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# Impact of past mining activities on water quality in a karst area in the Cévennes region, Southern France.

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10 **Abstract.** Sampling and analysis of groundwater and surface water were conducted to assess the potential impacts of abandoned mines on water quality in a karst area in Southern France. The results of multivariate statistical analysis and geochemical mapping revealed that water quality is affected by contaminated drainage from abandoned mine sites. Acid mine drainage with very high concentrations of Fe, Mn, Al, Pb and Zn was identified in a few samples collected from mine openings and near waste dumps. In general, neutral drainage with elevated concentrations of Fe, Mn, Zn, As, Ni and Cd was observed  
15 due to buffering by carbonate dissolution. The contamination is spatially limited around abandoned mine sites, suggesting that metal(oid)s are sequestered in secondary phases that form under near-neutral and oxidizing conditions. However, the analysis of seasonal variations in trace metal concentrations showed that the transport of metal contaminants in water is highly variable according to hydrological conditions. During low flow conditions, trace metals are likely to be rapidly sequestered in Fe-oxyhydroxides and carbonate minerals in the karst aquifer and the river sediments, while low or no surface runoff in  
20 intermittent rivers limits the transport of contaminants in the environment. On the other hand, significant amounts of metal(loid)s can be transported under high flow conditions, primarily in dissolved form. Dissolved metal(loid) concentrations in groundwater remained elevated despite dilution by uncontaminated water, likely as a result of the increased leaching of mine wastes and the flushing of contaminated waters from mine workings. This work shows that groundwater is the main source of contamination to the environment and highlights the need to better understand the fate of trace metals in karst water  
25 systems.

**Keywords.** Trace metals, mine drainage, groundwater, seasonal variations, compositional data analysis, Croix-de-Pallières.

