Hydrogeochemistry of thallium and other potentially toxic elements in neutral mine drainage at the decommissioned Pb-Zn Raibl mine (Eastern Alps, Italy)

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ABSTRACT

Decommissioned mines represent a worldwide concern due to the potential long-term effects related to the dispersion of potentially toxic elements (PTEs) in the environment. In this study, 176 water samples were collected in the period 2018–2021 at the carbonate-hosted Pb-Zn Raibl mine which is affected by neutral mine drainage (NMD). The post-flotation tailings are the main source of PTEs (Zn, Pb and especially Tl) in the river drainage system. Compared to other dissolved PTEs (Zn, Pb, Cd), Tl was found to be more mobile, reaching concentrations up to $120\,\mu g\,L^{-1}$ in waters flowing in the tailings impoundments. Modelling results suggest that Tl is mainly present in the Tl(I) ionic and mobile form thus suggesting that relevant natural attenuation processes for this element are not expected in the investigated area. In contrast, Zn and Pb attenuation pathways appeared to be governed by pH-dependent speciation and sorption processes, whereas elevated Zn concentrations were likely also limited by hydrozincite precipitation. Metalloids such as As and Sb were almost entirely released into the slightly alkaline waters of the mine drainage system, which are generally characterised by longer residence time or standing waters whereas As and Sb concentrations were negligible in the tailings-seepage waters. However, intense rainy events may increase PTE concentrations of one order of magnitude, especially in the tailings impoundment groundwater as a result of a rise in the water table, and PTE total dissolved loads of three orders of magnitude, in the main stream during high flow events, thus representing the most critical factor in regulating the remobilisation and downward dispersion of PTEs in the river drainage system.

1. Introduction

In the last decade there has been growing worldwide concern regarding Thallium (Tl) as an emerging natural or anthropogenic contaminant. In spite of its potential toxicity to ecosystems and humans through natural geological pathways (Peter and Viraraghavan, 2005; Campanella et al., 2019), this element is often given little thought by the regulation authorities. Thallium (Tl) is a relatively rare heavy metal with an average concentration of $0.9\,mg\,kg^{-1}$ (Rudnick and Gao, 2003) in the upper continental crust. The chemical behaviour of Tl resembles that of chalcophile elements (Cu, Pb, Zn, Hg, Sb and As) on the one hand and that of the alkali metals (K, Rb, Cs and Na) on the other (Liu et al., 2016). In freshwater, Tl is highly mobile and toxic at very low concentrations ranging from a few $\mu g\,L^{-1}$ to $mg\,L^{-1}$ (Peter and Viraraghavan, 2005; Tatsi et al., 2015; Belzile and Chen, 2017) and is found in two oxidation states, the most abundant monovalent Tl(I) (Vink, 1993) and the most uncommon, toxic but less bioavailable trivalent Tl (III) (Ralph and Twiss, 2002). Bioaccumulation and biomagnification along the trophic chain can occur in areas affected by elevated geochemical anomalies due to both natural and anthropogenic sources, posing a potential issue for environmental quality. For this reason, the areas affected by high Tl concentrations in several environmental matrices need to be investigated in the field to identify the main sources of contamination, focusing on the main geochemical mechanisms in regulating the behaviour and fate of Tl along with other associated potentially toxic trace elements (PTEs).

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In general, the mineral phases that can host notable amounts of Tl mainly belong to sulphide and sulfosalt ore deposits, among which the most relevant are sphalerite, which may have a Tl concentration up to 1800 mg kg^{-1} (Henjes-Kunst et al., 2017; Pimminger et al., 1985), galena (George et al., 2016), pyrite (George et al., 2019) and other Fe sulphides, jarosite (Garrido et al., 2020) or Tl-bearing sulfosalt minerals (Pimminger et al., 1985; Biagioni et al., 2013). Thallium (Tl) can also be found in K-bearing minerals, such as alkali feldspars or micas, and in coal (Kaplan and Mattigod, 1998 and references therein).

Primary sources of Tl in the environment are related to mining, burning coal, cement plants, electronics, etc. (Belzile and Chen, 2017). The contamination deriving from mining activities is one of the major global sources of PTEs in the environment, affecting several environmental matrices including soils, sediments, water, air, and biota even in very large areas (e.g., Acquavita et al., 2022; Barago et al., 2020; Giani et al., 2012; Hudson-Edwards et al., 2011). In Europe, mining of carbonate-hosted Pb-Zn ores such as those from the Alpine (Barago et al., 2021; Brigo et al., 1977; Pimminger et al., 1985) and Silesian districts (Viets et al., 1996), or of the volcanogenic hydrothermal deposits from the Serbo-Macedonian metallogenic province (Bačeva et al., 2014), which have largely been decommissioned, can represent one of the major sources of Tl in the environment. The ores in these mining sites, from which PTEs can be released, still contain high amounts of Tl as a trace element posing a potential environmental risk.

The water-rock interaction in decommissioned mine galleries as well as the weathering of waste rocks or tailings deposits produced during mining and metallurgical activities may favour the release of dissolved Tl and other PTEs, reaching concentrations well above the suggested values from the available environmental and toxicological guidelines (Casiot et al., 2011; Ghezzi et al., 2019; Jabłońska-Czapla et al., 2016; Pavoni et al., 2017, 2018). In fact, such guidelines are often missing in the case of Tl. In Italy, threshold limits for Tl are only provided for groundwaters (2 μg L^{-1}), whereas no quality guidelines are defined in the case of surface freshwaters. Generally, regarding freshwater quality guidelines (CCME, 1999), some authors suggest that these guidelines should be revised downward (e.g. to 0.087 μg L^{-1}) since scientific evidence has highlighted the serious toxic effects on a wide variety of aquatic organisms, even at lower Tl concentrations (Campanella et al., 2019; Tatsi et al., 2015). Since the remediation of decommissioned mining districts is usually very difficult to manage, as well as being expensive, the potentially harmful effects related to the occurrence of Tl and other PTEs may persist in these areas for decades, for example, the Montevecchio Pb-Zn mining district (Cidu et al., 2011) where PTE concentrations are still remarkably high even after almost 50 years of flushing.

The potentially harmful effects caused by mining mainly depend on the chemical composition, the mineralogical assemblage of the ore deposit, and the mineral processing steps adopted to recover the elements of economic interest. The release of PTEs in water draining decommissioned mining districts is mainly due to physico-chemical alteration processes at the water-rock interface of the ore as well as leaching of waste-rocks, tailings or smelter slags. Moreover, the mobility of PTEs is governed by several factors including mineral stability, Eh-pH boundary conditions and exposure to weathering among the most important water parameters. The physico-chemical boundary conditions, especially in terms of pH and Eh, can control PTE speciation in water. Oxidising conditions and higher values of pH, derived from the dissolution of carbonate host rocks, which have a crucial role in buffering acid mine drainages (AMD), can promote the oxidation and carbonatation of sulphides to more stable mineral forms (e.g., galena to cerussite: PbS - > PbCO$_3$) with subsequent attenuation of the release of PTEs in the dissolved phase.

The adsorption of PTEs to Fe oxy-hydroxides (from amorphous ferrihydrite to crystalline goethite) has been widely investigated as this process strongly influences the cation hydrochemistry by limiting the mobility and dispersion of dissolved PTEs (Dzombak and Morel, 1990).

High pH values usually promote the transformation of Fe sulphides (e.g., pyrite: FeS$_2$) to oxidised forms (e.g. ferrihydrite) which can notably scavenge PTEs from solution through sorption processes. PTE adsorption occurs at different pH values, as reported for ferrhydrite: Cr^{+3} > Pb^{+2} > Cu^{+2} > Zn^{+2} > Cd^{+2} > Ag$^+$ > Ca^{+2} ≈ Tl$^+$, from the most to the less sorbed cations (Coup and Swedlund, 2015; Gustafsson, 2009). However, PTEs are only transitorily scavenged since low pH values can induce the dissolution of Fe oxy-hydroxide minerals with subsequent release of previously adsorbed PTEs.

