Mobility and fate of Thallium and other potentially harmful elements in drainage waters from a decommissioned Zn-Pb mine (North-Eastern Italian Alps)

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ABSTRACT

The potential impact of decommissioned mining areas on the quality of water resources is an issue of major concern for local communities. Acid mine drainage resulting from hydrolysis and oxidation of metal sulphides associated with mineral veins or mining wastes is often responsible for leaching large amounts of potentially harmful elements (PHEs) in solution, which can be dispersed into the surrounding environment and affect the quality of the recipient water bodies.

The aim of the present study was to investigate the geochemical properties of the mine drainage waters at the decommissioned Salafossa mine (North-Eastern Italian Alps), to highlight anomalous concentrations of PHEs outflowing from the currently flooded galleries and to elucidate their speciation.

In spite of the Zn-Pb sulphides still present in the body ore, there is no evidence of acid drainage waters from the mine galleries as a result of the buffering effect produced by carbonate host rocks. Due to their high mobility, however, Zn and Tl are present in solution mostly in ionic form. Conversely, the less mobile Pb, is preferably partitioned in the solid phase. Additionally, the oxidising conditions of the drainage waters also allow the precipitation of some PHEs (As, Cd, Pb, Tl, Zn) in the form of Fe-Mn oxy-hydroxides and carbonates, which accumulate at the bottom of the mine galleries as fine "sediments" or concretions. Drainage waters inside the mine were found to be highly enriched in Zn (up to 16 mg L^{-1}), Fe (up to 5 mg L^{-1}) and Tl (up to 260 μg L^{-1}). Their concentrations, however, are partially diluted in the mine due to a mixing with less mineralised waters before being discharged into the Piave River, the major tributary downstream from the mining area. Although drainage waters are still characterised by high concentrations of Tl (about 30 μg L^{-1}) at their outflow, dilution in the Piave River seems to be the only natural process mitigating the impact of PHEs within the drainage basin.

1. Introduction

Mining activity and related mineral processing are generally considered among the major anthropogenic sources of potentially harmful elements (PHEs) and other contaminants in the environment (Callender, 2004). The resulting environmental contamination is mainly due to the presence not only of major metal(oid)s mined but also of other minor constituents of sulphides which are highly toxic (As, Cd, Hg and Tl). Decommissioned mining sites represent the usual case studies in environmental sciences, especially regarding the dispersion and geochemical mobility of PHEs which can cause contamination of soils (Rodríguez et al., 2009; Nannoni et al., 2011), sediments (Bačeva et al., 2014; Ospina-Alvarez et al., 2014; Resongles et al., 2014; Stefanowicz et al., 2014), waters (Alderton et al., 2005; Nordstrom, 2011; Ramani et al., 2014; Tatsi and Turner, 2014) and vegetation (Dinelli and Lombini, 1996; Zhao et al., 2003; Xiao et al., 2004a).

The physico-chemical alteration of tailing deposits, deriving from extractive processes employed to recover Zn and Pb from *sphalerite* (ZnS) and *galena* (PbS) respectively, are the cause of several environmental issues (Stefanowicz et al., 2014; Concas et al., 2006; Rodríguez et al., 2009; Ramani et al., 2014). Mine drainage waters, enriched in PHEs deriving from sulphide oxidation processes at decommissioned
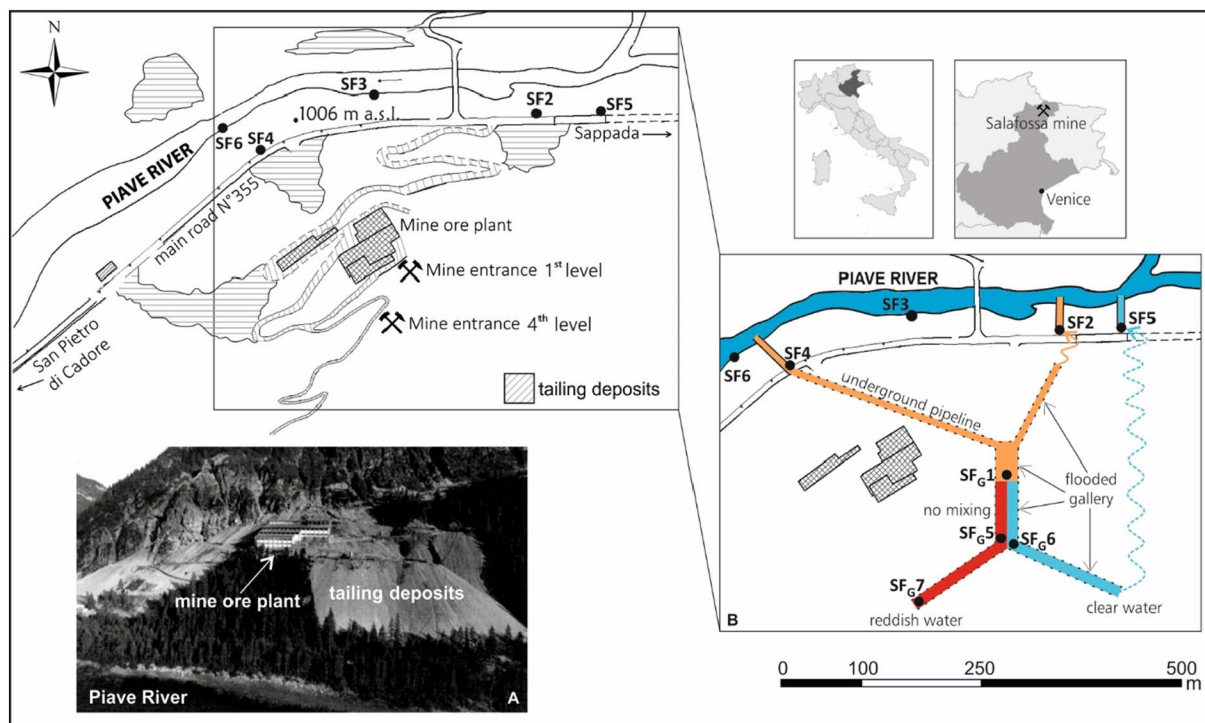

Fig. 1. Index map of the Salafossa mining area with the location of the sampling points where water samples were collected. A. Photography from Veneto Region archives. B. Scheme of the lower flooded gallery where mixing and dilution processes occur.

mining sites, can have a negative impact on the surrounding environment, both in acid and alkaline conditions (Xiao et al., 2003; Blowes et al., 2004; Concas et al., 2006; Moreno and Neretnieks, 2006; Cánovas et al., 2007; Lecomte et al., 2017).

The pH of the drainage waters strongly depends on the relationship between sulphide hydrolysis and oxidation, which promote a pH decrease, and the buffering capacity of carbonates, which is in turn responsible for a pH increase. Despite the neutralisation degree linked to the dissolution process of calcareous and dolomitic rocks, mine drainage waters are often characterised by high concentrations of PHEs (Blowes et al., 2004) such as Fe, Mn, As, Pb, Cu, Zn and Tl.

According to the *Agency for Toxic Substances and Disease Registry* (ATSDR, 1992; 2014), Tl is typically present in the environment as inorganic compounds and in combination with other elements, such as O and S. This element is generally associated with minerals containing K, Zn, Fe, Pb and Cu sulphides (*i.e. sphalerite*, ZnS; *pyrite*, FeS_2; *galena*, PbS; *chalcopyrite*, $CuFeS_2$), and, in some of them (*lorandite*, $TlAsS_2$; *avicennite*, Tl_2O_3) it also reaches major concentrations (Kazantzis, 2000; Peter and Viraraghavan, 2005; Kabata-Pendias, 2011). In addition, the oxidisable fraction of Zn-Pb ore represents the major source of Tl dispersion in the environment (Karbowska et al., 2014).