## 1. Introduction

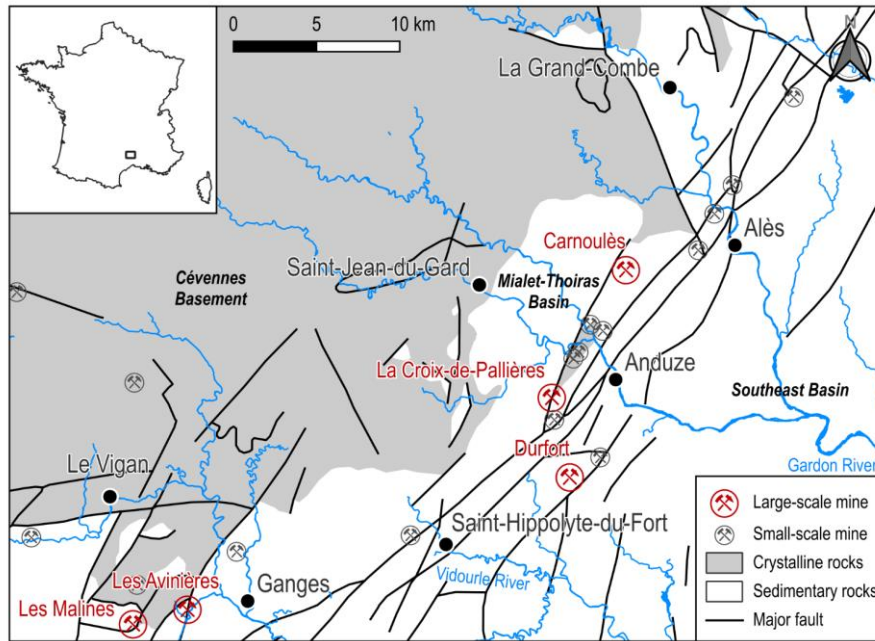
Abandoned metal mines are recognized as major sources of metal(loid)s in the environment and may pose a threat to the surrounding waters, soils and living organisms for decades or even centuries after mine closure (Doumas et al., 2018; Elbaz-Poulichet et al., 2017; Gutiérrez et al., 2016; Tomiyama and Igarashi, 2022). The metal contamination is primarily caused by mine drainage, which results from the alteration of sulfide minerals when exposed to oxygen, water and microorganisms (Nordstrom et al., 2015; Simate and Ndlovu, 2014). Abandoned mines are particularly affected by mine drainage because of the large quantities of sulfide minerals that are exposed to oxygen and water in waste rock dumps, tailings deposits, mine workings and open pits (Lottermoser, 2010). Historic mine wastes generally contain higher amounts of metal(loid)s than modern wastes due to the lower processing efficiency and mining of higher grade ores in the past (Bevandić et al., 2022; Kuhn and Meima, 2019). The oxidation of sulfide minerals may produce acid mine drainage with extremely high concentrations of SO<sub>4</sub>, Fe, Mn and Al, and elevated concentrations of trace metals such as Cu, Cr, Ni, Pb and Zn (Lottermoser, 2010; Simate and Ndlovu, 2014). However, neutral pH conditions can be maintained in settings where the acidity is neutralized by the dissolution of acid-buffering minerals, primarily carbonate minerals (Nordstrom et al., 2015). Although a variety of trace metals are insoluble and strongly sorbed under pH of 6-9, neutral drainage may still contain significant concentrations of sulfate and metal(loid)s such as Zn, Mn, Ni, As, Mo, Cd or Sb (Nordstrom et al., 2015). Compared to acid mine drainage, neutral mine drainage has only been recently recognized as a potential source of environmental pollution (Carvalho et al., 2017; Cidu et al., 2009; Navarro et al., 2015; Nordstrom et al., 2015; Valencia-Avellan et al., 2017; Vriens et al., 2020). As such, neutral mine drainage in carbonate aquifers has received attention only recently, with studies documenting karst groundwater pollution from coal mines (Gammons et al., 2013; Ren et al., 2021; Tao et al., 2012) and metal mines (Cidu et al., 2009; Doveri et al., 2021; Fang et al., 2021; Huang et al., 2019; Qin et al., 2021, 2019). Carbonate karst aquifers are a major source of water supply in many regions of the world including the Mediterranean Basin, Central and Western Europe, Southern China, Eastern USA, Central America, the Caribbean Region and the Middle East (Goldscheider et al., 2020; Stevanović, 2019). Groundwater flow in karst aquifers occurs in large conduits developed by karstification as well as in micropores and small fissures, often referred as the matrix (Hartmann et al., 2014). Karst groundwater resources are particularly vulnerable to surface contamination, because pollutants can easily enter the aquifer and be transported rapidly in the conduits without significant attenuation (Goldscheider et al., 2020). In the case of mining pollution, the source of contamination may be located within karst areas (i.e. carbonate-hosted mineral deposits) or upstream in adjacent non-karst areas such as those underlain by mineralized basement rocks. The fate of metal(loid)s in karst groundwater is controlled by chemical and physical processes. Karst groundwater is characterized by near-neutral pH with a high buffering capacity and oxidizing conditions (White, 2018). Under these conditions, trace metals are poorly soluble and are likely to be sorbed onto

colloids and particles (Cholet et al., 2019; Vesper, 2019). In the aquifer, trace metals can be scavenged by secondary minerals including Fe-Mn oxyhydroxides, metal carbonates and sulfate minerals (Du Preez et al., 2016; Friedrich et al., 2011; Newsome et al., 2021; Vesper, 2019). In particular, significant amounts of trace metals can be sequestered in Fe and Mn oxyhydroxides  
60 such as goethite, ferrihydrite or birnessite occurring as coatings on cave walls and in stream bed sediments (Friedrich et al., 2011; Vesper, 2019). It has been suggested that trace metals are primarily transported as suspended particles during storm flow (Vesper, 2019; White, 2018). Physical processes related to groundwater flow play a major role in the transport of trace metal contaminants by flushing dissolved, colloidal and particulate forms and diluting concentrations with uncontaminated water (Vesper, 2019). However, understanding the transport of contaminants in karst aquifers remains challenging due to the  
65 complexity of groundwater flow and the high variability in hydrological conditions.