The purpose of this research was to investigate the water chemistry in a Mississippi Valley-type (MVT) carbonate-hosted Pb-Zn decommissioned mine in the Alpine district, focusing on the geochemical behaviour of Tl and other PTEs in a complex environment notably affected by mining. In particular, the objectives were: a) to monitor the occurrence of dissolved PTEs in surface freshwaters, in waters draining abandoned mine galleries and groundwaters into the tailings impoundments b) to investigate the temporal variability of dissolved PTEs and their relation to local hydrological features c) to understand the role of different hydrological conditions on Tl and other PTE mobility from the mine galleries and tailings impoundments to the river drainage system.

1.1. Environmental setting

The Raibl mining district is located in a narrow north-south (N-S) trending valley near the village of Cave del Predil (Friuli Venezia Giulia, Italy; lat. 46.44150, long. 13.56904; 900 m a.s.l.) close to the borders with Slovenia and Austria in the Julian Alps, a south-eastern sector of the Alps (Fig. 1). The Rio del Lago is the stream which flows along the valley from S to N and, after the confluence with the Rio Freddo stream, it becomes the Slizza River which conveys into the Gail–Drava–Danube River system. The average annual rainfall in the period from 2007 to 2021 was 2240 mm/year, with a min-max rainfall of 1490–2980 mm/year and the average annual air temperature was 7.8 °C (ARPA FVG – OSMER and GRN data set; http://www.meteo.fvg.it). Summer and winter are the driest seasons, and autumn and spring the rainiest.

Although the Raibl mining district may have been active from the pre-Roman Era, the first documented activity dates from 1320 and the mine has been closed since 1991. The mine galleries extend inside Monte Re for 500 m and 480 m above and below the village of Cave del Predil, respectively, organised with 19 underground levels below the village for a total of >120 km of galleries. The galleries below the 13th level (−240 m from level zero) were flooded when the dewatering system was recently interrupted. The main water outflow of the underground mine system is the Bretto gallery (sampling site DBR: 250–300 L/s; Fig. 1), a 5 km gallery starting from the 13th level, which discharges directly into the Koritnica River, which flows into the Isonzo/Soča River, in Slovenia. In contrast, a part of the mine drainage system above the level of the village of Cave del Predil (sampling site: DPL) drains into the Rio del Lago stream, which flows in Italy towards Austria. An estimated 4 million metric tons of mineralised waste-rocks and tailings from the flotation plant operating at the Raibl mining district were disposed from 1976 to 1991 in tailings impoundments set up on the western bank of the Rio del Lago stream. Those impoundments are located 1.5 km N with respect to the mine entrance and are characterised by the following dimensions: 1200 m length, 100 m width and a maximum height of 25 m (Barago et al., 2021). Currently, the potential dispersion of water enriched in PTEs from the tailings impoundments to the Rio del Lago stream represents an issue of concern.

The early Mesozoic carbonate-hosted Pb-Zn (Sangster, 1976) mining district of the Eastern Alps represents one of the most historical and studied metallogenic provinces in Europe. The four Pb-Zn mines of Bleiberg (Austria), Mežica (Slovenia), Raibl and Salafossa (Italy) produced >75 % of the total Pb and Zn extracted from the Alps (Brigo et al., 1977). Currently, these deposits are of subeconomic interest, and the mines were decommissioned at the end of the twentieth century.
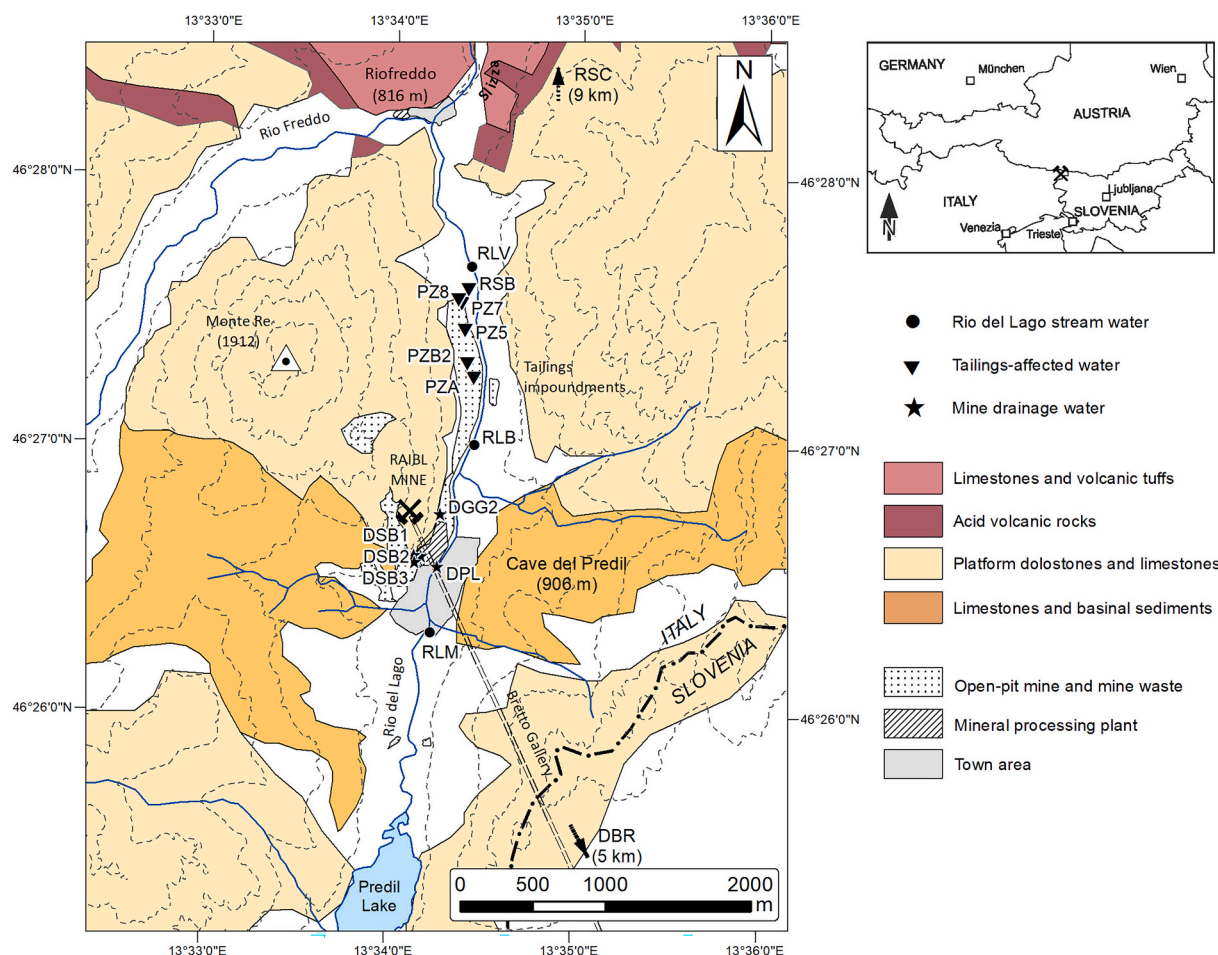
Fig. 1. Geological map of the Raibl mining district (modified after Desio et al., 1967) with the names and locations of the sampling stations related to various waterbodies.