Tl compounds are generally characterised by high water solubility and the element is mainly present as a monovalent ion (Tl^+) in aqueous systems; in addition, the trivalent ionic form (Tl^{3+}) also exists under strongly oxidising conditions (Vink, 1993). In the presence of strongly reductive conditions, Tl can precipitate as sulphide (Tl_2S) whereas, in oxidising environments, its trivalent ionic form (Tl^{3+}) can precipitate as a hydroxide ($Tl(OH)_3$). Moreover, Tl can be the subject of adsorption processes in aqueous solutions, especially in the presence of Fe and Mn oxides and hydroxides, or it can be bioconcentrated by vegetation tissues in aquatic as well as terrestrial environments (Pavoni et al., 2017).

Following several authors (Xiao et al., 2004a and Xiao et al., 2004b; Queirolo et al., 2009; Xiong, 2009; Xiao et al., 2012; Tatsi and Turner, 2014; Petrini et al., 2016), high Tl concentrations were often found in soil, drainage water and tailing samples collected near many mine sites. The presence of Tl in surface water and groundwater represents a very

important issue for human health due to the extremely high toxicity of this element, which is comparable to that of Pb and Hg even when it exists at a low concentration (Kazantzis, 2000; Peter and Viraraghavan, 2005; Campanella et al., 2016). Tl intoxication can occur through several pathways of exposure, such as dermal absorption, inhalation and ingestion. Although this element is usually excreted in the urine, it can accumulate in the bones, kidneys and central nervous system, thus going from acute to chronic toxicity effects (U.S. EPA, 2009). In the first case, symptoms depend on the individual age, pathway of exposure and metal dose and consist of vomiting, diarrhoea, temporary hair loss, negative effects on the central nervous systems and other organs, such as heart, lungs, liver and kidneys. Chronic intoxication occurs after a long-term exposure to low concentrations as was the case of the mineralised area nearby Lanmuchang (Guizhou, China), where the presence of tailings, heavily enriched in Tl along with Hg and As, caused chronic Tl poisoning of the population with hundreds of deaths. Tl intoxication was mainly caused by high concentrations in drinking water and the content of Tl in the urine of the population remained persistently high (153–2,668 µg L^{-1}) after several years, (Xiao et al., 2004a and Xiao et al., 2004b). Moreover, the consumption of vegetables grown in contaminated soils has also contributed to the poisoning of humans as highlighted by Tl concentrations in urine samples which were positively correlated to those of crop samples (Xiao et al., 2007). Anorexia, headache, abdominal pain, alopecia, blindness and death are all symptoms of chronic Tl poisoning (Zhang et al., 1998).

In this work, part of the results of an interdisciplinary study aimed to assess the environmental impact of the PHEs around the decommissioned Salafossa mine (North-Eastern Italian Alps) is presented. A previous study has dealt with the PHEs availability in soils by considering the differences between vegetated and not vegetated soil samples (Pavoni et al., 2017). The purpose of the present work was to investigate the geochemical properties of the mine drainage waters outflowing from the mine galleries which represent the main pathway of the dispersion of Tl and other PHEs in the groundwater and surface waters of the Piave River, the major tributary of the entire drainage basin. There is particular interest in relation to the potential impact that

these elements can have on the exploitable water resources and, as a consequence, on the health of the population living downstream from the decommissioned mining area.

2. Materials and methods

2.1. Study area

The Salafossa decommissioned mining area is located in the eastern Dolomites belonging to the Alps (Fig. 1) in the Veneto region (North-Eastern Italy) and is included in the Piave River drainage basin. The Salafossa mineralisation was one of the largest Pb-Zn-containing ore deposits in Europe. Zinc and Pb were mainly present as sulphides: *sphalerite* (ZnS) and *galena* (PbS). In addition to the sulphides of mining interest, *pyrite* and *marcasite* (FeS$_2$) were also present (Assereto et al., 1977). The mineralogical characterisation performed on soil samples collected in the external area of the mine revealed the presence of *pyrite* (FeS$_2$) and other minerals. *Dolomite* (CaMg(CO$_3$)$_2$) and *quartz* (SiO$_2$) reflect the lithological characteristics of the study area, whereas *hematite* (Fe$_2$O$_3$), *goethite* (FeOOH) and *sulphur* (S) are the results of sulphide oxidation processes (Pavoni et al., 2017). The mineral deposit belongs to a unique ore body included in the Ladinian-Carnian dolomites of the Lower Triassic age (Assereto et al., 1977).

Mining activity started around 1550, but it was only around 1960 when the richest veins of the minerals were discovered. Approximately 32 km of galleries, in 9 levels from 1,071 to 1,215 m above sea level (a.s.l.), and five shafts were dug to access the ore bodies and transport the ore to the surface. Deep drilling revealed that the ore is 750 m long and 200 m wide with a thickness of 30 m below the surface. From the Salafossa mineral deposits, a little more than 11 million tons of *tout-venant* (raw material) were extracted with an average content of 0.9% Pb and 4.7% Zn. On the whole, 92,000 tons of Pb and 482,000 of Zn were recovered from the mineral deposits (Zas Friz, 1999). The mining activity continued until 1985, the year of its final closure.

Currently, heterogeneous deposits constituted by the remains of excavated rock mixed with mineralised tailings generated during mineral processing are present in the external area of the mine. This waste material was frequently used in the construction of the access road to the dumping area, dropped on the mine slopes or accumulated near the banks of the Piave River, thus contributing to contaminant dispersion (Fig. 1A). Moreover, the residual sludge enriched in PHEs deriving from the mineral extraction was usually dumped into the river freshwaters during mining activity. The decommissioned mine galleries are not currently monitored and the drainage waters flowing out represent the primary means by which PHEs could be conveyed into the Piave River, mainly in dissolved form.

2.2. Field work and sample preparation

Water samples were collected from the main drainage points of the mine outflowing into the Piave River (SF2, SF4 and SF5) in November 2011 and in June and October 2014. Average stream velocities were measured on site by means of a Swoffer Model 3000 Current Velocity Meter-Flowmeter. In addition, one sediment sample (SF3) and two freshwater samples (SF3 and SF6) were recovered from the riverbanks (Fig. 1). A second group of waters were sampled in two galleries (hereafter, referred to the letter "G" in the sampling point labels) related to the corresponding mine levels in November 2014. Water (SF$_G$4), sediments (SF$_G$2A, SF$_G$2B and SF$_G$2C) and mineral concretions (SF$_G$3) deriving from dripping drops of water were sampled from the forth level of the mine (1,120 m a.s.l.). The mineral concretion sample appeared intensively reddish in the centre, fading concentrically to white. In the first and lowest mine gallery (1,071 m a.s.l.), the bottom was flooded by a stream that fed the main drainage points outside the mine. The waterflow was characterised by an apparent reddish colour, which testified to the occurrence of oxidation processes. By moving

upstream along the main gallery, the confluence between two different types of water was easily recognised, since the first one was clear (SF$_G$6) whereas the second appeared intensively reddish (SF$_G$5). Further water and sediment samples (SF$_G$1) were collected along the so-called "mixing zone" between the two types of water. The last water sample (SF$_G$7) was collected at the head of the gallery which functioned as a source point for the reddish stream (Fig. 1).

