

(Editores)
Rodrigo Álvarez García
Almudena Ordóñez Alonso

RECURSOS MINERALES Y
MEDIOAMBIENTE: UNA HERENCIA
QUE GESTIONAR Y UN FUTURO
QUE CONSTRUIR

LIBRO JUBILAR
DEL PROFESOR
JORGE LOREDO



Universidad de Oviedo
Universidá d'Uviéu
University of Oviedo

2020

UNIVERSIDAD DE OVIEDO

HOMENAJES

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medioambiente: una herencia
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MOBILITY OF THALLIUM AND OTHER TRACE ELEMENTS IN MINE DRAINAGE WATERS FROM TWO CARBONATE-HOSTED LEAD-ZINC ORE DEPOSITS IN THE NORTHEASTERN ITALIAN ALPS

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ABSTRACT

The ore deposits mined at Salafossa and Raibl (northeastern Italian Alps) were two of the largest Pb-Zn mineral deposits in Europe where the two metals were mainly present as sulphides (sphalerite and galena). Currently, the two mining districts are decommissioned and their galleries were partially flooded after the mine closure. In this context, water-rock interaction and the oxidation of sulphides are often responsible for increasing the mobility and dispersion of potentially toxic trace elements in the surrounding environment. Among minor constituents of sulphides, Tl is one of the most toxic elements and there is great concern regarding its occurrence, behaviour and fate in areas affected by both active and decommissioned mining activity. The geochemistry of the mine drainage waters was investigated at the two mining districts with the final aim of providing further information regarding their chemical composition, highlighting anomalous Tl and other trace element concentrations. In spite of the oxidation of sulphides which appears to occur, the buffering effect related to carbonate host rocks prevents the formation of acid mine drainage at both the investigated sites. Drainage waters were, however, found to be enriched in Zn, Pb and Tl (maximum of 16204, 80.1 and 261 $\mu\text{g L}^{-1}$ at Salafossa and 5243, 70.1 and 80.1 $\mu\text{g L}^{-1}$ at Raibl, respectively). Although drainage waters are diluted after being discharged into their respective riverine systems, Tl still remained at high levels in the freshwater downstream from the mines, especially at Raibl. There, the Tl-enriched

groundwater flowing into the tailing ponds appears to affect the chemical composition of the freshwater of the Rio del Lago stream.

1. INTRODUCTION

Decommissioned mining sites are globally recognised as one of the major anthropogenic sources of potentially toxic elements (PTEs) in the environment (e.g. Zhang *et al.*, 1998; Rodríguez *et al.*, 2009; Cidu *et al.*, 2012). Indeed, the extraction activity of Zn and Pb from sulphides have often led to the accumulation of extended tailing deposits found to be enriched in other PTEs (such as As, Cd, Hg and Tl) which can be minor constituents of sulphides. Natural weathering of these deposits can promote PTE dispersion and the subsequent contamination of various environmental compartments including soils, sediments, water and vegetation (Zhao *et al.*, 2003; Xiao *et al.*, 2004a; Rodríguez *et al.*, 2009; Fellet *et al.*, 2012; Campanella *et al.*, 2016; Petrini *et al.*, 2016; Pavoni *et al.*, 2017, 2018).

Water draining from abandoned mine tailing deposits commonly represents the most effective vehicle for PTE mobility and adverse effects on the environment as a result of acid mine drainage (AMD) have been reported in several studies (e.g. Xiao *et al.*, 2003; Concas *et al.*, 2006; Lecomte *et al.*, 2017). However, near-neutral and alkaline conditions might also occur when the dissolution of carbonatic host rocks promotes neutralisation processes driven by carbonates in solution (e.g. Cidu *et al.*, 2012; Petrini *et al.*, 2016; Pavoni *et al.*, 2018).

There is a growing interest on the part of the scientific community with regards to the occurrence, mobility and behaviour of Tl in water systems affected by abandoned mining activity, where elevated concentrations of Tl (1-88 mg L⁻¹) have been measured (Peter and Viraraghavan, 2005). Due to its extremely high toxicity (Xiao *et al.*, 2003; Peter and Viraraghavan, 2005; Cvjetko *et al.*, 2010), Tl has been included among the USEPA priority pollutants (USEPA, 2014) and its presence in the environment is of great concern. Thallium compounds generally show high solubility in water and the element can naturally occur as Tl(I) and Tl(III). According to Vink (1993), Tl(I) is very mobile, stable in solution form over a wide range of pH and predominates in natural water systems (Belzile and Chen, 2017). On the other hand, the behaviour of Tl(III) is similar to Al and its occurrence in solution is observed at high pH values when the formation of oxy-hydroxide complexes is favoured (Vink, 1993).