This study is focused on the Triassic carbonate-hosted strata-bound Pb-Zn Raibl mine. The classification of these ore deposits is still controversial (Brigo et al., 1977; Henjes-Kunst et al., 2017; Leach et al., 2010; Schroll, 2005). The MVT (or Alpine-type) low-temperature hydrothermal Pb-Zn ore deposit of Raibl is hosted in thick and massive Triassic dolomitic reefs located on the Adriatic passive continental margin. Other lithologies such as marls and volcanic rocks are notably less abundant in the study area. Structurally, the deposit of Raibl is similarly controlled by the Triassic to Early Jurassic extensional fault activity associated with the Pangea breakup (Doglioni, 1988). The paragenesis of the ore deposits is mainly composed of primary sulphides such as sphalerite (ZnS), galena (PbS) and iron sulphides (mainly pyrite and marcasite: FeS_2). Regarding the occurrence of Tl, the element appears to be preferentially hosted in colloform sphalerite, and likely to a lesser extent in galena and Fe sulphides (Brigo and Cerrato, 1994; Melcher and Onuk, 2019; Schroll et al., 1994). Unusually, elevated Tl-content in inclusions found in dolomite and sphalerite could presumably be related to Tl-bearing jordanite ($Pb_4As_2S_7$) microphases (Brigo and Cerrato, 1994; Pimminger et al., 1985; Venerandi, 1966). An upper oxidised zone is mainly constituted by Fe oxy-hydroxide secondary minerals such as ferrihydrite or goethite. Similarly, the deepest areas of the deposit present abundant secondary carbonate minerals (e.g., smithsonite: $ZnCO_3$, hydrozincite: $Zn_5(CO_3)_2(OH)_6$ and cerussite: $PbCO_3$) formed by leaching of the primary sulphides under ambient conditions. Among gangue minerals, dolomite and barite prevail (Brigo et al., 1977).

2. Materials and methods

2.1. Sampling strategy

In this research, 16 sampling sites were selected at the decommissioned mining district and monitored between 2019 and 2021. In detail, 14 stations were sampled monthly for 1 year, including 3 piezometers (PZB2, PZ5, PZ7), which were sampled monthly for 2 years and 2 stations (DGG2, RSC), which were only sampled sporadically. In addition, results from two preliminary sampling campaigns performed in 2018 were also included in this study for a total of 176 water samples.

The sampling stations were divided into three groups (Fig. 2): (a) *mine galleries and drainage water*: drainage water outflowing into the Rio del Lago stream in front of the mine entrance (DPL) and in the Koritnica River (Slovenia) from the Bretto gallery (DBR), respectively; seepage water flowing from the upper sector of the mine (DGG2); water from three distinct mine galleries at the "zero-level" (DSB1, DSB2, DSB3) which converge in the main outflow (DPL). (b) *Tailings-affected water*: groundwater from the tailings impoundments taken from the external and internal tailings dams mainly consisting of waste rocks (PZA, PZB2, PZ5, PZ7 and PZ8) and a creek at the northern side of the impoundments (RSB). (c) *Surface freshwater from Rio del Lago - Slizza stream*: upstream from the mining site (RLM), immediately downstream from the mine and the tailings impoundments (RLB and RLV, respectively), and further downstream in the Slizza River (RSC) just before the border with Austria, 9 km N. The stream in RLM and RLB stations was found often
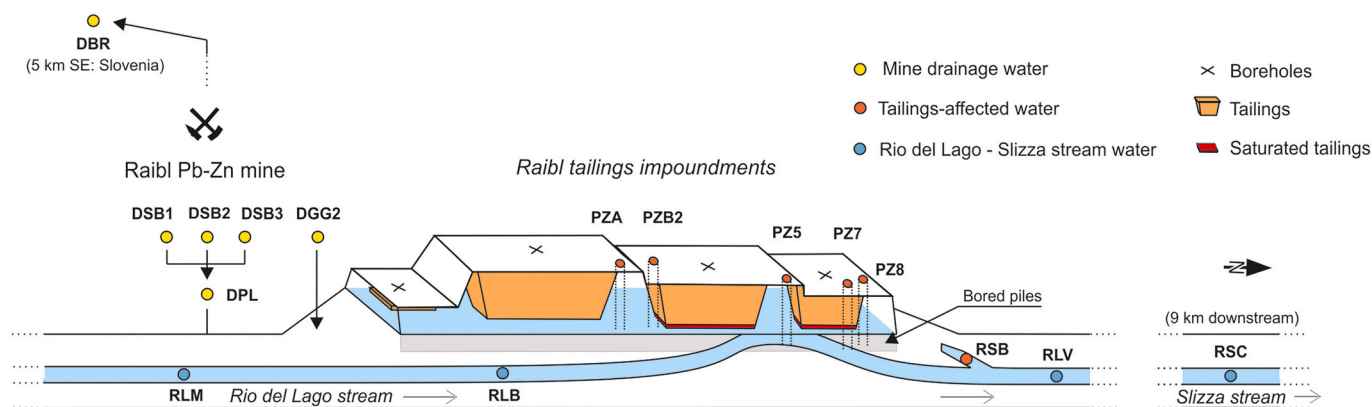
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Fig. 2. Schematic representation of the decommissioned Raibl mining district showing the location of the monitored stations for different groups of water. The orange area represents the possible volumes of tailings stored in the ponds based on boreholes and geophysics (Barago et al., 2021).

dry.

Groundwater sampling was performed in dynamic mode using a full submersible pump, which was inserted into each piezometer. In detail, groundwater samples were collected following 15 min of purging for the stabilisation of the physico-chemical parameters. All the water samples were filtered *in-situ* (syringe filters Millipore Millex HA, 0.45 μm pore size, mixed cellulose esters) and three aliquots of 100 mL each were collected for different chemical analyses in pre-conditioned (hot suprapure HNO_3 (VWR), ≥ 69 %, 10 % v/v, heated at 50 °C for 12 h and rinsed with Milli-Q water and the water sample before sample collection) PTFE containers. Moreover, blank samples were collected on each sampling day. Water samples for PTEs and major cation determinations were acidified (1 % *v/v*) with HNO_3 (69 % v/v, VWR). Samples were transported to the laboratory in a cooler filled with ice packs and then stored at a temperature of 4 °C in a cold, dark room. In addition, the main physico-chemical parameters (temperature, pH, oxidation/reduction potential (ORP), dissolved oxygen (DO), electrical conductivity (EC) and total dissolved solids (TDS)) were measured *in situ* using a portable multiprobe meter (Hanna HI98194). Total dissolved load (TDL) was calculated as the product between the dissolved PTE concentration in the filtered water sample and the water discharge from the gauge station located downstream from the tailings impoundments as per data provided by the Deputy Commissioner for the Raibl mining area.

2.2. Analytical measurements

The concentrations of Ca, Mg, K, Na and Zn were determined using an Optima 8000 ICP-OES Spectrometer equipped with an S10 Autosampler (PerkinElmer, USA). The instrument was calibrated using standard solutions (ranging between 1 and 100 mg L^{-1}) prepared by the dilution of a multistandard solution for ICP analysis (Periodic Table MIX5, Merck). Quality control was done by 1) analysing laboratory-fortified samples that are a subset of the samples prepared by spiking multistandard solutions with known amounts of trace elements (depending on the trace element concentrations in the samples) (Periodic Table MIX1, Merck) in actual water samples; and 2) by laboratory-fortified blanks which consist of a multistandard solution prepared by dilution. Both control solutions were analysed every 10 samples with recoveries ranging between 74 and 130 %. Concentrations of PTEs (As, Ba, Cd, Fe, Ge, Mn, Pb, Sb, Tl, Zn) were quantified using an ICP-MS Spectrometer (NexION 350x, PerkinElmer, USA) equipped with an ESI SC Autosampler. The instrument was calibrated using standard solutions (ranging between 0.5 and 500 μg L^{-1}) prepared by dilution from a multistandard solution for ICP analysis (Periodic Table MIX1 and MIX2, Merck). The analysis was performed in KED (Kinetic Energy Discrimination) mode to avoid and minimise cell-formed polyatomic ion interference. Quality control was performed in the same manner as ICP-OES with a multistandard solution (Multi-element quality control standards for ICP, VWR) prepared by dilution, with recoveries ranging between 83 and 92 %. Moreover, Sc, Y and Ho were used as internal standards for quality control in order to evaluate potential matrix effects. The precision of the ICP-OES and ICP-MS analyses expressed as RSD% was <5 % and 3 %, respectively.