The main physico-chemical parameters (temperature, pH, redox potential Eh, electrical conductivity EC and dissolved oxygen) both for the drainage waters collected in the external area of the mine and inside the mine galleries (Table S1) were measured *in situ* through portable probes (pH-meter PH25, Conductivity meter CM 35+ and Oxygen meter OXI 45P by Crison Instruments). At each sampling point, two aliquots of the same water were collected for the analysis of major ions and PHEs, respectively. For PHEs determination, water samples had been previously filtered through glass fibre prefilter and surfactant-free cellulose acetate (SFCA) (0.45 μm, Minisart Plus 17829Q, Sartorius) and acidified using 5% solution of ultrapure nitric acid (HNO$_3$, 69% w/w) to 50 mL of the original sample to preserve the original characteristics of the water.

The sediment samples were frozen, freeze-dried (Coolsafe 55-4 SCANVAC) and finely ground. These samples were then acid-digested through a total dissolution in a closed microwave system (Milestone, MLS 1200) using *aqua regia* (a mixture of ultrapure HNO$_3$ (65% w/w) and HCl (37% w/w), 1:3) and HF (48%, w/w) according to USEPA 3052 method. Mineralisation was performed through two heating steps. In the second step, H$_3$BO$_3$ was added to buffer the excess of HF. The extracts obtained from the mineralisation process were filtered through syringe filters (0.45 μm, GHP Acrodisc 25 mm) before analytical determinations.

2.3. Analytical measurements

The concentrations of Ca, Mg, K, Na, Zn, Fe, Ba, Mn, Pb, As, Cd, Cu and Tl in water samples (Tables S2, S3, S4 and S5) were determined by means of Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES, Ciros Vision, Spectro Ametek Instruments) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS, Mod. XSeries2, Thermo Scientific) according to the EPA 6010D and EPA 6020B methods, respectively. The calibration standard solutions were prepared by dilution (1,000 mg L^{-1} and 10,000 mg L^{-1}) of mono and multi-element standard solutions (CPI International). The calibration curve quality was verified using standard solutions (Ultrascientific and CPI International, for ICP-OES and ICP-MS respectively) and certified reference materials (ICP multi-element standard VI Merck, SPS-SW1 and SPS-SW2, Spectrapure). The precision of the measurements as relative standard deviations for the analysis was always < 5%.

Anions (Tables S4 and S5) were determined by Ion Chromatography (IC) (ICS 1100 Dionex, Thermo Scientific) (APAT CNR IRSA, 2003). The calibration curves were obtained using standard solutions (Merck), prepared by dilution (1,000 mg L^{-1}) and the quality was verified using standard solutions (Merck and Icus 3058 Custom Standard, Ultrascientific). The precision of the measurements as relative standard deviations for the analysis was always < 10%.

With regard to CO$_3^{2-}$ and HCO$_3^-$, the determination was performed using potentiometric titration (TIM 870 Radiometer Analytical) (APAT CNR IRSA, 2003). The measurements were obtained after electrode calibration using standard solutions (Radiometer – pH 4.00, 7.00 and 10.00; Merck – pH 7.00). The precision of the measurements as relative standard deviations for the analysis was always < 5%.

The concentrations of Ca, Mg, H, Fe, Mn, As, Pb, Cu, Cd, Zn and Tl in sediment samples (Table S6) were determined by ICP-OES (Optima 8000 Spectrometer, equipped with a S10 Autosampler, Perkin Elmer, USA). The measurements were conducted using calibration curves obtained by dilution (range 0–100 mg L^{-1}) of the standard solutions for ICP-OES analyses (Sigma-Aldrich, USA). Samples exceeding this range
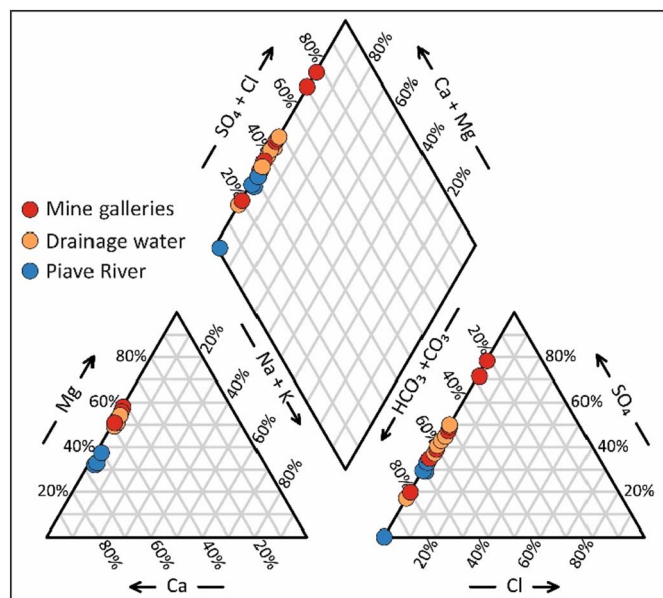
Fig. 2. Piper diagram showing the hydrochemical facies of the three types of waters collected from the mine galleries, the drainage outflow and the main river.

$$CaCO_{3\,(s)} \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \tag{1}$$

$$PbS + 2O_2 \longrightarrow Pb^{2+} + SO_4^{2-} \tag{2}$$

$$ZnS + 2O_2 \longrightarrow Zn^{2+} + SO_4^{2-} \tag{3}$$

$$4FeS_2 + 10H_2O + 15O_2 \rightarrow 4FeO(OH) + 16H^+ + 8SO_4^{2-} \tag{4}$$

$$ZnS + 8Fe^{3+} + 4H_2O \longrightarrow Zn^{2+} + 8Fe^{2+} + SO_4^{2-} + 8H^+ \tag{5}$$

$$ZnS + 2H^+ \rightarrow Zn^{2+} + H_2S \tag{6}$$

The results of the PHEs analyses (Tables S2 and S3) have highlighted the presence of a significant amount of Fe, Mn, Pb, Tl and Zn. These elements generally reach the highest concentrations in those samples collected in the mine galleries where the drainage waters are in direct contact with mineralised rock.

Due to a lack of appropriate national guidelines for the chemical composition of waters draining mineral deposits, the only comparison which can be made is with the Italian regulatory threshold limits for contaminated groundwater (Italian Legislative decree 152/2006 according to EU Directive 2000/60/EC). Zinc reaches maximum values of 16,204 µg L^{-1}, exceeding the limit values (3,000 µg L^{-1}) in some water samples collected in the mine galleries, especially in those reddish waters, which seem to represent the most effective pathway in terms of transport and diffusion of dissolved PHEs. Due to the strong mobility of Zn in the aqueous phase, high concentrations are also evident in the drainage waters collected in the external area of the mine, whereas the Pb concentration clearly decreases in correspondence of the mixing zone inside the main gallery to reach values below the detection limit in the Piave River freshwaters.

Thallium also exceeds the threshold limit value of 2 µg L^{-1} in all samples where the maximum concentration of 261 µg L^{-1} was detected in the reddish water source area (SF$_G$7). This value is comparable to the average concentration (340 µg L^{-1}) found in contaminated groundwater within a Tl-mineralised area in China (Xiao et al., 2003). The amount of Tl decreases with the distance away from the mineralised area to background levels and the physico-chemical boundary conditions change to increasing pH and decreasing electrical conductivity (EC) values. In fact, according to Xiao et al. (2003), the release of this element in solution is strongly promoted by acid drainage waters and controlled by Tl mineralisation, water-rock interaction and hydrogeological conditions (Xiao et al., 2003; Liu et al., 2017). However, the Salafossa drainage waters are very rich in Tl but, at the same time, they exhibit alkaline values of pH (up to 8.21). In these environmental conditions, water alkalinity is mainly due to the buffering effect supplied by carbonates (HCO$_3^-$, CO$_3^{2-}$) deriving from the dissolution of calcareous and dolomitic host rocks (Banks et al., 2002; Navarro-Flores and Sola, 2010; Navarro et al., 2015). In addition, the absence of acid drainage waters can also be due to the prevalence of *sphalerite* and *galena*, whose oxidation does not imply a pH decrease. Generally, neutral mine drainage can result from either high neutralisation potential or a low extent of sulphide mineral oxidation (Heikkinen et al., 2009). Moreover, since our main interest was focused on drainage waters, we cannot exclude that more acidic environmental conditions can occur locally in the mine gallery system, which can be favoured by a longer residence time of waters in contact with the mineralised rock. To support this hypothesis, the only sample of stagnant waters collected at the bottom of the upper level gallery (SF$_G$4), which is not flooded, provided a very acidic pH value (pH = 2.24) and an extremely high Tl concentration (310 µg L^{-1}). The intensive weathering of sulphide minerals, testified by the elevated concentration of SO$_4^{2-}$ (3,201 mg L^{-1}), is responsible for the release of Tl and other PHEs (20,906 µg L^{-1} of Zn, 98.84 µg L^{-1} of Pb, 736,002 µg L^{-1} of Fe and 489 µg L^{-1} of Mn) in solution.