The Cévennes region is located on the southeastern edge of the Massif Central mountains in France. The region was an important Pb-Zn mining area from the mid 19th to the late 20th century (Fig. 1). The long history of mining has left a legacy of abandoned mine sites which pose a potential threat to water quality in the old mining districts (Casiot et al., 2009; Dumas et al., 2018; Ebengue Atega et al., 2022; Elbaz-Poulichet et al., 2017; Escarré et al., 2011; Resongles et al., 2014). Previous  
70 studies in the area have mainly focused on the contamination of surface waters and sediments with metal(loid)s. The speciation and transport of trace metals in surface waters have been studied in detail at the abandoned Carnoulès Mine (Casiot et al., 2009, 2003) and throughout the Gardon River watershed (Resongles et al., 2015, 2014). However, little is known about the potential impacts of abandoned mines on groundwater quality. Groundwater is a major source of water supply in the region and a number of public supply wells contain significant concentrations of metal(loid)s (As, Sb, Pb), occasionally exceeding  
75 drinking water standards (GEODERIS, 2019). Moreover, public concerns have been raised about the potential effects of mining pollution on public health, while this issue has long been ignored by the authorities (Mésini, 2018). A number of former mining sites have experienced land use changes to residential, agricultural or recreational areas, causing an increased exposure to potentially toxic metals. A recent study conducted by the French Public Health Agency showed an association between mining pollution and biological levels of Pb, As and Cd in local residents (Cochet et al., 2018a, 2018b). In this  
80 context, groundwater quality studies around abandoned mine sites are urgently needed in the Cévennes region.

The objective of this study is to assess the potential impacts of past mining activities on surface water and groundwater quality in a karst area. For this purpose, water samples were collected in a variety of sampling sites and geochemical data were compiled from a recent governmental study. The geochemical dataset includes physico-chemical, major ion and trace metal data for a high density of sampling points around abandoned mining sites. Statistical analysis for compositional data,  
85 geochemical mapping and analysis of seasonal variations were used to develop a conceptual model of the fate and transport

of metal(loid)s in karst groundwater. This study provides an overall picture of the processes that control contaminated mine drainage in karst aquifers.



**Fig. 1.** Location of abandoned Pb-Zn mines and geological context of the Cévennes border. Small-scale mines produced hundreds to thousands of tonnes of metals, large-scale mines produced over tens hundreds of tonnes of metals.

## 2. Study area

The study area covers an area of about 180 km<sup>2</sup> in the southeastern edge of the Massif Central. The elevation ranges from 90 590 meters above sea level in the northwest to less than 100 meters above sea level in the southeast (Fig. 2). The uplands are dominated by trees and shrubs (green oaks, maritime pines, chestnuts), while the flat low-lying areas are mostly occupied by vineyards, cereal crops and meadows. The climate is Mediterranean with a long dry period during summer and rainfall events mainly concentrated during autumn and spring. The Cévennes region is subject to heavy rainfall events during autumn with typically hundreds of millimeters of precipitation in a few hours. The annual precipitation is 1176 mm and the mean annual 95 temperature is 13.6°C for the period 1981-2010 at the Généragues station (Fig. 2). The northern part of the study area is drained by the southern tributaries of the Gardon River, which is a tributary of the Rhône River, and the southern part is drained by the northern tributaries of the Vidourle River, a little coastal river (Figs. 1 and 2). In the region, the rivers are characterized by a Mediterranean hydrological regime with low or no flow during summer and high flow during the rest of the year. Flash floods may occur in autumn and to a lesser extent in spring in response to heavy rainfall events (Fig. 3; Vinet, 100 2008).

Geologically, the study area is located in the Cévennes border, a tectonic unit that separates the Cretaceous and Tertiary sedimentary rocks of the Southeast Basin from the outcropping crystalline basement rocks of the Massif Central (Gouin and

Bailly, 2011; Henry et al., 2001) (Fig. 1). The Cévennes border consists of Triassic and Jurassic sedimentary rocks affected by the NNE-SSW-trending Cévennes fault system which has been active since late Hercynian times (Barbarand et al., 2001).

