	max	20.7	8.3	1140	10.9	2.63	128	28.9	15.9	487	128
	av	**15.1**	**7.0**	**545**	**8.7**	**1.05**	**74**	**17.0**	**12.3**	**203**	**86**
BS5 (n=7)	min	11.8	6.7	356	6.6	0.82	55	7.9	9.9	67	138
	max	15.6	8.3	437	10.0	1.60	88	12.5	15.3	113	238
	av	**14.2**	**7.8**	**407**	**8.8**	**1.09**	**71**	**10.4**	**13.3**	**91**	**171**
BS6 (n=8)	min	11.0	7.9	391	9.1	1.08	68	7.7	13.3	62	159
	max	25.9	8.3	567	10.8	2.21	86	13.6	17.9	124	187
	av	**15.4**	**8.2**	**449**	**9.8**	**1.34**	**78**	**10.9**	**15.4**	**89**	**175**
BS7 (n=11)	min	11.4	6.6	353	6.8	0.88	54	7.5	10.0	56	108
	max	15.7	8.3	676	32.7	3.08	89	14.6	37	106	229
	av	**13.2**	**7.8**	**449**	**12.6**	**1.62**	**73**	**10.9**	**17.0**	**83**	**169**
BS8 (n=4)	min	12.5	7.4	1520	129	11.6	99	31.9	292	75	281
	max	18.4	7.7	3430	486	24.3	107	66	830	171	299
	av	**14.7**	**7.5**	**2220**	**273**	**20.0**	**102**	**44**	**492**	**108**	**291**

(b)

		Li µg/L	Be µg/L	Al µg/L	V µg/L	Cr µg/L	Mn µg/L	Fe µg/L	Co µg/L	Ni µg/L	Cu µg/L	Zn µg/L	As µg/L	Sr µg/L	Mo µg/L	Ag µg/L	Cd µg/L	Sn µg/L	Sb µg/L	Ba µg/L	Tl µg/L	Pb µg/L	Th µg/L	U µg/L
BS1 (n=4)	min	12.0	0.43	2500	3.3	6.6	1400	152000	9.5	101	6.2	400	93	547	< 0.1	0.05	2.81	< 0.04	4.5	10.0	59	11.3	0.95	3.8
	max	16.5	0.67	5500	10.8	11.6	1970	320000	15.9	154	44	53	529	769	1.33	0.26	3.18	< 0.04	27.6	23.7	115	36	2.58	7.7
	av	**14.4**	**0.54**	**4300**	**6.4**	**8.6**	**1700**	**212000**	**13.5**	**126**	**24.3**	**480**	**273**	**688**	**0.58**	**0.13**	**2.97**	**< 0.04**	**13.9**	**14.9**	**89**	**23.8**	**1.57**	**6.3**
BS2 (n=13)	min	1.74	0.01	< 20	< 0.03	0.20	156	16.5	1.30	11.4	3.00	19	0.19	139	< 0.1	0.04	0.22	< 0.04	0.56	10.0	9.2	< 0.2	0.13	0.02
	max	11.9	1.14	11000	15.4	18.9	5590	550000	38	227	171	2300	447	1090	2.86	0.25	12.7	0.40	28.8	56	170	31.9	7.5	18.2
	av	**5.5**	**0.35**	**3300**	**6.2**	**5.2**	**1400**	**214000**	**13.2**	**76**	**44**	**430**	**211**	**387**	**1.33**	**0.09**	**2.64**	**0.13**	**10.4**	**29.2**	**90**	**10.6**	**4.8**	**5.8**
BS3 (n=5)	min	0.87	0.01	< 20	< 0.03	< 0.1	63	12.3	0.34	2.80	< 1	< 7	< 0.03	91	< 0.1	< 0.02	0.05	< 0.04	0.19	32.6	9.3	< 0.2	0.01	0.01
	max	1.21	0.10	< 20	2.00	2.00	110	114	0.97	8.8	2.00	11	2.00	154	0.4	0.21	0.10	< 0.04	0.58	53	25.0	0.50	0.06	0.56
	av	**1.02**	**0.04**	**< 20**	**0.43**	**0.59**	**89**	**59**	**0.58**	**5.7**	**< 1**	**< 7**	**0.48**	**112**	**0.2**	**0.07**	**0.08**	**< 0.04**	**0.44**	**46**	**14.9**	**0.27**	**0.03**	**0.18**