Major anions were determined on bulk samples by Ion Chromatography (IC) using a Dionex ICS-3000 equipped with an ASRS 300 electrolytic suppressor. The precision of the IC analysis expressed as RSD% was <10 %. The IC was calibrated with standard solutions (ranging from 0.1 to 100 mg L^{-1}) prepared via the dilution of two different 100 mg L^{-1} standards (Anion multi-element standard I e II, Merck). Quality control was done by analysing of a different multistandard (Dionex™ Retention time standards for Ion Chromatography, ThermoFisher) every 10 samples, with recoveries ranging between 85 and 101 %. Regarding alkalinity, CO_3^{2-} and HCO_3^- were determined by titration with 0.01 N HCl (APAT and IRSA-CNR, 2003).

2.3. Geochemical modelling

Saturation indexes (SI) and chemical speciation were calculated with the chemical equilibrium models provided by Visual Minteq (Gustafsson, 2014). The SI parameters, calculated from the ion activity product (IAP) and the solubility product (K_{sp}), indicate whether elements could precipitate in determined mineral phases starting from a solution with known physico-chemical parameters and chemical composition. Only the water samples where all the parameters were measured were used to simulate speciation.

2.4. Exploratory multivariate data analysis

A 3-way principal component analysis (3W-PCA) obtained using the Tucker-3 algorithm (Smilde et al., 2004) was used as an unsupervised exploratory chemometric tool for the identification of relationships within objects (different groups of water samples collected at the decommissioned mining district), variables and conditions (sampling campaigns performed monthly throughout 2020) (Oliveri et al., 2020). Prior to multivariate analysis, a log-transform was applied to those variables that did not show a normal distribution. Systematic differences between the experimental variables were minimised by applying column autoscaling (j-scaling) to data matrices (Smilde et al., 2004). Multivariate data processing was performed using the CAT (Chemometric Agile Tool) package, based on the R platform (The R Foundation for Statistical Computing, Vienna, Austria) and freely distributed by Gruppo Italiano di Chemiometria (Italy) (Leardi et al., 2019).
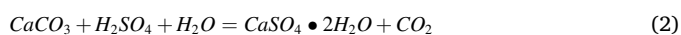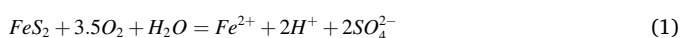
3. Results and discussion

3.1. Physico-chemical characterisation and the major ions of waters

The average pH of the investigated water samples ranged between 7.7 and 8.3 (Table 1, Table S1), indicating overall near-neutral to slightly alkaline conditions due to the dissolution of dolostones and limestones, which represent the main lithologies in the area. The average pH of tailings-affected water was closer to neutral (7.7 ± 0.3) than the drainage waters from the mine (avg. 8.3 ± 0.2) and the stream water (avg. 8.2 ± 0.2), suggesting the aquifer has strong pH buffering capacities. The average temperature ranged between 7.6 and 10.9 °C. Tailings-affected water showed lower EC (297 ± 77 µS cm^{-1}) and TDS (Total Dissolved Content) (155 ± 42 mg L^{-1}) values with respect to the mine drainage water, possibly due to longer water-rock interaction and low-flow conditions inside the mine. However, the lowest average TDS value was found in the stream water (avg. 126 ± 29 mg L^{-1}) indicating strong dilution processes promoted by rainfall and a shorter water-rock interaction compared to the mine drainage water in the galleries (226 ± 67 mg L^{-1}).

Generally, reducing conditions were not observed during this study, although Petrini et al. (2016) detected bulk redox potential (ORP) values near to 0 mV within the mine galleries, most likely due to the role of organic oxidisable matter that occurs as intercalations of dark bituminous layers within the carbonate rocks. All the investigated water samples showed positive ORP and relatively high concentrations of dissolved oxygen (DO: 7.3–8.9 mg L^{-1}).

In the Piper diagram (Piper, 1944; Fig. 3), the distribution of the major anions (Cl$^-$, SO$_4^{2-}$, HCO$_3^-$) and cations (Mg^{2+}, Ca^{2+}, Na$^+$, K$^+$) (Table 2, Table S1) confirmed the hydrofacies identified in a previous study (Petrini et al., 2016).

Freshwater samples from the stream belonged to the Ca-HCO$_3$ hydrofacies whereas there is an evident shift to the Ca–Mg–SO$_4$ hydrofacies for the mine drainage and tailings-affected water samples reflecting higher sulphur availability due to sulphide oxidation (1) or gypsum dissolution (2), initially precipitated as a secondary mineral during limestone neutralisation of the sulphate-rich AMD (Petrini et al., 2016), according to the following Eqs. (1) and (2):

$$FeS_2 + 3.5O_2 + H_2O = Fe^{2+} + 2H^+ + 2SO_4^{2-} \tag{1}$$

$$CaCO_3 + H_2SO_4 + H_2O = CaSO_4 \bullet 2H_2O + CO_2 \tag{2}$$

Very low concentrations of Na$^+$ and K$^+$ reflect the scarcity of silicate minerals and the predominance of calcite and dolomite among the main mineral constituents of the host rock. In contrast, high concentrations of Ca^{2+} and Mg^{2+} were observed, especially in water from the mine galleries, testifying to a long residence period and prolonged water-rock interactions. Regarding sulphates, a notable variability was observed within the investigated water samples, generally reaching values >50 mg L^{-1} (Table 2, Table S1). Under certain environmental conditions, especially during rainy periods or spring thaw, the water table inside the tailings impoundments can sufficiently rise to interact and leach inner

and slightly altered sulphide-rich tailings beds, leading to high concentrations of dissolved sulphates (max SO$_4^{2-}$ in PZ5: 277 mg L^{-1}; Table S3, Fig. S1). This variability showed that the deepest sector of the tailings beds inside the impoundments are characterised by the lowest sulphur availability, potentially related to the advanced oxidation aging of the deepest tailings in the saturated zone. In contrast, results showed that more surficial tailings can still release sulphur as sulphate, indicating possibly high enough amounts of Fe-sulfides such as pyrite or marcasite that can be oxidised being sources of PTEs.

According to the Ficklin diagram (Plumlee et al., 1999) in Fig. 3, all the waters collected at Raibl fall in the "near-neutral" field confirming strong pH buffering effects as the result of carbonate dissolution processes. The majority of water samples in the area of the tailings impoundments and from the mine drainage system fall into the "high-metal" area whereas all the Rio del Lago and Slizza freshwaters belong to the "low-metal" area. The diagram also highlights the difference between the three groups of water samples in terms of pH. Mine waters were more slightly alkaline and enriched in Ca^{2+} and Mg^{2+}, partially overlapped with more near-neutral and metal-rich tailings-affected waters and less enriched stream waters. Thus, no acid mine drainage (AMD) occurs at the decommissioned mining district of Raibl, which appeared to be characterised by a neutral mine drainage (NMD).

3.2. Potentially toxic trace elements: distribution and behaviour

Despite the notable spatial and temporal variability in the distribution of PTEs, the lowest concentrations were found in the waters of the Rio del Lago stream located upstream from the mine and the tailings impoundments (station: RLM, max concentration: Zn = 2.80 and Tl = 0.06 µg L^{-1}; Table S3). In contrast, the water affected by the presence of tailings showed the highest concentrations and variability of metals in the mining district, especially in the case of Zn, Tl and Pb (Table 3: Zn = 2349 ± 2519, Tl = 38.3 ± 25.5 and Pb = 35.1 ± 17.0 µg L^{-1}; Table S2). Thallium and Pb concentrations are very high if compared to the Italian national regulatory limits for groundwaters (D.Lgs. 152/2006: Tl = 2 µg L^{-1}, Pb = 10 µg L^{-1}). Drainage water from the mine also displayed elevated concentrations of PTEs and appeared to be especially enriched in metalloids such as As and Sb (18.6 ± 27.0 and 2.40 ± 2.03 µg L^{-1}, respectively). Conversely, the tailings-affected waters exhibited concentrations of As and Sb one order of magnitude lower (1.4 ± 0.5 and 0.34 ± 0.20 µg L^{-1}) with respect to the drainage water from the mine. The stream water, although diluted, appeared to be mostly affected by metals, especially in the case of Pb and Tl (16.9 ± 11.1 and 5.0 ± 5.8 µg L^{-1}, respectively), whereas As, Sb and Cd occurred with very low concentrations (< 1 µg L^{-1}). The similar distribution of metals (Zn, Pb, Tl) and Ba as well as the differences with metalloids (As, Sb, Ge) and Cd (Fig. 4) was also confirmed by the 3W-PCA (explained with a variance up to 56.5 %, Fig. 5). Zinc (Zn), which is the most abundant metal of the ore assemblage, was by far the most abundant dissolved trace element in water (Table 3), often being more abundant than common major cations such as K$^+$ and Na$^+$ (max Zn = 14,933 µg L^{-1}; Table S3). In addition to Zn, Tl is an element of growing interest due to its high toxicity. The Tl

Table 1

Average physico-chemical parameters measured on the different groups of waters collected at the decommissioned Raibl mining district. ORP: redox potential, EC: Electrical conductivity, TDS: Total dissolved solids, DO: Dissolved oxygen, T: Temperature.