105 This fault system was reactivated as a strike-slip fault during the Eocene Pyrenean Orogeny and especially as a normal fault during the Oligocene extension (Arthaud and Séguret, 1981; Séranne, 1999). Transgressively overlying the crystalline basement, the Triassic rocks consist of about 150 m of conglomerate and sandstone overlain by marl with gypsum, and alternating layers of marl, sandstone and dolostone (Berger, 1972; Bruxelles, 1997). The Triassic sedimentary rocks are covered by Lower Jurassic deposits of the Hettangian that consist of 10-15 m of argillaceous limestone overlain by up to 150 m

110 of dolostone. The Hettangian is overlain by the Sinemurian limestone that ranges from argillaceous to siliceous in composition (100-250 m), itself covered by the Carixian argillaceous limestone (10-20 m). North of the study area, the Pallières Horst forms the eastern boundary of the small Triassic-Jurassic Mialet-Thoiras Basin. The Pallières Horst is composed of Hercynian granite capped by Triassic sandstone and bounded to the west by the mineralized fault zone of the Croix-de-Pallières (Fig. 2). East of the horst, the sequence continues upwards with the marl-dominated Domerian-Bajocian interval overlain by up to

115 100 m of Bathonian dolostone. Upper Jurassic (Oxfordian-Portlandian) limestones outcrop in the northeastern part of the study area, underlain by Callovian marls. West of the Cévennes fault system, the outcropping rocks of the Southeast Basin consists of Lower Cretaceous (Berriasian-Barremian) rocks dominated by marl and limestone, covered in places by Tertiary Oligocene rocks mainly consisting of lacustrine conglomerate, marl and limestone. Alluvial deposits composed of silt, sand, gravel and pebble occur along the Gardon River and are particularly extensive in the lowlands of the Southeast Basin.

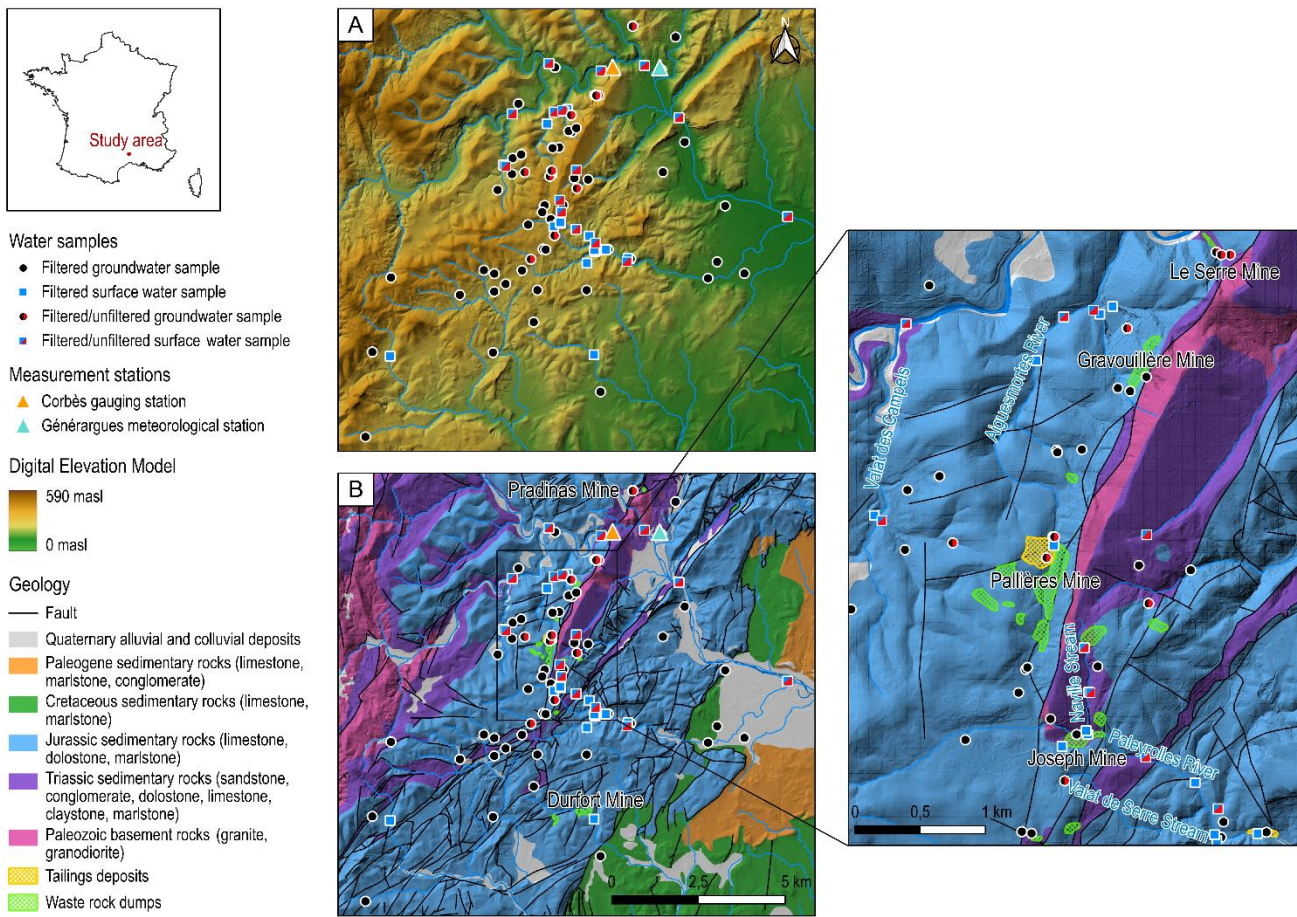
120 The Pb-Zn deposits are mainly hosted in carbonate rocks and are typical of Mississippi Valley-Type (MVT) deposits (Gouin and Bailly, 2011; Henry et al., 2001; Leach et al., 2006). The mineralization consists mainly of pyrite, galena and sphalerite within the Lower Jurassic dolostones of the Hettangian (Pallières Mine) and Lotharingian (Durfort Mine) (Gouin and Bailly, 2011; Maton et al., 2008). Sulfide mineralization also occurs in Late Triassic rocks as sandstone-hosted Pb deposits (Pradinas Mine) (Berger, 1972). Although mining dates back to Roman times, the main period of activity was from the mid