BS4 (n=11)	min	< 0.06	0.01	< 20	< 0.03	< 0.1	23.0	5.8	0.39	2.14	< 1	13	0.14	40	< 0.1	< 0.02	0.17	< 0.04	0.39	8.9	3.18	< 0.2	0.01	0.03
	max	3.9	0.13	2600	0.19	1.89	287	19500	20.0	62	273	6500	1.78	161	0.34	0.04	18.1	< 0.04	2.99	53	93	22.4	0.03	4.4
	av	**1.19**	**0.05**	**400**	**0.04**	**0.23**	**101**	**1880**	**4.4**	**14.4**	**40**	**1000**	**0.40**	**113**	**0.19**	**< 0.02**	**3.21**	**< 0.04**	**1.76**	**40**	**19.8**	**2.79**	**0.02**	**0.72**
BS5 (n=7)	min	0.69	0.01	< 20	< 0.03	< 0.1	< 0.2	12.7	0.08	1.97	< 1	< 7	0.22	90	0.23	< 0.02	0.03	< 0.04	0.85	35	3.7	< 0.2	0.01	0.08
	max	1.02	0.01	32	< 0.03	0.20	38	35	0.55	5.9	2.00	36	0.44	216	0.43	0.04	0.36	< 0.04	2.41	47	8.7	0.30	0.02	0.67
	av	**0.83**	**0.01**	**< 20**	**< 0.03**	**0.13**	**21.2**	**23.2**	**0.41**	**3.5**	**1.08**	**17**	**0.30**	**141**	**0.30**	**< 0.02**	**0.17**	**< 0.04**	**1.65**	**40**	**5.8**	**< 0.2**	**0.01**	**0.31**
BS6 (n=8)	min	0.10	0.01	< 20	< 0.03	< 0.1	1.03	6.5	0.14	0.86	< 1	< 7	0.29	102	0.25	< 0.02	0.01	< 0.04	1.40	37	1.60	< 0.2	0.01	0.29
	max	1.00	0.10	60	0.04	0.15	30.8	141	0.44	6.0	3.6	24	0.84	228	1.87	0.04	0.21	< 0.04	2.17	106	5.41	0.34	0.06	0.66
	av	**0.78**	**0.06**	**23**	**< 0.03**	**0.13**	**12.3**	**34**	**0.31**	**2.94**	**1.36**	**13**	**0.58**	**181**	**0.56**	**< 0.02**	**0.11**	**< 0.04**	**1.76**	**51**	**3.8**	**< 0.2**	**0.03**	**0.40**
BS7 (n=11)	min	0.64	0.01	< 20	< 0.03	< 0.1	0.42	14.1	< 0.1	1.51	< 1	< 7	0.38	91	0.25	< 0.02	0.03	< 0.04	1.10	35	3.24	< 0.2	0.01	0.08
	max	1.50	0.01	28	1.22	0.20	389	57	0.91	8.3	3.09	22	1.56	231	0.87	0.16	0.09	< 0.04	3.20	104	7.1	0.30	0.07	1.25
	av	**0.89**	**0.01**	**< 20**	**0.16**	**0.12**	**53**	**28.3**	**0.30**	**3.5**	**1.95**	**13**	**0.70**	**152**	**0.39**	**0.05**	**0.06**	**< 0.04**	**1.75**	**48**	**5.0**	**< 0.2**	**0.03**	**0.47**
BS8 (n=4)	min	5.3	0.01	< 20	0.38	0.15	223	40	0.56	2.31	1.99	14	3.4	478	1.12	< 0.02	0.02	< 0.04	0.53	29.4	0.17	0.21	0.01	0.38
	max	13.8	0.01	249	1.65	0.22	330	75	1.08	8.5	19.2	40	7.3	876	1.84	0.03	0.07	0.05	1.62	52	1.01	0.41	0.01	1.10
	av	**8.8**	**0.01**	**< 20**	**1.00**	**0.18**	**281**	**52**	**0.73**	**5.5**	**10.0**	**21**	**5.8**	**653**	**1.37**	**< 0.02**	**0.03**	**< 0.04**	**1.02**	**37**	**0.53**	**0.29**	**0.01**	**0.64**