If compared with the results obtained from other mining districts

were diluted with milliQ water. The precision of the measurements as relative standard deviations for the analysis was always < 5%.

Qualitative chemical analyses (EDS) were obtained by using a Leica Stere-oscan 430i EDS. These analyses were performed on two sub-samples, the reddish and the white, from the mineral concretion (SF$_G$3) collected from the upper gallery level. In addition, X-Ray Diffraction (XRD, SIEMENS STOE-D500) analyses were performed on the same samples for mineralogical characterisation to support the geochemical data.
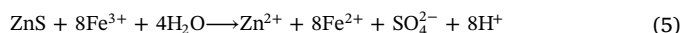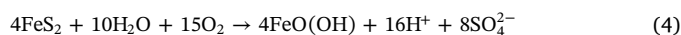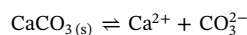
3. Results and discussion

3.1. Chemical characterisation: major ions and PHEs

Water samples collected at the Salafossa mine site are generally characterised by high contents of calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO$_3^-$) and sulphate (SO$_4^{2-}$) (Tables S4 and S5). The representation in Fig. 2 of the composition of the water samples in the Piper diagram (Piper, 1944) identifies the main hydrochemical facies as alkaline earth sulphate and alkaline bicarbonate groups, except for the Piave River freshwaters, which belong to the alkaline earth bicarbonate group. Moreover, water samples plot along one side of the diamond in the Piper diagram: this trend is often an indication of mixing processes between chemically different waters, as it occurs in the mine gallery and when the drainage waters outflow into the Piave River freshwaters.

The relative abundance of Ca^{2+}, Mg^{2+} and HCO$_3^-$ results from dissolution processes of calcareous and dolomitic rocks (formula (1)), whereas SO$_4^{2-}$ derives from *sphalerite* and *galena* hydrolysis, oxidation and dissolution processes under oxidising conditions (formulas (2) and (3)). Sulphide oxidation process can lead to acid mine drainage, especially in the presence of *pyrite* (FeS$_2$) (formula 4) (Banks et al., 2002; Alderton et al., 2005; Sangita et al., 2010); on the contrary, the oxidative processes do not cause a pH decrease when the metal is present in divalent form.

Actually, as regards the *sphalerite* oxidation process, the reaction can take place under both oxidising, mediated by O$_2$ or Fe^{3+} (formulas (3) and (5)), and reductive conditions in presence of H$^+$, which can lead to the formation of hydrogen sulphide (H$_2$S) (formula (6)).

Table 1
Range of pH values and concentrations of Zn, Pb, Tl, Fe and Mn ($\mu g\ L^{-1}$) in water samples collected in sulphide-rich ore mining sites as reported in literature (nd: not determined).

Location	Type of ore	$\mu g\ L^{-1}$ Zn	$\mu g\ L^{-1}$ Pb	$\mu g\ L^{-1}$ Tl	$\mu g\ L^{-1}$ Fe	$\mu g\ L^{-1}$ Mn	pH	Reference
Salafossa (Italy)[md]	PbS-ZnS	< 2.5–16,204	< 2.5–388	< 2.5–261	< 5–10,023	< 1–344	7.15–8.21	This work
Salafossa (Italy)[r]		2.5–178.79	< 2.5	2.5–6.06	5.00–12.68	< 1.00	8.15–8.35	
La Rioja (Argentina)[r]	FeS$_2$	6.1–421,000	0.2–670	< 0.002–1,260	0.11–1,220	3.77–580	3–7.91	Lecomte et al., 2017
Raibl (Italy)[md]	PbS-ZnS	< 5–6,600	0.17–9.7	< 0.05–30.0	< 10– < 200	0.4–3	7.9–8.1	Petrini et al., 2016
Raibl (Italy)[r]		< 1–876	0.14–40.1	< 0.05–4.8	< 100	< 1	8.0–8.3	
Alaşehir (Turkey)[md]	HgS	3.4–1,675	0.07–3.7	nd	0.025–670,950	2.03–1,672	2.55–2.75	Gemici, 2008
Odiel (Spain)[r]	Iberian Pyrite Belt	1,300–41,700	< 7–267	nd	300–235,600	900–32,100	2.92–5.05	Cánovas et al., 2007
Tinto (Spain)[r]		2,200–152,300	< 7–698	nd	70–280,400	700–54,700	2.22–5.01	
Sardinia (Italy)[r]	PbS-ZnS	0.1–710	17–800	< 0.07–8.9	20–240,000	0.02–98	4.45–8.02	Concas et al., 2006
Lanmuchang (China)[md]	Hg-Tl ore	nd	nd	59.00	150.00	2.90	3.8	Xiao et al., 2003
Lanmuchang (China)[r]		nd	nd	0.12–33	< 3–780	19–270	6.2–8.6	
Monteponi (Italy)[md]	PbS-ZnS	92–57,400	7–470	nd	nd	467,512	6.5–8.2	Cidu et al., 2001

r = river; md = mine drainage.

(Table 1), the concentration range of Zn, Pb, Tl, Fe and Mn in drainage and riverine waters are similarly very high and in the same order of magnitude. In particular, the Raibl Pb-Zn mining district located further east in the Julian Alps, close to the border between Italy and Slovenia and in a similar geo-mineralogical context, exemplifies an environmental situation comparable to that of the Salafossa mine in terms of PHEs abundance deriving from the oxidation of sulphides minerals and of pH values of the drainage waters (Petrini et al., 2016).