Thallium poisoning was found to be mainly related to elevated concentrations of Tl in drinking water and/or in water supplied for agricultural activities (Zhang *et al.*, 1998; Xiao *et al.*, 2004b, 2007; Campanella *et al.*, 2016; D'Orazio *et al.*, 2020; Liu *et al.*, 2020). Even at low doses, Tl can cause serious health problems, as Tl(I) can easily interfere with K-dependent processes (Campanella *et al.*, 2019; Duan *et al.*, 2020). Although Tl is usually excreted through the urine, it can accumulate in the human body and chronic intoxication has been reported in China (SW Guizhou Province) and Italy (northern Tuscany) where elevated concentrations of Tl have been measured in the urine of the local inhabitants (153-2668 µg L⁻¹, Xiao *et al.*, 2007; 0.046-5.44 µg L⁻¹, Campanella *et al.*, 2016).

The goal of this work is to make a preliminary comparison of the occurrence, distribution and mobility of Tl and other PTEs in the drainage waters at the two Pb-Zn decommissioned mining districts of Salafossa (Pavoni *et al.*, 2018) and Raibl. Future investigation will be conducted at Raibl as a part of a doctoral research Project. Knowledge of the geochemical properties of the water draining these mine deposits is fundamental in order to provide further information on the general status of the environment and scientific support for environmental management, risk assessment and mitigation strategies.

2. MATERIALS AND METHODS

2.1. Study area

The early Mesozoic Pb-Zn mining district of the Eastern Alps represents one of the most historical and studied metallogenic provinces in Europe. These four Pb-Zn mines in Bleiberg (Austria), Raibl and Salafossa (Italy) and Mežica (Slovenia) produced more than 75% of the total Pb and Zn extracted from the Alps (Brigo *et al.*, 1977) (Table 1). Currently, these deposits are of subeconomic interest and the mines have been decommissioned.

Table 1 - The four main carbonate-hosted Pb-Zn ore deposits in Europe

Location	Original resource (estimate) – tons (Melcher and Onuk, 2019)	Ore grade Pb/Zn (Brigo <i>et al.</i> , 1977)
Bleiberg (Austria)	43 x 10 ⁷	Pb = 1%; Zn = 5%
Mezica (Slovenia)	34 x 10 ⁷	Pb = 1÷3%; Zn = 1%
Raibl (Italy)	18 x 10 ⁷	Pb = 1%; Zn = 5%
Salafossa (Italy)	10 x 10 ⁷	Pb = 1%, Zn = 6%

This study is focused on the Mid-Late Triassic strata-bound ore deposits of Salafossa and Raibl, which are located in the northeastern Italian Alps, near the villages of Sappada and Cave del Predil, respectively, southward with respect to the “Periadriatic/Insubric Lineament”, a regional W-E trending fault which divides the Adriatic plate from the European plate (Fig.1 and Fig.2).

The Pb-Zn ore deposits of Salafossa and Raibl are hosted in thick, Ladinian to Lower Carnian, massive dolomitic reefs located on the Adriatic passive continental margin. Structurally, the Pb-Zn ore deposits of Salafossa (Lagny, 1975; Assereto *et al.*, 1977 and references therein) and Raibl (Doglioni, 1988) are similarly controlled by the Triassic to Early Jurassic extensional fault activity associated with the Pangea breakup. Due to the similarities among the four mines (Brigo *et al.*, 1977), and assuming that the interpretation of Henjes-Kunst *et al.* (2017) on the Bleiberg ore deposit is also valid for Raibl and Salafossa ores, the ore deposits from our studied sites may have originated from a mixing between a poorly characterised hydrothermal base metal-bearing fluid and low temperature seawater with a high content of bacteriogenic sulphur.

The paragenesis of the primary ore deposits is mainly composed of sphalerite, galena and iron sulphides (mainly pyrite, marcasite and

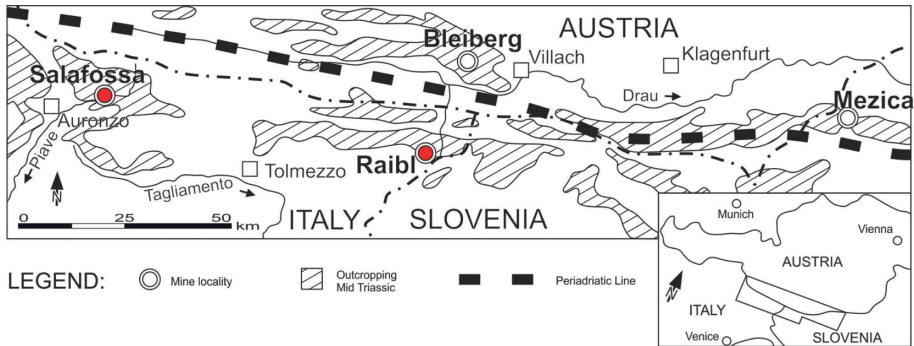


Fig. 1. Location of the four main Pb-Zn carbonate hosted ore deposits in the SE Alps domain, after Brigo et al. (1977)