125 19th century to the late 20th century and the peak of production was reached after the Second World War. The Pallières Mine was the largest in the area producing approximately 80,000 t of Zn, 34,000 t of Pb, 30 t of Ag, 520 t of Cd and 28 t of Ge between 1844 and 1971 (Gouin and Bailly, 2011). More than one million tonnes of tailings were generated and stored on site and significant quantities of waste rocks were piled up around shafts. Portable X-ray fluorescence (pXRF) measurements indicated that these wastes contain 3-18 wt.% Fe, 0.1-15 wt.% Pb, 0.05-5 wt.% Zn, 110-4,500 ppm As, 60-1,200 ppm Cu and

130 up to 180 ppm Cd (GEODERIS, 2019). The second largest mine in the area, the Durfort Mine, produced approximately 20,000 tonnes of metals (mainly Zn) between 1939 and 1971, a large part of the ore was processed at the Pallières Mine (Maton et al., 2008). The Joseph Mine was worked from 1845 to 1955 and produced 24,000 t of ore containing 4.5 wt.% Pb during the

main period of activity from 1948 to 1955 (Maton et al., 2008). The mining operations produced a large waste rock pile from the mine floor to the Paleyrolle River below which contains 3-20 wt.% Fe, 0.2-12 wt.% Pb, 600-1600 ppm As, 250-  
135 500 ppm Zn and up to 850 ppm Sb (GEODERIS, 2019). Small-scale mining operations were conducted at the Gravouillère Mine, Pradinas Mine and Le Serre Mine in the late 19th-early 20th centuries (Fig. 2). Significant amounts of wastes are still present on site, with metal(loid) contents commonly ranging from hundreds to thousands ppm (GEODERIS, 2019).

In the area, the main aquifer systems are developed in the Lower Jurassic carbonate rocks and the alluvial deposits along major rivers (Berger, 1972; GEODERIS, 2019). The Hettangian dolostone and Sinemurian limestone are well karstified and  
140 contain significant groundwater reserves (Bruxelles, 1997). Fracture measurements conducted during the sampling campaigns suggest two potential preferential flow paths with a N-S direction parallel to the Cévennes fault and a E-W direction perpendicular to the fault (Fig. S1). A number of perennial and intermittent springs discharge from these aquifers in the Mialet-Thoiras Basin including the Pont de Salindre Spring which is used for public water supply. The Bathonian dolostone also contains important groundwater resources that are used for water supply at the Moulin du Baron Spring. The two karst springs  
145 used for drinking water contain detectable amounts of As and Pb (several  $\mu\text{g/L}$ ) and are subject to strict water quality controls. The alluvial aquifers along the Gardon River are the main source of drinking water in the area. These Quaternary deposits have a good permeability ( $K=10^{-2}$  to  $10^{-3}$  m/s) and the pumping wells are often located close to the river banks (Berger, 1972). The wells generally contain detectable concentrations of As, Pb and Sb due to inflow from the Gardon River and adjacent contaminated aquifers.