Considering the characteristics of each sampling point in terms of the chemical composition of the drainage waters, some information on the hydrogeochemistry can be provided by the relationships observed between pairs of chemical components (Figs. S1 and S2). However, these relationships should be treated as purely indicative, referring to few sampling points and being influenced by the elevated concentrations found in the SF_G7 water sample. Thallium and Zn concentrations increase proportionally with the increase of Ca and SO_4^{2-}, thus suggesting carbonate dilution and sulphide hydrolysis/oxidation processes, respectively (Liu et al., 2017) (Fig. S1). A significant correlation between Tl concentrations with those of Ca ($R^2 = 0.920$, $P < 0.001$, $n = 11$) and SO_4^{2-} ($R^2 = 0.903$, $P < 0.001$, $n = 11$) represents an index of the contribution of water-rock interactions to water geochemistry (Xiao et al., 2003; Liu et al., 2017). Excluding the Piave River freshwater samples, the correlation between Zn and Tl is highly significant ($R^2 = 0.998$, $P < 0.001$, $n = 10$) and confirms the mutual availability of these PHEs in the aqueous phase of the waters flowing out of the mine (Fig. S2). The same is not true for Pb, whose concentrations are generally low in the samples collected in the mine gallery (7.14 $\mu g\ L^{-1}$ and 6.84 $\mu g\ L^{-1}$ in SF_G5 and SF_G7 respectively) and lower than the detection limit in the external drainage waters. A good correlation ($R^2 = 0.999$, $P < 0.001$, $n = 7$) also exists between Fe and Mn when present in detectable concentrations. Moreover, these elements are also significantly correlated with Zn ($R^2 = 0.999$, $P < 0.001$, $n = 7$) and Tl ($R^2 = 0.998$, $P < 0.001$, $n = 7$ for Fe and $R^2 = 0.997$, $P < 0.001$, $n = 7$ for Mn). Iron and Mn reach high concentrations with maximum values of 5,843 $\mu g\ L^{-1}$ and 344 $\mu g\ L^{-1}$ in the sample collected at the reddish water source area (SF_G7). Sample SF_G1_2014 is undoubtedly enriched with Fe, Mn and Pb, whereas Zn and Tl concentrations are lower than those recorded in the water sample collected at the source area of the reddish drainage water (SF_G7) located further upstream. Therefore, the water sample SF_G1_2014 may be considered an outlier since its composition (10,023 $\mu g\ L^{-1}$ of Fe, 388 $\mu g\ L^{-1}$ of Pb and 334 $\mu g\ L^{-1}$ of Mn) is very different from the corresponding water sample collected at the same point in 2011. The most appropriate explanation for this evidence is an artefact due to sampling operations. Indeed, sample SF_G1_2014 was collected last on the way back to the exit of the mine. As a consequence, the abnormally high PHEs concentrations may be due to the resuspension of fine material

deposited on the flooded gallery bottom as a result of having been previously walked on.

3.2. Mixing and dilution processes

The chemical composition of drainage waters (Tables S2, S3, S4 and S5) at the Salafossa mine appears significantly influenced by mixing and dilution processes in their flow to the Piave River. In the lower gallery, the clear and reddish waters do not mix for a long stretch after the confluence zone but they flow in parallel (Fig. 1B). Indeed, water samples SF_G5 and SF_G6 result very different. The clear waters (SF_G6) appeared to be characterised by a flow discharge greater than that of the reddish waters (SF_G5). As regards the physico-chemical parameters measured *in situ* (Table S1), the two waters do not show significant difference in temperature (8.01 °C in SF_G5 and 7.20 °C in SF_G6) and pH (7.56 in SF_G5 and 8.00 in SF_G6) whereas the EC value in the reddish waters is almost double compared to that of the clear waters (945 $\mu S\ cm^{-1}$ in SF_G5 and 420 $\mu S\ cm^{-1}$ in SF_G6). This difference means a different content of total dissolved solids, and related density which in turn, can affect the mixing process between the two types of water. As a consequence, the more marked are the differences in terms of water discharge and density, the more disadvantaged the mixing process will be and will occur downstream, also because of a narrowing of the gallery section after the confluence.

According to their location in the mining area, the water samples can be split into three categories: i) waters collected in the galleries; ii) external drainage waters; and iii) freshwaters from the Piave River. The PHEs contents tend to decrease from the inner part of the galleries towards the external area of the mine.

In fact, dilution represents a very effective natural process able to mitigate high and potentially toxic concentrations of PHEs, contrary to what has been reported for other similar environments. According to Concas et al. (2006), groundwater and stream water in the Rio Piscinas (Sardinia, Italy) hydrogeological basin were found to be highly enriched in PHEs. Acidic and strongly metal contaminated groundwater (780 $mg\ L^{-1}$, 570 $\mu g\ L^{-1}$ and 8.90 $\mu g\ L^{-1}$ for Zn, Pb and Tl respectively) flooded into the Irvi stream (a Piscinas stream affluent) without showing as strong a dilution as Salafossa. The PHEs content still remains elevated (710 $mg\ L^{-1}$, 280 $\mu g\ L^{-1}$ and 8.40 $\mu g\ L^{-1}$ for Zn, Pb and Tl respectively) even when the dilution in the Irvi stream freshwaters occurs.

When plotted on a Ficklin diagram (Plumlee, 1999), the water samples were classified as "near-neutral, high metal" and "near-neutral, low metal" waters (Fig. 3). The Ficklin diagram shows the sum of dissolved PHEs (Zn, Cu, Cd, Pb, Co, Ni) plotted against pH value. The results obtained are only indicative since some of these elements were found to be below the detection limit and reported as equal to half of
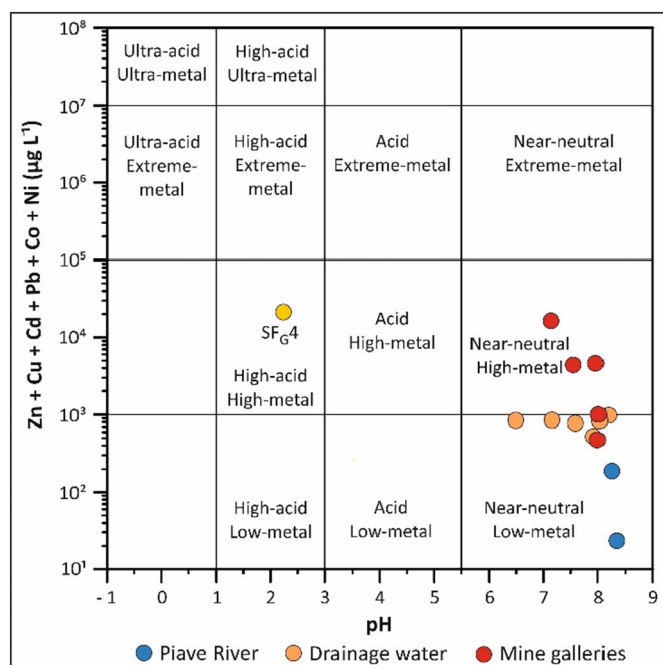
Fig. 3. Ficklin diagram of the Salafossa drainage waters showing the sum of dissolved PHEs (Zn, Cu, Cd, Pb, Co, Ni) plotted against pH value.

Fig. 4. Effect of dilution process observed for Zn and Tl in the drainage waters flowing from the inner part of the mine towards the Piave River.

Fig. 5. Effect of dilution process observed for Pb, Fe and Mn in the drainage waters flowing from the inner part of the mine towards the Piave River.

these limits in the graphical representation. Although a few of the water samples with extremely low PHEs contents are considered in the construction of the Ficklin diagram, the resulting classification confirms the dilution process. The water samples collected in the mine galleries (SF$_G$7 and SF$_G$5) fall in the field of "high-metal" waters. Afterwards, the mixing with the clear water (SF$_G$6) at the confluence zone, the drainage water (SF2, SF4 and SF5) and the Piave River freshwater (SF3 and SF6) samples move to the field of "low-metal". The only exception is represented by the stagnant water sample (SF$_G$4) which is classified as "high-acid, high-metal" according to its low pH value and extremely high PHEs concentrations.

The highest concentrations of Fe, Mn, Pb, Tl and Zn were found in the reddish water samples, both at its source area (SF$_G$7) and near the mixing zone (SF$_G$5). These reddish waters, enriched in PHEs, are first diluted due to being mixed with the clear waters which are low in PHEs contents. A better representation of the spatial evolution of these mixing and dilution processes may be seen by reporting the results of the sampling points according to the related distance from the external area of the mine (Figs. 4 and 5). As a first approximation, the PHEs concentration trend does not seem to be the same for all the elements. It is possible to distinguish two trends, one describing the behaviour of Zn and Tl (Fig. 4) and a second for Fe, Mn and Pb (Fig. 5), respectively.