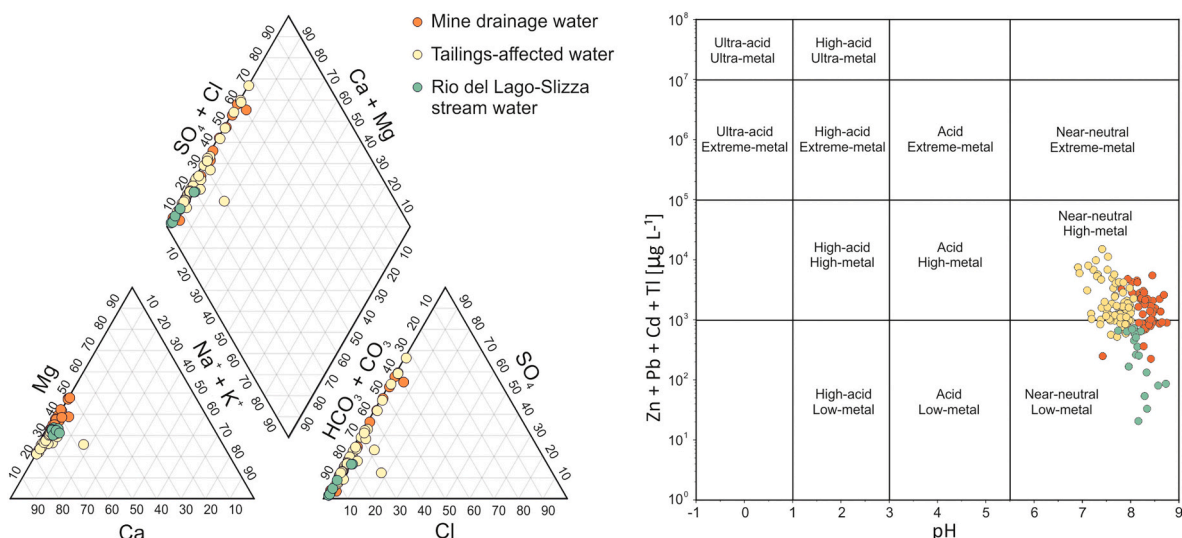|	Mine drainage water (n = 54)	Tailings-affected water (n = 96)	Stream water (n = 26)
pH	8.3 ± 0.2	7.7 ± 0.3	8.2 ± 0.2
ORP (mV)	191 ± 50	176 ± 59	191 ± 51
EC (µS cm^{-1})	446 ± 135	297 ± 77	238 ± 54
TDS (mg L^{-1})	226 ± 67	155 ± 42	126 ± 29
DO (mg L^{-1})	8.9 ± 1.4	7.3 ± 1.0	8.9 ± 1.0
T (°C)	8.6 ± 2.0	9.9 ± 2.7	9.6 ± 3.6

Fig. 3. Piper and modified Ficklin diagrams of the different groups of water collected at the decommissioned Raibl mining district.

Table 2
Average major cation and anion concentrations (mg L^{-1}) in the different groups of water collected at the decommissioned Raibl mining district. Anions were analysed on a subset of data.

	n	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	HCO$_3^-$	SO$_4^{2-}$	Cl$^-$	F$^-$
Mine drainage water	54	67.8 ± 19.1	27.4 ± 10.9	1.06 ± 0.38	1.22 ± 1.98	177 ± 26	88.6 ± 62.5	1.47 ± 1.00	0.14 ± 0.08
Tailings-affected water	96	50.4 ± 14.1	12.2 ± 1.9	1.13 ± 0.25	0.83 ± 2.40	168 ± 10	58.4 ± 67.0	2.37 ± 2.93	0.07 ± 0.03
Stream water	26	40.0 ± 7.5	11.9 ± 2.3	1.36 ± 1.01	0.51 ± 0.52	164 ± 14	12.0 ± 11.7	2.86 ± 2.00	0.04 ± 0.03

Table 3
Average trace element concentrations (μg L^{-1}) in the different groups of water collected at the decommissioned Raibl mining district.

	Mine drainage water (n = 54)	Tailings-affected water (n = 96)	Stream water (n = 26)
Zn	1795 ± 1262	2349 ± 2519	341 ± 256
Tl	16.7 ± 14.1	38.3 ± 25.5	5.0 ± 5.8
Pb	11.5 ± 6.9	35.1 ± 17.0	16.9 ± 11.1
Ba	38.9 ± 17.5	56.2 ± 25.2	28.4 ± 16.3
Cd	1.26 ± 0.89	1.46 ± 2.38	0.28 ± 0.18
As	18.6 ± 27.0	1.4 ± 0.5	0.7 ± 0.3
Sb	2.40 ± 2.03	0.34 ± 0.20	0.16 ± 0.07
Ge	0.68 ± 0.35	0.42 ± 0.41	0.09 ± 0.07
Fe	10.03 ± 8.53	8.07 ± 8.79	6.41 ± 8.33
Mn	0.32 ± 0.20	0.28 ± 0.56	0.33 ± 0.59

concentration range is 0.02–120 μg L^{-1} overall. Maximum concentrations were found in the tailings-affected groundwater, especially at PZ5 (120 μg L^{-1}; Table S3), where extensive interactions between the water table and the saturated tailings beds occurred.

The understanding of PTE behaviour in water systems, especially those affected by mining, is quite complex, since the distinctive geochemical characteristics of different elements strongly govern speciation, mineral-water partitioning as well as PTE mobility and fate. Hereafter, hydrochemical data of dissolved elements are presented together with geochemical modelling results calculated using Visual Minteq (Gustafsson, 2014). The highest concentrations of Zn, Pb and Tl were observed in the near-neutral tailings-affected waters (average pH of 7.7 ± 0.3) where a large amount of metal-bearing waste minerals is present. The dissolution and sorption processes that regulate their mobility are mainly pH dependent (Fig. 6). With respect to release processes affecting Pb, and to a lesser extent Zn, modelling speciation showed that there is a negative correlation between pH and the relative