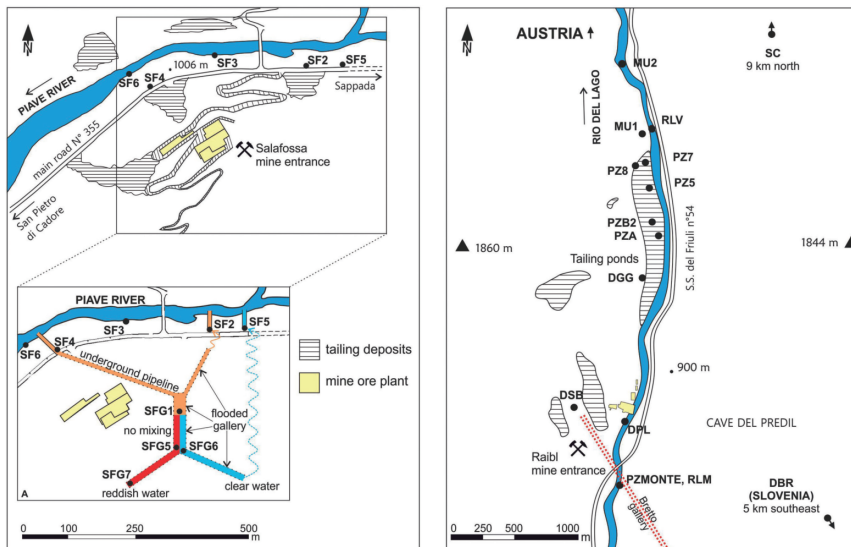


Fig. 2. Index map of the Salafossa (left) and Raibl (right) decommissioned mining districts along with the location of the sampling stations where various types of water samples were collected

melnikovite). Thallium appears to be preferentially hosted in sphalerite, and likely to a lesser extent, in galena (Schroll *et al.*, 1994; Melcher and Onuk, 2019). An upper oxidized zone, usually constituted by secondary minerals such as hydrated iron oxide, is present at Raibl and almost entirely lacking at Salafossa. Lower zones of both mines are enriched in secondary carbonatic minerals (e.g. smithsonite) formed by leaching of the Pb-Zn ore body.

Sulphosalts are rare and the probable presence of Tl-bearing jordanite and gratonite can be found in Raibl ore deposits (Pimminger *et al.*, 1985), whereas

geocronite can be found as an inclusion in galena at Salafossa (Lagny *et al.*, 1974). Among the “gangue” minerals, dolomite and barite prevail. Traces of detrital quartz, alkali feldspar, clay and tuffaceous fragments can be found in “gangue” minerals only at Salafossa, where the ore body is tectonically in contact with the basement and Permian units (Brigo, 1977 and references therein).

Although the Raibl mining district was likely in use from the pre-Roman Epoch, the first documented activity dates from the fourteenth century and the mine ceased all activity in 1991. The mining district is located in a narrow N-S valley dipping northward. The Rio del Lago stream flows from south to north and, after the confluence with the Rio Freddo stream, it becomes a tributary of the Slizza River which conveys into the Austrian Gail–Drava–Danube river system. The Raibl mine extends for approximately 110 km of galleries which were partially flooded when the dewatering system was interrupted (in 2008–2009). The water circulation is governed by mine voids of high porosity and hydraulic conductivity. The main water outflow is the Bretto gallery (DBR; 250–300 L s⁻¹, Petrini *et al.*, 2016) which connects a 5 km underground gallery to the lower level of the mine drainage system discharging directly into the Koritnica River which flows in the Isonzo/Soča River, in Slovenia.

Information concerning the decommissioned mining district of Salafossa has been reported elsewhere (Pavoni *et al.*, 2017, 2018). Heterogeneous deposits with mineralised tailings are present in the external area both at Raibl and Salafossa. Unlike Salafossa, where the residual sludge enriched in PTEs was usually discharged into the Piave River, at Raibl, during the period from 1976 to 1991, this material accumulated in tailing ponds set up on the western bank of the Rio del Lago stream. Those impoundments are located 1.5 km north with respect to the mine entrance. They are characterised by the following dimensions: 1200 m in length, 100 m width and a maximum height of 25 m and they store up to 2 million m³ of flotation mill tailings. Currently, they represent the principal source of release and transport of dissolved PTEs in the Rio del Lago stream.