The dilution process is evident in the case of Zn and Tl, whose concentrations decrease more than one order of magnitude at the mixing zone into the gallery (SF$_G$1). In the external area of the mine (SF2 and SF4), Zn and Tl contents further decrease, thus testifying to a complete mixing. When these drainage waters are discharged into the Piave River, a second dilution process occurs and Zn and Tl concentrations decrease to reach values that are lower than the detection limit at sampling point SF3 (Fig. 4). Conversely, the freshwaters collected from the Piave River at SF6, just downstream from the two confluence points of the drainage waters achieved a relatively high Zn concentration whereas the Tl content appears diluted (6.06 μg L^{-1}) compared to the main drainage point (SF4, 29.58 μg L^{-1}). This evidence can be due to a greater water discharge noted at SF4 than at the point located further upstream (SF2). The dilution trends for Zn and Tl are comparable with the results obtained from the preliminary investigation performed in 2011, which is an indication that this behaviour is
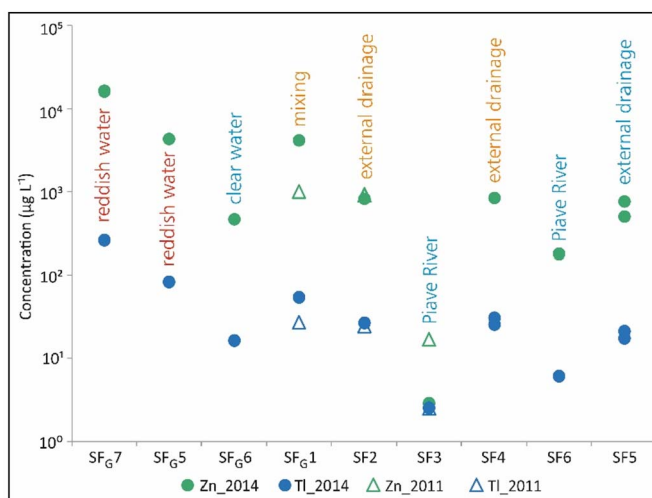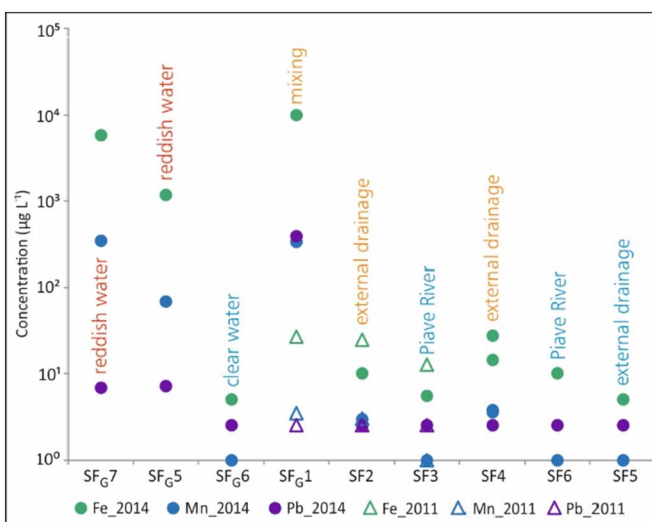
persistent in the Salafossa mine drainage waters. The essential difference consists of the higher concentrations observed in 2014, which are possibly related to a different sampling period, especially as regards rain falling in the area and affecting the recharge and circulation of the groundwater in the mine (Fig. 4). Although relatively high Zn and Tl concentrations were recorded at sampling point SF5, this was not considered in the evaluation of the dilution process since its chemical composition seems to be different from that of other drainage water samples. It can be noticed that the PHEs content at sampling point SF5 is comparable to that of the clear water collected in the mine gallery (SF$_G$6), suggesting a possible relationship between the two sampling points. In fact, moving upstream along the related gallery up to its head, it was possible to verify that the stream flowing along the bottom is fed by waters flowing from the gallery roof, due to the presence of fracture zones in the rocky mass which facilitate water circulation.

In contrast with Zn and Tl, Fe, Mn and Pb show a different trend of dilution (Fig. 5). Although their concentrations are lower, the dilution trends of Fe and Mn are comparable to those of Zn and Tl considering the water samples collected in the preliminary campaign in 2011. Contrary to what we expected, the water samples collected in 2014 did not seem to be affected by a dilution process when the clear (SF$_G$6) and reddish (SF$_G$5) waters mix with each other in the mine gallery. Indeed,

in downstream mixing zone (SF$_G$1), PHEs show higher concentrations than those of the source area (SF$_G$7). Specifically, whereas the Mn content is comparable to that at the source area, significant differences exist in the case of Fe, whose concentration doubles from 5,843 µg L^{-1} in SF$_G$7 to 10,023 µg L^{-1} in SF$_G$1, and Pb, whose concentration increases from 6.84 µg L^{-1} in SF$_G$7 to 388 µg L^{-1} in SF$_G$1. However, external drainage waters (SF2 and SF4) reach lower concentrations due to the mixing and subsequent dilution processes.

As reported previously for Zn and Tl, when the drainage waters convey into the Piave River, the Mn and Pb concentrations are also further diluted up to values lower than the detection limit whereas Fe persists in the fluvial waters, although in low concentrations (Fig. 5).

The main difference between the two-time series of data (2011 and 2014) consists of a different content of Fe, Mn and Pb in the water samples collected in the mixing zone (SF$_G$1). As stated above, the difference between the two water samples may be due to perturbations unintentionally induced during sampling. We can suppose that the perturbation could lead to the resuspension of colloidal particles which, since they are not retained by the 0.45 µm filter, are responsible for the increase of PHEs content in the aqueous phase. This aspect is also confirmed by the chemical composition of the sediment sample collected near the mixing zone (SF$_G$5) which is highly enriched in Fe (247,642 mg kg^{-1}), Zn, (71,659 mg kg^{-1}), Tl (73.31 mg kg^{-1}), Pb (1,760 mg kg^{-1}) and Mn (1,716 mg kg^{-1}) (Table S6). In addition, high concentrations of As and Cd, which were not present in the drainage waters, were found in sediments covering the bottom of the galleries (Fig. 6). Arsenic, Cd, Pb, Tl and Zn exceed the threshold limit values posed by Italian regulations (Italian Legislative decree 152/2006 according to EU Directive 2000/60/EC) for soils set aside for industrial use. Fig. 6 also allows to compare the PHEs content in sediments collected in the mine galleries and from the riverbank (SF3_2011). Although these concentrations are below the Italian regulatory threshold values, PHEs and, especially, Fe (16,752 mg kg^{-1}) were also significantly present in river sediments, thus assessing the general contamination of the area surrounding the dismissed mine.

Despite the drainage waters outflow can be influenced by several factors, knowing the water flow and the average PHEs concentration in the water samples collected in June and October 2014 at the sampling point SF4, a rough estimation of the amount of PHEs that is transported to the Piave River has been calculated. Considering an average water flow of 0.07 m^3 s^{-1}, the highest value of the amount of metal which flows into the Piave River freshwaters during a year is obtained for Zn (1,771 kg y^{-1}) followed by Tl (60.54 kg y^{-1}), Fe (44.65 kg y^{-1}) and Mn (7.76 kg y^{-1}).
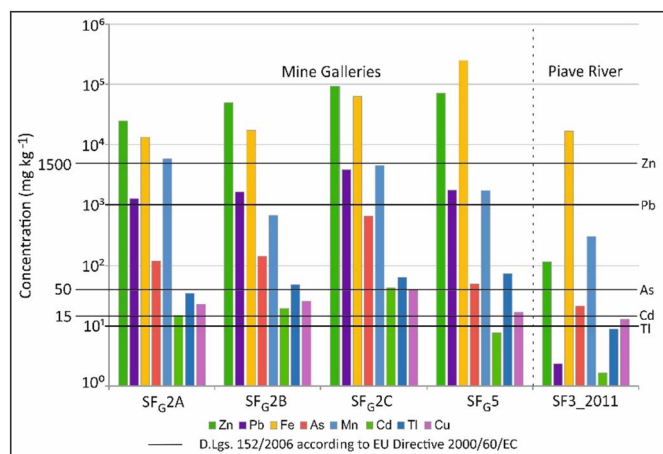

Fig. 6. Comparison of PHEs concentrations observed in fine sediment samples collected at the bottom of the mine galleries and at the banks of the Piave River.