abundance of dissolved ionic Zn^{2+} and Pb^{2+} forms, which is consistent with both field observations (Fig. 6a and b) and the 3 W-PCA output (Fig. 5). However, Pb was present in its ionic form Pb^{+2} only up to 12–13 %, whereas the remaining dissolved fraction was in the carbonate form. Presumably, Pb and to a lesser extent Zn natural attenuation is governed by adsorption processes due to their affinity with Fe-oxyhydroxides (HFO) at pH > 7 (Coup and Swedlund, 2015; Dzombak and Morel, 1990). In addition, the attenuation of Pb does not likely depend on cerussite precipitation (SI PbCO$_3$ < 0), whereas high concentrations of Zn appeared to be buffered by hydrozincite, a hydrated Zn-carbonate (SI Zn$_5$(CO$_3$)$_2$(OH)$_6$ max = 6.85, min = −10.12; Fig. 6c) and less by smithsonite (ZnCO$_3$) precipitation (SI ZnCO$_3$ max = 1.38, min = −2.12). Minimum SI values of Zn carbonates are found in stream water indicating that their potential transport and consequent dissolution to the stream water could be one of the main sources of Zn in water. This is consistent with modelling results and corrosion morphologies of smithsonite found by Miler et al. (2022) at the Mežica Pb-Zn mining area
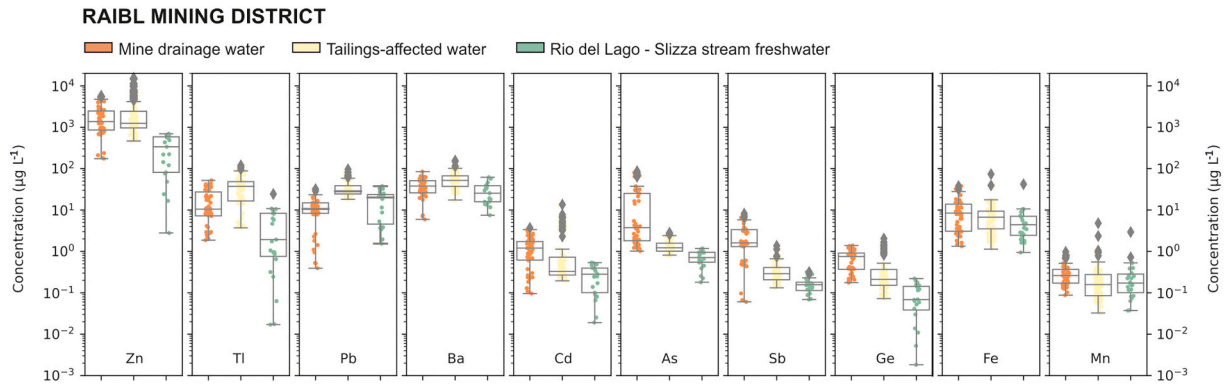
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Fig. 4. Boxplot of potentially toxic trace element compositions in the mining district.

in Slovenia, which belongs to the same metallogenic province, indicating that smithsonite can be very soluble in slightly alkaline stream waters. Reasonably hydrozincite could behave similarly to smithsonite.

Although Tl is a trace component in the Raibl tailings, because its concentrations are at least two orders of magnitude lower in comparison to Zn and Pb (Barago et al., 2021), Tl was very abundant in the water matrix. Such high Tl mobility can be explained by two geochemical processes: 1) The modelling results indicate that negligible amounts of poorly mobile species of Tl(III) are expected. On the contrary, Tl should be found mainly in the more mobile Tl(I) form. In detail, the mobile Tl^{+1}

ion (> 97 %; Fig. 6b) is expected to prevail among the Tl(I) dissolved species, while the sulphate ($TlSO_4^-$) should occur only to a lesser extent (3 %). 2) Natural attenuation processes of Tl in comparison to other PTEs (As, Pb, Zn) are also expected to be scarce, since Tl removal is not likely to be accomplished by Tl-mineral precipitation, as suggested by modelling results performed in this study, neither by adsorption processes (e.g., onto HFO), which are expected to be weak (Coup and Swedlund, 2015).

Arsenic (As) concentrations were generally low and consistent with previous studies (Petrini et al., 2016), even in the tailings-affected water
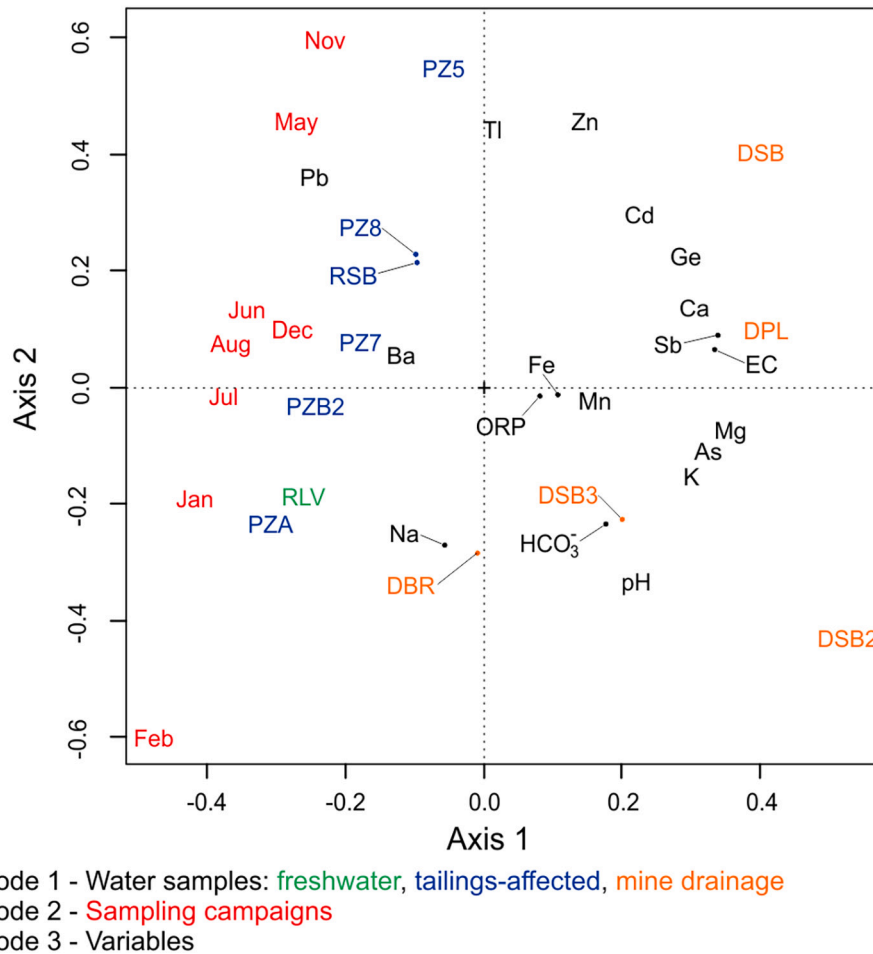

Mode 1 - Water samples: freshwater, tailings-affected, mine drainage
Mode 2 - Sampling campaigns
Mode 3 - Variables