2.2. Sampling strategy

Several water samples were collected both at Raibl and Salafossa (Pavoni *et al.*, 2018). The following samples were recovered at the Raibl district: mine drainage waters (DPL and DBR outflowing into the Rio del Lago stream and in the Koritnica River, in Slovenia, respectively), waters from abandoned mine galleries (DSB and DGG) and surface freshwaters from Rio del Lago, upstream (RLM) and downstream from the mine and the tailing ponds (RLV) and in the Slizza River (SC) near the border with Austria, 9 km further north from the mining area. Groundwater samples were collected in dynamic mode from piezometers upstream from the mine (PZM), within the impoundments (PZA, PZB2, PZ5, PZ7 and PZ8) and outside these tailing ponds (MU1 and MU2). At Salafossa, water samples were collected from the main drainage points of the mine outflowing into the Piave River (SF2, SF4 and SF5), whereas a second group of waters were sampled in two galleries (referred to the letter “G” in the labels): the SFG6 sample was clear whereas the SFG5 sample appeared intensively reddish. A further water sample (SFG1) was collected along the so-called “mixing zone” between the two types of water. The last water sample (SFG7) was collected at the head of the gallery, the source point for the reddish stream.

Water samples were immediately filtered (syringe filters Millipore Millex HA, 0.45 µm) and several aliquots were collected for different chemical analyses. Water samples for trace element determination were acidified (1% v/v) with ultrapure HNO₃ (69% v/v, VWR). In addition, the main physico-chemical parameters (temperature, pH, Eh and EC) were measured *in situ* using portable probes (pH-meter PH25 and Conductivity-meter CM 35 from Crison Instruments). The same procedures were followed for the Salafossa mine (Pavoni *et al.*, 2018).

2.3. Analytical measurements

Details on the analytical determination of major ions and trace elements in the water samples collected at Salafossa were previously reported in Pavoni *et al.* (2018). Regarding the water samples from Raibl, the concentrations of Ca, Mg, K, Na and Zn were determined using an Optima 8000 ICP-OES Spectrometer (PerkinElmer, USA). Concentrations of Fe, Mn, Pb and Tl were quantified using a NexION 350x ICP-MS Spectrometer (PerkinElmer, USA). The analysis was performed in KED mode (Kinetic Energy Discrimination) to avoid and minimise cell-formed polyatomic ion interferences. Potential matrix effects were evaluated by the analysis of laboratory-fortified samples obtained by spiking 1 or 10 µg L⁻¹ of trace elements in water samples collected in the field and acceptable recoveries were obtained (99-102%). The precision of the ICP-OES and ICP-MS analyses expressed as RSD% was always <5% and <3%, respectively.

Anions were determined by Ion Chromatography (IC) using a Metrohm 883 Basic IC Plus equipped with a Metrohm 863 Compact autosampler and a Metrosep A Supp 5-250/4.0 anionic column. The precision of the IC analysis expressed as RSD% was <10%. Regarding CO₃²⁻ and HCO₃⁻, the determination was performed using potentiometric titration (APAT CNR IRSA, 2003).

2.4. Exploratory multivariate data analysis

Experimental data were analysed by principal component analysis (PCA) for both the Salafossa and Raibl mining sites in order to identify the relationships within samples, variables and between samples and variables (biplots) (Oliveri *et al.*, 2019). Multivariate data processing was performed after column autoscaling using the CAT package (Chemometric Agile Tool, based on the R platform and freely distributed by Gruppo Italiano di Chemiometria, Italy, (Leardi *et al.*, 2019).

3. RESULTS AND DISCUSSION

3.1. Major ions and trace elements

Water samples collected at the Salafossa and Raibl mining districts generally showed elevated concentrations of Ca²⁺, Mg²⁺, HCO₃⁻ and SO₄²⁻ (Table 2) most likely due to the dissolution of carbonatic rocks and oxidation processes involving sphalerite, galena and iron sulphides, respectively (Liu *et al.*, 2017). Water sample compositions both from Salafossa and Raibl were plotted in the Piper diagram (Fig. 3, Piper, 1944) and belong to the Ca-HCO₃ and Ca-SO₄ groups. Although the oxidation of sulphides can lead to the formation of AMD (e.g. Concas *et al.*, 2006; Campanella *et al.*, 2017), water samples exhibited alkaline pH values (Table 2) as a result of the buffering effect supplied by