**Fig. 2.** Topographical and simplified geological maps of the study area showing the location of sampling sites and measurement stations.

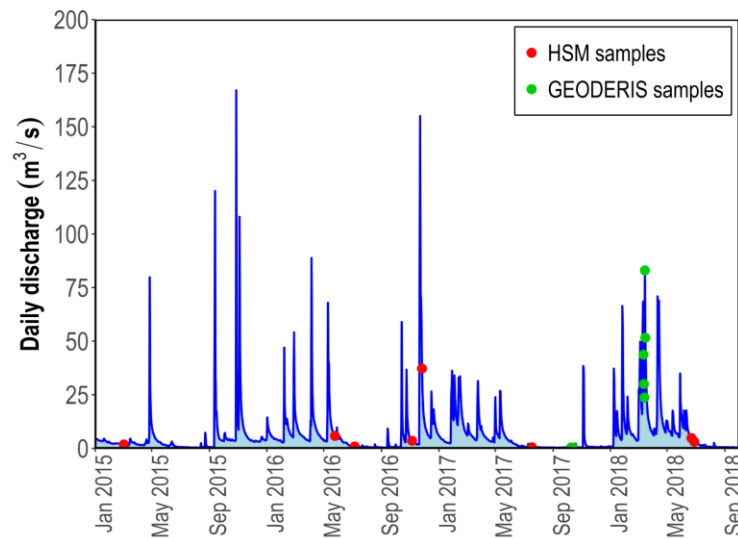
### 150 3. Material and methods

#### 3.1. Water chemistry data

The dataset contains physico-chemical measurements, major and trace element data for 120 filtered water samples and 44 unfiltered water samples collected at 90 different sampling sites from March 2015 to June 2018 (Figs. 2 and 3, Tables S1 and S2). Groundwater sampling sites included karst springs, wells completed in karst and alluvial aquifers, mine openings (e.g. shafts, adits), and leachates from waste materials; surface water sampling sites included intermittent streams and perennial rivers (Fig. 2). A total of 76 filtered water samples were collected by HydroSciences Montpellier (HSM) during six sampling campaigns, with two samples collected at eight sampling points during different hydrological conditions (Fig. 3). The hydrological conditions during sampling were defined based on the discharge values obtained at the Corbès gauging station on the Gardon Saint-Jean River (Figs. 2 and 3). Low and high flow conditions were defined as periods when discharge values are below the lower quartile and above the upper quartile, respectively; medium flow conditions as periods when discharge values are in the interquartile range. Temperature (T), pH and specific conductivity (SC) were measured on site using calibrated probes. Water samples were collected in acid-washed polyethylene bottles and included (1) one unfiltered

and unacidified aliquot for alkalinity determination, (2) one filtered and unacidified aliquot for anion analyses, (3) one filtered and acidified (with 1% suprapur HNO<sub>3</sub>) aliquot for major cation, minor and trace metal analyses. The samples were filtered  
165 in the field with 0.22 µm cellulose acetate filters using disposable plastic syringes in order to remove suspended sediments and obtain comparable results between the different flow conditions. The sample bottles were stored at 4°C until analysis. Chemical analyses were conducted at the HydroSciences Montpellier Laboratory and the AETE-ISO platform (OSU OREME/University of Montpellier). Alkalinity (as HCO<sub>3</sub><sup>-</sup>) was determined by acid titration using an automatic titrator (Mettler Toledo G20). Major anions (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>) were measured by ion chromatography (DIONEX ICS-1000). Major  
170 cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>), silica (Si) and trace metals (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mo, Mn, Ni, Pb, Rb, Sb, Sn, Sr, Tl, U, V and Zn) were analyzed by inductively-coupled plasma mass spectrometry (ICP-MS; Thermo Scientific iCAP Q). Concentrations were determined with external calibration using In and Bi as internal standards to correct potential sensitivity drifts. Analytical quality was checked by analyzing international certified reference water (CNRC SLRS-6). Accuracy was better than 5% relative to the certified values and analytical error (relative standard deviation) was better than 5% for  
175 concentrations ten times higher than the detection limits.