Fig. 5. Plot resuming the results of 3W-PCA performed on different water sampling stations at the Raibl mining district. Months and sampling stations were selected only when all the data were available.
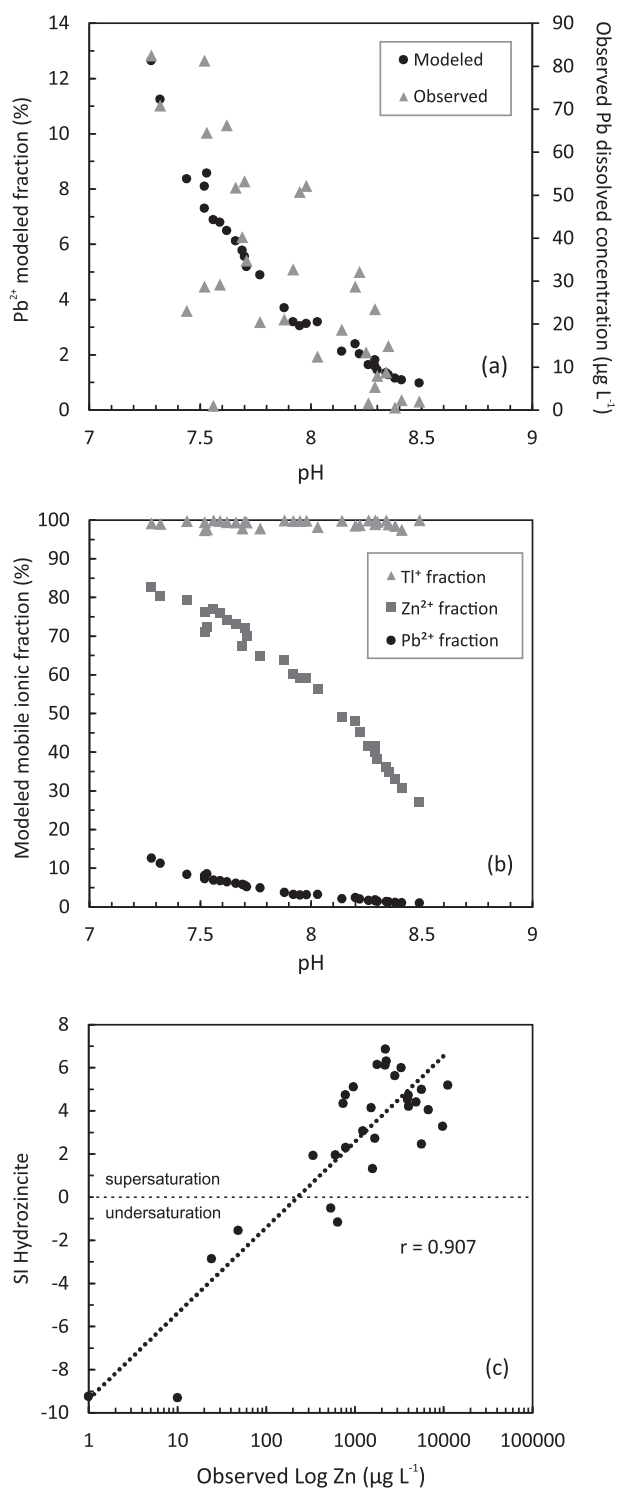
Fig. 6. (a) Observed Pb dissolved concentrations and modelled Pb^{2+} ionic fraction; (b) comparison of modelled ionic and mobile fractions of Tl^{+1}, Pb^{+2} and Zn^{+2}; (c) relation of observed Zn concentrations and hydrozincite saturation index ($Zn_5(CO_3)_2(OH)_6$).

where the PTE-bearing tailings can reach up to almost 1500 mg kg^{-1} of As in the solid phase (Barago et al., 2021). The absence of As can be related to its strong co-precipitation or adsorption on the HFOs as suggested for other similar decommissioned mining sites (Álvarez-Quintana et al., 2020; Cidu et al., 2011). However, high concentrations of As (DSB2: 74.4 ± 7.58 µg L^{-1}; Table S2) were found in the mine drainage water, which also appeared to be enriched in Sb. The occurrence of high

concentrations of dissolved As and Sb could be related to relatively high pH values (~8.5) of standing oxygenated water, which induced the desorption of As, and possibly Sb (mainly As(V) and Sb(V) species) from Fe oxide surfaces (Smedley and Kinniburgh, 2002; Leuz et al., 2006). Little is known regarding the hydrogeochemistry of Germanium (Ge). It is believed that Ge distribution resembled that of As and Sb, perhaps indicating that metalloids could be characterised by similar behaviour in this mining environment. However, Ge depletion in the tailings-affected waters may also be related to the depletion of Ge-bearing sphalerite in the flotation tailings, similar to Cd.

3.3. Tailings as a source of Thallium

In Fig. 7, Zn and Tl concentrations are presented together among all the investigated sampling stations. Generally, dissolved Zn reached concentrations two orders of magnitude higher with respect to Tl; such absolute values are consistent with the high Zn availability from the tailings and its generally high mobility. The average Tl/Zn chemical ratio in water upstream from the tailings impoundments, including mine drainage waters, was nearly constant among the stations (Tl:Zn ≃ 1:100, expressed as 1 %). Changes in the Tl/Zn ratio were then observed inside the tailings impoundments. In detail, in the southern upgradient sectors of the impoundments (piezometer: PZA) the interaction between the tailings and the water table remains scarce, explaining the unaltered general Tl/Zn ratio in the corresponding groundwater. Such low interaction is explained by a greater distance between the tailings and the groundwater table, of approximately 4–8 m, in the southern sectors (Barago et al., 2021). Conversely, from PZB2 to the downgradient PZ5, PZ7 and PZ8 groundwaters, the tailings become more saturated as the tailings beds are deeper and the water table is shallower (Fig. 2). This may explain the increase in the Tl concentrations (PZ7 and PZ8: Tl = 43.1 ± 10.3 and 53.6 ± 19.4 µg L^{-1}), together with Tl/Zn ratios (up to 3.4 %). Somewhat similarly the same anomaly was found between Tl and the other main PTEs such as Pb and Cd (Table S2). This positive anomaly of Tl indicates that the tailings represent an active source of this element, and their leaching promotes Tl mobilisation, even 3–4 fold more than other monitored sites in the Raibl district. Such a release of Tl is of concern since a significant amount of dissolved Tl may eventually occur downstream, posing a potential risk for the general quality of the fluvial ecosystem. Although there is no direct evidence that the tailings impoundments represent an active and constant source of contamination affecting the Rio del Lago - Slizza river system, some minor springs of the Rio del Lago, located immediately downgradient with respect to the tailings impoundments and likely fed by the groundwaters below them (RSB), were characterised by very high Tl concentrations (46.8 ± 9.75 µg L^{-1}) and a higher Tl/Zn ratio (2.2 %). This evidence suggests that tailings are responsible for the release of dissolved PTEs with a subsequent contamination of the main stream of the Rio del Lago (RLV: 9.7 ± 5.3 µg L^{-1}; Tl/Zn = 1.5 %). Downstream along the river, Tl concentrations, as well as the other PTEs, were attenuated by dilution as evidenced by a decrease in their concentrations by one order of magnitude (1.01 ± 0.06 µg L^{-1}) at 9 km downstream in the Slizza freshwaters (RSC station; Table S2). However, the geochemical signature was still observable (RSC: Tl/Zn = 1.7 %). As previously discussed, elevated values of Tl/Zn were reasonably related to differences in the attenuation pathways of the different elements. High values of Tl/Zn can be explained by the higher affinity of Tl for the dissolved phase, which was consistent with negligible attenuation pathways. On the other hand, in the case of Zn, its decrease can be attributed to natural attenuation processes such as sorption, precipitation of Zn-bearing secondary minerals such as hydrozincite and pH dependent speciation (Fig. 6a and b) and, consequently, increasing the Tl/Zn ratio.