carbonates in solution (Banks *et al.*, 2002; Navarro and Sola, 2010; Navarro *et al.*, 2015). Regarding PTEs, significant amounts of dissolved Pb, Tl and Zn were detected especially in the groundwater collected from the tailing ponds at Raibl and in the samples from the mine galleries at Salafossa where the water flows directly in contact with the mineralised rock (Table 2). Due to a lack of appropriate guidelines for water draining mineral deposits, a comparison was provided with the Italian regulatory threshold limits for groundwater (Italian Legislative Decree 152/2006 according to EU Directive 2000/60/EC) (Fig. 4). Zinc was found to be notably present at both sites, exceeding the limit value (3000 $\mu\text{g L}^{-1}$) in one of the piezometers in the tailing ponds at Raibl (PZ5, 5243 $\mu\text{g L}^{-1}$) and at the source of the reddish water (SFG7, 16204 $\mu\text{g L}^{-1}$) representing the main pathway of transport and diffusion of PTEs at Salafossa (Pavoni *et al.*, 2018).

Thallium also exceeded the threshold limit value of 2 $\mu\text{g L}^{-1}$ in all the sampling sites at Salafossa with the only exception being the Piave River freshwater collected upstream from the mining district (SF3, Tl <LOD). As already pointed out in previous research (Petrini *et al.*, 2016), equally elevated concentrations of Tl were found at Raibl, where Tl systematically exceeded the threshold limit with the lone exception being the water samples collected upstream from the mining district (PZM and RLM) and one of the freshwater samples collected downstream (SC), most likely due to intense dilution effects.

Major differences between the two investigated sites were found for dissolved Pb, which is subjected to intense dilution effects at Salafossa (Pavoni *et al.*, 2018). Conversely, notably high concentrations of Pb were found at Raibl, where the element often exceeded the threshold limit of 10 $\mu\text{g L}^{-1}$, especially in the tailing ponds.

Table 2. Physico-chemical parameters and concentrations of the major ions and trace elements in the water samples collected at the Salafossa and Raibl decommissioned mining districts (LOD: limit of detection, n.d.: not determined).

		freshwater		mine drainage		mine gallery		groundwater
		Salafossa	Raibl	Salafossa	Raibl	Salafossa	Raibl	Raibl
T	$^{\circ}\text{C}$	5.30 - 5.80	6.30 - 7.90	6.50 - 8.00	9.90 - 10.5	7.20 - 8.70	7.80 - 8.10	7.40 - 8.90
pH		8.15 - 8.26	7.74 - 8.16	7.20 - 8.06	8.29 - 8.75	7.15 - 8.00	8.07 - 8.69	7.30 - 7.86
Eb	mV	291 - 312	159 - 171	305 - 326	162 - 175	-76 - 390	190 - 218	152 - 193
EC	$\mu\text{S cm}^{-1}$	406 - 520	187 - 327	464 - 489	294 - 410	420 - 1335	419 - 625	195 - 297
Ca ²⁺	mg L ⁻¹	45.1 - 47.0	32.9 - 56.5	38.9 - 40.4	38.8 - 50.9	34.8 - 122	37.6 - 80.4	32.4 - 55.5
Mg ²⁺	mg L ⁻¹	14.2 - 17.2	9.65 - 16.5	27.1 - 29.1	14.1 - 22.0	24.8 - 89.7	12.5 - 35.1	10.3 - 12.7
Na ⁺	mg L ⁻¹	1.42 - 1.75	1.03 - 4.40	0.30 - 0.38	0.96 - 1.51	0.26 - 0.88	0.45 - 0.65	1.17 - 1.85
K ⁺	mg L ⁻¹	0.40 - 0.47	1.04 - 2.09	0.14 - 0.25	0.40 - 0.67	0.11 - 1.69	0.17 - 0.44	0.81 - 21.1
Cl ⁻	mg L ⁻¹	<LOD	2.77 - 6.90	<LOD - 0.48	0.94 - 1.19	2.20 - 2.70	0.73 - 12.1	2.08 - 15.5
SO ₄ ²⁻	mg L ⁻¹	58.0 - 68.0	1.24 - 22.5	90.0 - 104	25.2 - 63.2	71.0 - 532	7.38 - 178	2.78 - 50.4
CO ₃ ²⁻	mg L ⁻¹	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
HCO ₃ ⁻	mg L ⁻¹	168 - 168	134 - 211	166 - 179	97.0 - 111	163 - 173	167 - 168	110 - 164
Fe	$\mu\text{g L}^{-1}$	5.50 - 10.1	2.88 - 4.40	<LOD - 27.6	1.62 - 22.8	<LOD - 5843	2.44 - 14.6	2.65 - 73.7
Mn	$\mu\text{g L}^{-1}$	<LOD	0.27 - 0.40	<LOD - 3.56	0.37 - 0.80	<LOD - 344	0.17 - 1.02	0.10 - 2.36
Pb	$\mu\text{g L}^{-1}$	<LOD	3.67 - 27.6	<LOD	7.79 - 8.87	<LOD - 80.1	10.2 - 21.3	1.10 - 70.1
Tl	$\mu\text{g L}^{-1}$	<LOD - 6.06	0.02 - 10.6	17.3 - 29.6	8.06 - 11.3	16.3 - 261	3.20 - 43.3	0.01 - 80.1
Zn	$\mu\text{g L}^{-1}$	2.84 - 179	2.80 - 632	501 - 843	712 - 866	465 - 16204	344 - 2508	1.10 - 5243