3.3. PHEs speciation in mine drainage waters

The chemical form of an element in an environmental system is strongly influenced by physico-chemical boundary conditions, especially in terms of pH and redox potential (Eh) (Table S1). From the mine galleries to the Piave River, the drainage waters show high values of pH (6.50–8.35) without significant variations. On the contrary, Eh values are more variable. This parameter exhibits a negative value (− 76 mV), indicating reductive conditions at the head of the gallery where the reddish water source is located (SF$_G$7). Moving downstream to the mixing zone, the Eh increases to 66 mV in the reddish water (SF$_G$5) and to 241 mV at the mixing zone (SF$_G$1) and the system moves to more oxidising conditions which remain stable in the external drainage points.

The Eh-pH diagrams for Zn, Pb, Tl, Fe and Mn, which are built using the Geochemist's Workbench software, considering pH, Eh, temperature measured *in situ* and major ion concentrations, are reported in Figs. 7, 8 and 9. Zinc, which derives from the *sphalerite* oxidation process, is highly mobile and tends to be partitioned in the aqueous phase in its divalent ionic form (Zn^{2+}). From the mixing zone to the reddish water source area, *i.e.* moving upstream from oxidising to reductive conditions, the water samples in the Eh-pH diagram plot closer to the *sphalerite* solid field (Fig. 7).

On the contrary, Pb tends to be partitioned in the solid phase due to its low mobility when present as a sulphide also justified by the low concentrations measured in the waters. The abundance of carbonate ions can favour the precipitation of Pb as *cerussite* (PbCO$_3$) under oxidising conditions (Fig. 7).

With regard to the speciation of Tl, the information is obtained from the Eh-pH diagram proposed by Vink (1993) at 25 °C which is higher than the temperature we measured in our sampling (Fig. 8). However, the stability fields are indicative that the behaviour of Tl in the drainage water samples appears similar to that described for Zn. Thallium is present in its monovalent ionic form (Tl$^+$) and the high concentrations observed are related to its high mobility in the aqueous phase. According to Lin and Nriagu (1998), monovalent ionic form (Tl$^+$) adsorption on the surface of iron hydroxides is disadvantaged at a low pH, increasing at circumneutral conditions. In addition, the ionic species of Zn and Tl tend to remain in the aqueous phase as the pH increases, reaching higher concentrations in drainage waters from mineralised areas (Cidu, 2011). The high mobility of Tl is also confirmed by its low affinity for suspended particles and little removal in terms of hydroxide precipitation (Law and Turner, 2011). As regards the waters draining the mine galleries at Salafossa, the high Tl concentration suggests that this element is predominantly present in the aqueous phase, similar to the Raibl mine site (Petrini et al., 2016). On the other hand, the relatively high amount of Tl in the sediment sample SF$_G$5 (73.31 mg kg^{-1}) could be indicative of potential adsorption on the surface of iron and in particular of manganese oxi-hydroxides. On the contrary, Fe and Mn tend to be partitioned in the solid phase (Fig. 9). Specifically with regard to Fe, most of the water samples fall in the stability field of *hematite* (Fe$_2$O$_3$). In fact, the oxidising conditions at the mixing zone and at the external drainage and fluvial sampling points can favour the oxidation of the dissolved divalent ions (Fe^{2+}) to the trivalent ionic form (Fe^{3+}) and the precipitation of iron oxi-hydroxides, which lead to a red colouring of the drainage water stream bed (Concas et al., 2006; Gemici, 2008; Lecomte et al., 2017). In addition, the oxidation of dissolved Fe^{2+}, under neutralisation processes, can lead to the precipitation of a mixture of phases of uncertain composition and crystallinity (Nordstrom, 2011). The exception is represented by the water sample collected at the reddish water source area (SF$_G$7), which is positioned on the boundary between the solid field of *hematite* and that of the divalent ionic form in the aqueous phase (Fe^{2+}). This evidence is due to a negative Eh value, which indicates reductive conditions and possible dissolution processes (Fig. 9). However, the speciation of Fe could also be affected by precipitating colloids which can lead to an increase of
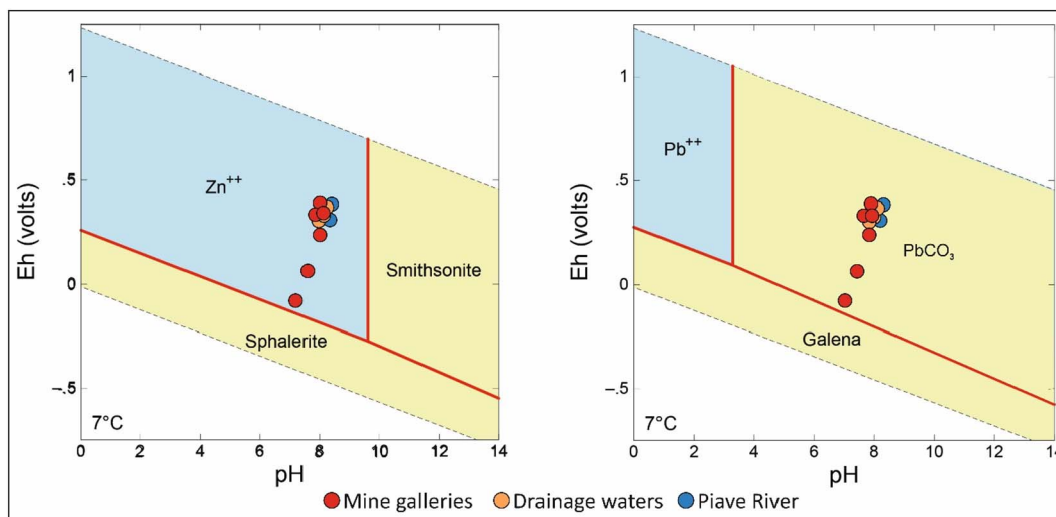
Fig. 7. Eh-pH diagram showing the predominant species in water for Zn and Pb according to the average composition and temperature measured at the sampling points.
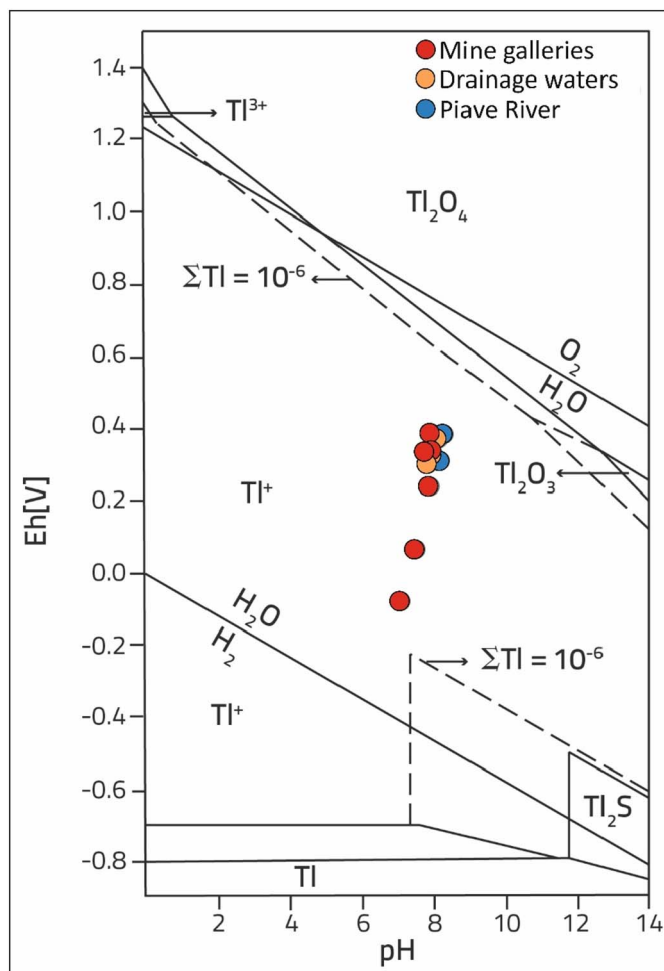