3.4. Temporal variability of PTE concentrations and total dissolved loads

In general, the temporal variability was characterised by high
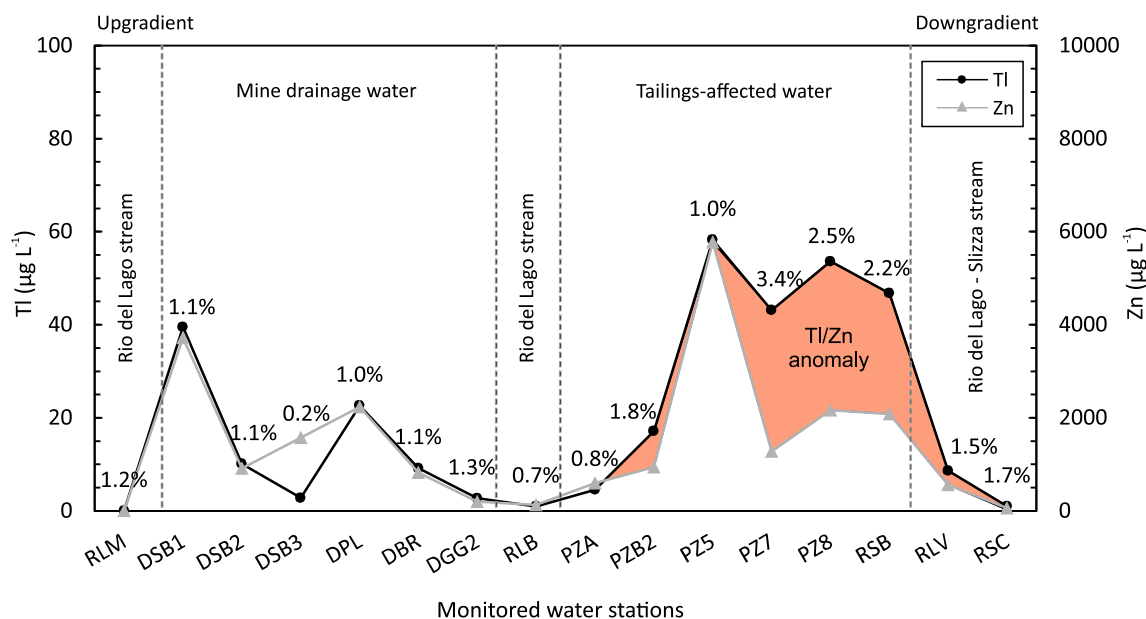
Fig. 7. Zinc and Tl concentrations in the different groups of waters collected upstream and downstream of the decommissioned Raibl mining district along the Rio del Lago Valley. The labels indicate Tl/Zn ratio (%).
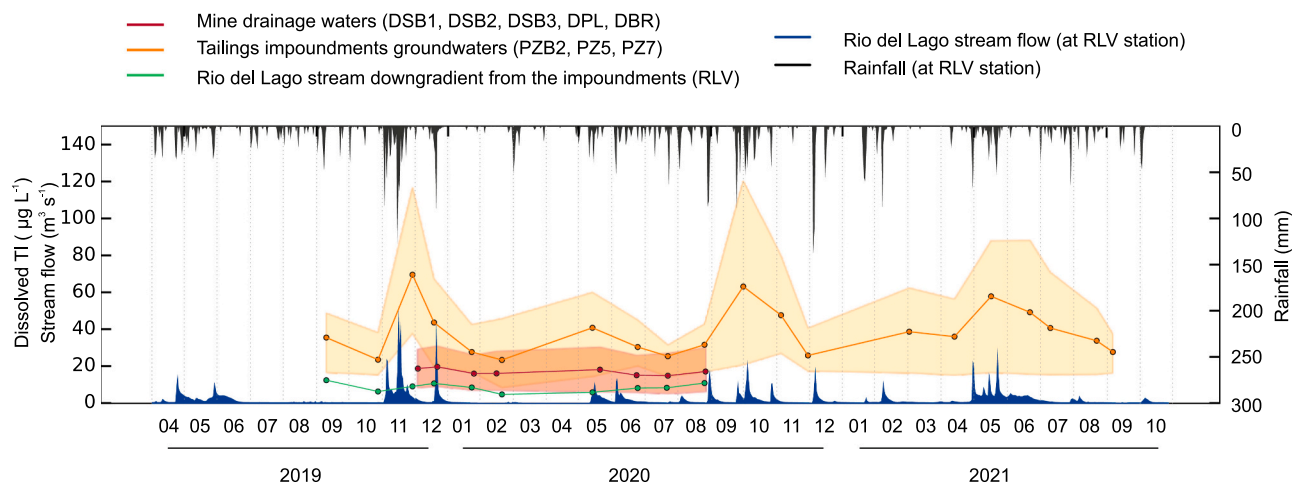

Fig. 8. Time series of dissolved Tl in the different groups of waters collected at the decommissioned Raibl mining district, represented with a 95 % confidence interval. Rainfall and stream flow data were provided by the commissioner station.

concentrations of dissolved Tl (Fig. 8) (and other PTEs, not presented) in the rainy seasons, which corresponded to autumn (November) and spring (May). This seasonal effect, which is responsible for the large standard deviations seen in Table 3 and S2, was also confirmed by the 3W-PCA output, also for Zn and Pb (Fig. 5). The major temporal variations appeared in the groundwaters entrapped in the tailings impoundments, especially when the water table rose as a consequence of intense precipitation and melting snow, which recharged the Rio del Lago stream water (Fig. 8). Such processes caused an extension of the saturated area to less deep and weathered volumes of tailings, with high potential in terms of secondary source of PTEs (Fig. S1). For instance, the minimum PTE concentrations at PZ5 were observed in winter, when snow fall is frequent and the Rio del Lago is in low-flow conditions (February 2020), and in autumn just before the beginning of the rainy season (October 2019) with concentrations ranging from 8.27 to 15.3 μg L^{-1}. In contrast, the maximum concentrations were found at PZ5 during the main rainfalls of the rainy seasons in November 2019 and October 2020 with values of Tl one order of magnitude higher than in the dry season, ranging from 117 to 120 μg L^{-1}.

Since the PTE concentrations in the Rio del Lago River downstream from the tailings impoundments (RLV), appeared moderately constant through the year (Tl: average = 8.65 ± 2.37, max = 12.4 μg L^{-1}), a general increase in the stream flow corresponded to an increase in the total dissolved load (TDL). Considering the average concentration of Tl mentioned above, under low flow conditions (100 L/s), the TDL of Tl was 70 g day^{-1}. In contrast, during high flow events when the Rio del Lago discharge can reach values higher than 50,000 L/s, the TDL transport can reach values higher than 37 kg day^{-1} of Tl, representing an increase of almost three orders of magnitude. In the same low and high flow conditions, the TDL of Zn calculated from the average concentration (563 μg L^{-1}) ranged from 4.8 to 2432 kg day^{-1}. Although the average PTE concentrations and TDL of the Rio del Lago are very low in comparison to other Pb-Zn mining districts characterised by acid drainages, such as the abandoned mining areas in SW Sardinia, Italy (De Giudici et al., 2018; Dore et al., 2020), during such high flow events the TDL of Zn strongly increased reaching values comparable to the extreme values found in the Rio Irvi (Sardinia), which was found to be characterised by a Zn TDL = 2370 kg day^{-1}. This suggests that intense rainfalls

and high flow events, which are not uncommon in the alpine environment, may not only represent a matter of concern for the structural stability of the tailings impoundments but also an environmental hazard. Indeed, very large quantities of dissolved (and particulate) PTEs can be dispersed although their concentrations remain quite constant, and transported over very long distances.

4. Conclusions

Significantly high PTE concentrations persist in the drainage water system of the decommissioned Pb-Zn Raibl mining district despite almost 30 years of flushing after extraction and processing activities shut down. Differences in the geochemical signature were found in different monitored waters: the water affected by the leaching of tailings showed very high concentrations of Zn, Tl and Pb, whereas the waters draining the mine galleries were also enriched in As and, to a lesser extent, Sb. This could be explained by differences in the residence time and higher pH conditions of the water, which can promote the mobility of metalloids such as As due to desorption from HFOs. Anomalous high concentrations of Tl were found in waters affected by post-flotation tailings leaching, with Tl/Zn ratios 3–4 fold higher with respect to mine drainage and riverine waters. This anomaly of Tl was similarly observed with regard to other main PTEs, indicating that tailings are the main source of dissolved Tl in the water at the investigated decommissioned mining district. This is reasonably supported by modelling results since negligible natural attenuation processes are expected for Tl, which appeared to be mainly present in its ionic mobile form Tl(I). In contrast, Zn and Pb concentrations were likely affected by attenuation processes due to sorption on Fe oxy-hydroxides and pH-dependent speciation. Moreover, elevated Zn concentrations were also likely limited by hydrozincite precipitation. Results from this research also reveal that leaching processes involving tailings and the subsequent release and dispersion of PTEs are promoted during periods of intense rainfall and high flow river conditions. During such events the concentrations of metals in the groundwater found in tailings impoundments can be heavily increased by one order of magnitude, whereas the total dissolved load (TDL) in the main stream, the Rio del Lago, can be magnified by three orders of magnitude.

CRediT authorship contribution statement

Nicolò Barago: Investigation, Software, Data curation, Visualization, Writing – original draft. **Elena Pavoni:** Investigation, Software, Writing – review & editing. **Federico Floreani:** Investigation. **Matteo Crosera:** Resources, Validation. **Gianpiero Adami:** Resources, Validation. **Davide Lenaz:** Resources, Supervision. **Stefano Covelli:** Conceptualization, Investigation, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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