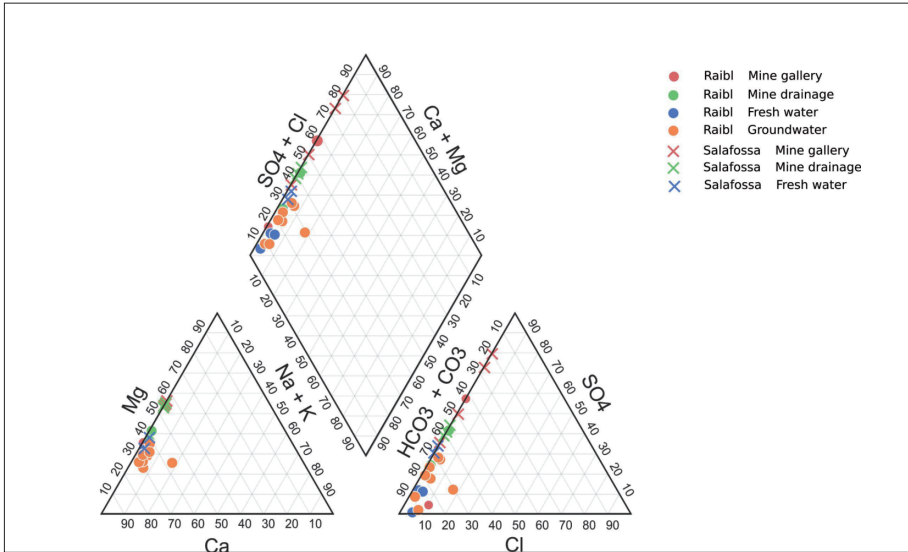


Fig. 3. Piper diagram showing the hydrochemical facies of all water samples collected from the mine galleries, the drainage outflow and the river freshwater at the Salafossa and Raibl mining districts

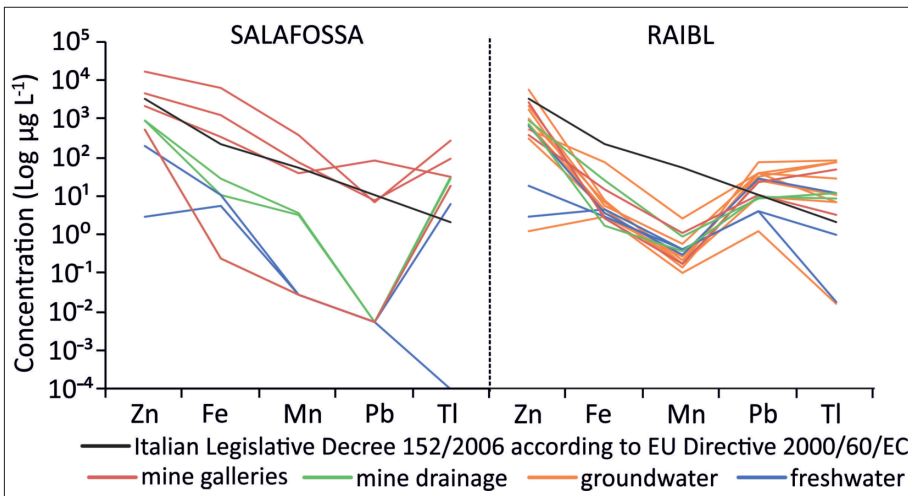


Fig. 4. Trace element patterns for all water samples collected at the investigated mine sites with respect to the Italian regulatory threshold limits (Italian Legislative Decree 152/2006 according to EU Directive 2000/60/EC).

3.2. Water-rock interactions and dilution processes

As an additional chemometric tool to the traditional evaluation of single parameters, a PCA was employed to depict major ion and PTE behaviour in the water samples collected from the two investigated mining sites, highlighting the relationships and differences among different types of water (Fig. 5). At Salafossa, the source of the reddish water (SFG7) displayed the highest PTE, SO_4^{2-} and EC levels since water-rock interactions under reductive conditions ($E_h = -76$ mV) may promote PTE dissolution and/or desorption processes (Xiao *et al.*, 2003; Liu *et al.*, 2017). The PCA output clearly denotes the influence of dilution responsible for the decrease in PTE concentrations from the inner part of the galleries to the external area at Salafossa (Pavoni *et al.*, 2018). Indeed, natural mitigation was provided by mixing processes involving the clear water in the mine galleries (SFG6) which appeared chemically comparable to the external drainage water (SF2, SF4 and SF5) and further dilution of the external drainage water into the Piave River freshwater, although dissolved Zn ($179 \mu\text{g L}^{-1}$) and Tl ($6.06 \mu\text{g L}^{-1}$) still remained elevated.