Fig. 8. Eh-pH diagram showing the predominant species for Tl in water (from Vink, 1993).

dissolved Fe (Nordstrom, 2011) since they are not retained by the filters.

The behaviour of Mn is similar to that described above for Fe. Most of the water samples are included in the solid field of *rhodochrosite* ($MnCO_3$) and they sometimes approach the solid field of *bixbyite* ($(Mn,Fe)_2O_3$). In addition, the abundance of Ca^{2+} ions can promote the precipitation of Mn in its carbonatic form in oxidising conditions. However, Mn is also present in bivalent ionic form in the aqueous phase (Mn^{2+}) at the mixing zone and at the reddish water source area (Fig. 9).

PHEs precipitation processes also occur in the gallery of the upper level, where mineral concretions have been recognised related to points of dripping waters. In Fig. 10, the chemical and mineralogical composition of the mineral concretion sample (SF_G3) is represented. The mineralogical analysis revealed the presence of *hydrozincite* ($Zn_5(CO_3)_2(OH)_6$), which is also confirmed by results of the qualitative chemical analyses performed on the white part of the sample where the main constituents are Zn and O. Conversely, the intense reddish colour visible on the central area of the mineral deposit is probably due to the presence of Fe at the surface in the form of poor crystalline (Fe-Mn oxy-hydroxides) or colloidal phases, neither of which are detectable by the X-Ray Diffraction (XRD) analyses.

4. Conclusions

The drainage waters flowing from the dismissed mine of Salafossa are not acidic due to the buffering effect produced by carbonate host rocks. They are highly enriched in Zn, Tl and Fe but their concentrations are strongly diluted first in the mine galleries and then after their confluence with the freshwaters of the Piave River. In particular, dilution in these freshwaters seems to be a natural process able to mitigate the possible negative impact of the PHEs within the drainage basin downstream the mine. Moreover, the precipitation of As, Cd, Pb, Tl and Zn is favoured by the oxidising conditions found in the drainage waters. As a consequence, these PHEs can accumulate in the mine gallery sediments in the form of Fe-Mn oxy-hydroxides and carbonates.

Future investigations should be focused on the presence of Tl and other PHEs in the shafts and fountains used by the local population as drinking water in the nearby villages downstream of the mine, which could represent a natural hazard for inhabitants. Moreover, further research should also investigate the mobility of the PHEs fraction associated with suspended particulate matter in the fluvial environment. As residual sludge enriched in PHEs was dumped into the Piave River when the mining activity at Salafossa was in operation, it is possible that a certain amount of PHEs was carried downstream to the Centro Cadore reservoir to eventually accumulate in the basin. Here, biogeochemical reactions at the water-sediment interface could favour their mobility and recycling and potential bioaccumulation in the aquatic trophic chain.
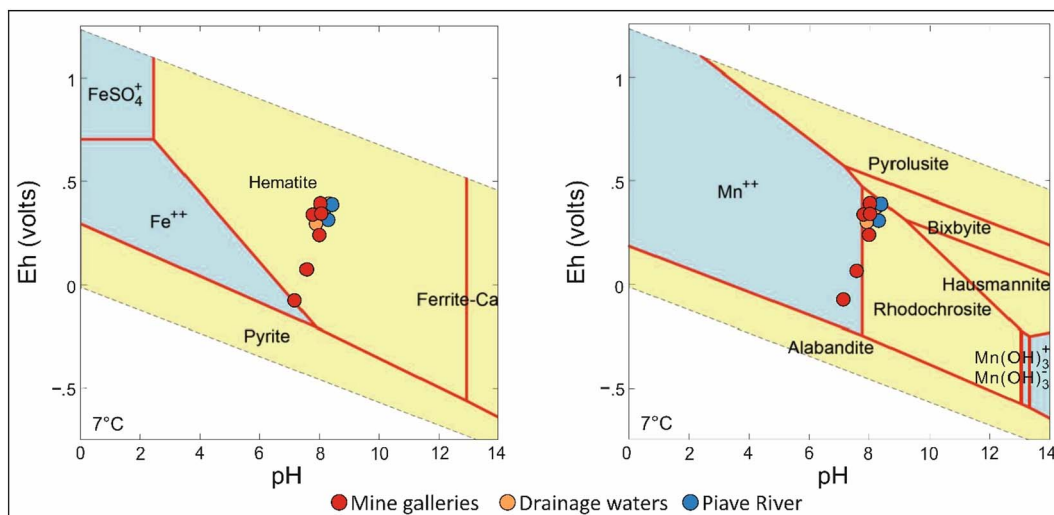
Fig. 9. Eh-pH diagram showing the predominant species in water for Fe and Mn according to the average composition and temperature measured at the sampling points.
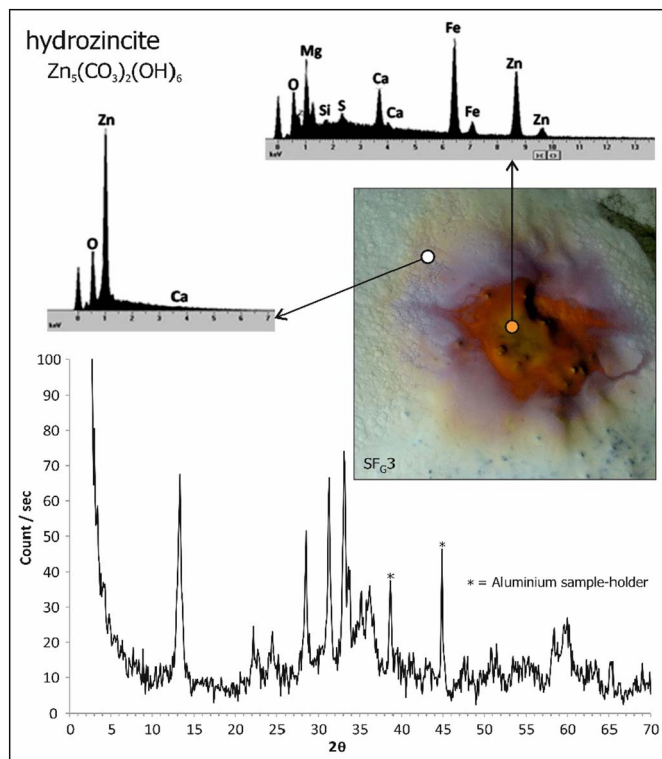

Fig. 10. Chemical and mineralogical composition of the mineral concretions sampled in the gallery of the upper level.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gexplo.2018.01.005.

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