Regarding Raibl, the different types of water are not particularly well distinguished in the PCA output, most likely due to a more complex water circulation system. However, the distribution of the water samples in the plot reflects their chemical composition. Zinc and Tl displayed a similar behaviour and were notably present in solution as well as SO_4^{2-} and Pb, especially in the mine galleries (2508, 43.3, $21.3 \mu\text{g L}^{-1}$ of Zn, Tl and Pb and 178 mg L^{-1} of SO_4^{2-} in sample DSB) which also showed high EC values ($625 \mu\text{S cm}^{-1}$ in sample DSB). On the contrary, extremely low concentrations were found upstream from the mine both in the Rio del Lago stream freshwater (RLM) and groundwater (PZM) which showed a very similar chemical composition, as also highlighted in the PCA output. In the tailing ponds, the highest concentrations of Zn ($5243 \mu\text{g L}^{-1}$), Tl ($80.1 \mu\text{g L}^{-1}$) and Pb ($70.1 \mu\text{g L}^{-1}$) were found at PZ5. Although decreasing, concentrations of Zn, Pb and Tl were still found to be very high in the sampling stations located downstream from the

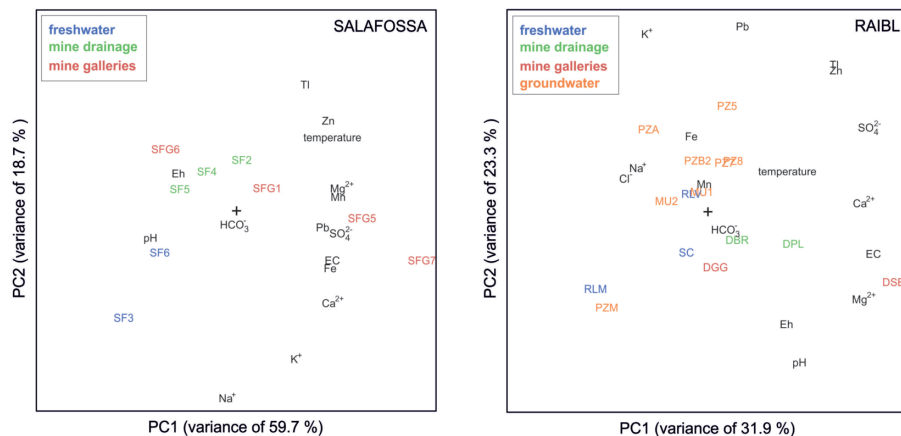


Fig. 5. Biplots summarising the results of PCA performed on different types of water samples collected at the Salafossa and Raibl decommissioned mining districts

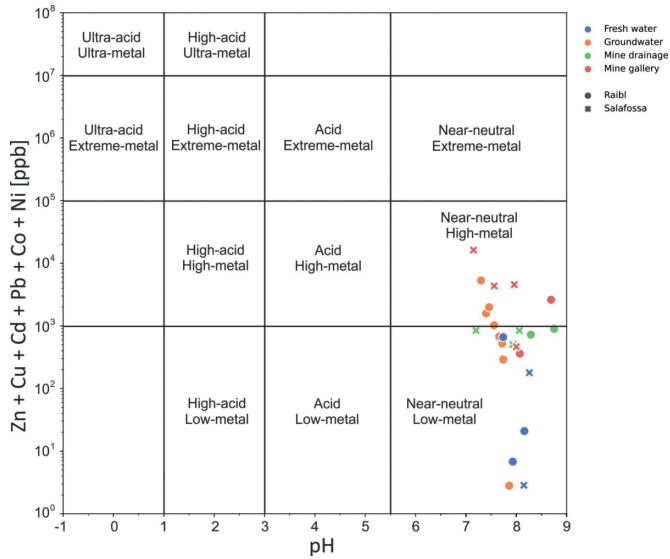


Fig. 6. Ficklin diagram of different water samples collected at the two investigated mining sites showing the sum of dissolved trace elements (Cd, Co, Cu, Ni, Pb and Zn) plotted against pH values. Fig. 7. Impacto en la producción de crudo, como consecuencia de la reducción de inversiones en 2020 (Rystad Energy, 2020)

tailing ponds (MU1 and MU2). This is especially evident at site MU1 where the chemical composition was similar to RLV, suggesting that the lack of impermeabilisation systems of the impoundments and the diffuse presence of mineral wastes allows for mixing processes between PTE-enriched groundwater and the Rio del Lago stream waters.

The Ficklin diagram (Ficklin *et al.*, 1992; Plumlee, 1999) illustrates the PTE content of different water samples collected at the two investigated mining districts which were classified as “near-neutral, high metal” and “near-neutral, low metal” water (Fig. 6).

The distribution of the water samples in the Ficklin diagram confirms the dilution processes, especially with regard to Salafossa. Indeed, the water samples collected in the mine galleries (SFG5 and SFG7) fall into the category of “high-metal” water, whereas the clear water at the confluence zone (SFG6), the external drainage water (SF2, SF4 and SF5) and the Piave River freshwater (SF3 and SF6) move to the field of “low-metal”. This is similar to the water samples collected at Raibl. There, the water samples from the mine galleries (DSB and DGG) and some of the water samples collected from the piezometers in the tailing ponds fall into the category of “high-metal”, whereas the external drainage water (DPL and DBR) and the Rio del Lago stream and Slizza River freshwater (RLM, RLV and SC) move to the field of “low-metal”.

With the exclusion of the source of the reddish water in the mine galleries at Salafossa, which is considered an outlier since its extremely high concentrations of Zn (16204 µg L⁻¹), Tl (261 µg L⁻¹) and SO₄²⁻ (532 mg L⁻¹), Zn

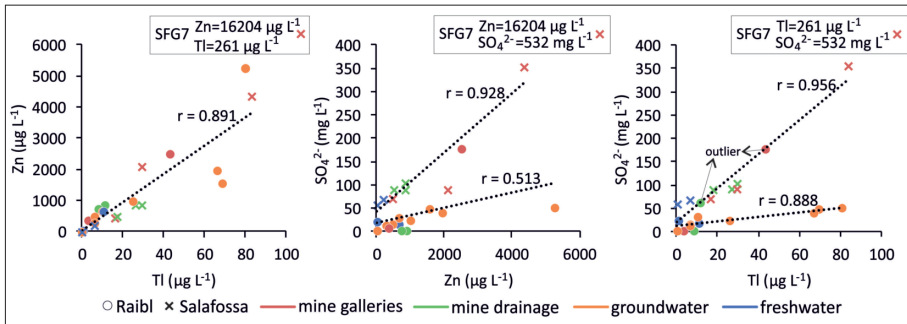


Fig. 7. Correlations between Zn, Tl and SO_4^{2-} in the water samples collected at the investigated mine sites

and Tl increase proportionally with the increase of SO_4^{2-} both at Salafossa ($r=0.928$ and $r=0.956$ for Zn and Tl, respectively) and Raibl ($r=0.513$ and $r=0.888$ for Zn and Tl respectively) (Fig. 7).

Significant correlations were also found between Zn, Tl and Ca ($r=0.658$ and $r=0.647$ for Zn and Tl respectively). These correlations testify to the contribution of the water-rock interactions since the oxidation of sulphides could explain the elevated concentrations of SO_4^{2-} (Xiao *et al.*, 2003; Liu *et al.*, 2017) which were found to be higher in the water samples collected in the mine galleries rather than those from the external area at the investigated mine sites. Most likely due to sphalerite being the common mineral source, dissolved Zn and Tl were found to be significantly correlated ($r=0.891$, Fig. 7) thus testifying to the mutual availability of these elements in solution.

4. CONCLUSIONS

Despite no evidence of AMD due to the buffering effect promoted by the dissolution of carbonatic host rocks, dissolved Zn, Pb and Tl reached high concentrations in the water draining the Pb-Zn orebodies and associated tailing deposits at the Raibl and Salafossa mining districts. This suggests that weathering and oxidation of sulphides in mine tailings, as well as water-rock interaction processes are occurring in the abandoned mine galleries at both mining districts and in the tailing ponds at Raibl. Intense dilution and mixing processes effectively mitigate PTE concentrations which notably decreased after outflowing into the Piave River and Rio del Lago stream freshwaters. However, Tl still remained at concentrations of concern ($> 2 \mu\text{g L}^{-1}$) in the freshwater downstream from both the mining districts. Moreover, quite high concentrations of Zn, Pb and Tl persisting in the groundwater, downstream from the tailing ponds (MU1) as well as in the freshwater collected downstream from the mine (RLV) at Raibl, suggest the groundwater is a passive contamination source for fluvial waters. Currently, dilution in the fluvial waters seems to be the only natural process able to mitigate the possible negative impact of these potentially toxic metals within the drainage basin downstream from the mine.

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