In addition to HSM data, publicly available data were compiled from GEODERIS, a public interest group in charge of post-mining issues in France (GEODERIS, 2019). The GEODERIS data include unfiltered and 0.45 µm filtered data for 44 groundwater and surface water samples collected at 27 different sites during low flow conditions in October 2017 (17 samples) and high flow conditions in March 2018 (27 samples) (Figs. 2 and 3, Table S2). These data include multiple  
180 samples collected during low and high flow conditions at sites that were expected to be impacted by mine drainage. Trace metal concentrations in filtered samples were representative of the truly dissolved fraction as well as the fraction sorbed on nanoparticles and colloids smaller than 0.45 µm (hereafter referred to as the dissolved fraction; Cholet et al., 2019; Vesper and White, 2003). In unfiltered samples, trace metal concentrations include both the dissolved and acid-extractable fractions. The acid-extractable fraction includes easily available trace metals associated with particles larger than 0.45 µm (e.g.  
185 amorphous oxyhydroxides), but does not include more stable particles (e.g. particulate sulfides). Details on sampling procedures and analytical methods are provided in GEODERIS, 2019. It is important to mention that GEODERIS samples were analyzed by ICP-AES for Al, Fe, Tl and Zn; ICP-MS was used for As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb and U. This difference in analytical methods explains the higher detection limits for Al, Fe and Zn for the GEODERIS data compared to the HSM data.



**Fig. 3.** Sampling campaigns and daily discharge measured at the Corbès gauging station on the Gardon Saint-Jean River from January 2015 to September 2018 (data from Banque HYDRO, <http://www.hydro.eaufrance.fr>).

190 3.2. *Statistical methods for compositional data*

The compilation of existing data is a common practice in geochemistry to increase the amount of data and strengthen the interpretation of the results. However, existing and newly acquired data have generally been obtained using different analytical methods, which often results in merged datasets with chemical variables having different detection limits (DL). Data below detection limits or censored data need to be numerically transformed for statistical analysis. It has long been known that simple substitution of censored data (e.g. by 0, DL or DL/2) may produce misleading statistical results, from basic descriptive statistics to advanced multivariate statistical techniques (Helsel and Cohn, 1988; Reimann et al., 2008). A variety of techniques have been developed to impute censored values in a dataset and improve the statistical treatment of the data (Helsel, 2011; Kowarik and Templ, 2016; Palarea-Albaladejo et al., 2014). In this paper, we imputed left-censored values based on the log-ratio expectation-maximization (EM) algorithm with the “lrEM” function of the R package “zCompositions” (Palarea-Albaladejo and Martín-Fernández, 2015). This method has the advantage of preserving the relative structure of compositional data.

Water chemistry data expressed as concentration values (e.g. mol/L, mg/L) are compositional in nature; each component being a proportion of a given total (Bondu et al., 2020; Buccianti and Pawlowsky-Glahn, 2005; Engle and Rowan, 2013; Owen et al., 2016). Compositional data contain relative information since a change in the abundance of one component changes the relative abundance of other components. Such data need to be transformed using the family of logratio transformations before applying the standard statistical techniques in the Euclidean space (Engle and Rowan, 2013; Filzmoser et al., 2018). In this paper, principal component analysis (PCA) was applied to centered logratio (clr) transformed data. The clr transformation is defined for a D-part composition  $x$  as:

$$\text{clr}(\mathbf{x}) = \left[ \ln\left(\frac{x_1}{g(\mathbf{x})}\right); \dots; \ln\left(\frac{x_D}{g(\mathbf{x})}\right) \right], \quad \text{where } g(\mathbf{x}) = \sqrt[D]{x_1 \dots x_D}$$

210 PCA of clr transformed data has been shown to reveal the true variability of the data (Engle and Blondes, 2014; Filzmoser et al., 2018; Reimann et al., 2008). The clr transformation was performed using the “clr” function of the package “robCompositions” and the PCA was conducted using the “prcomp” function in R.

## 4. Results and discussion

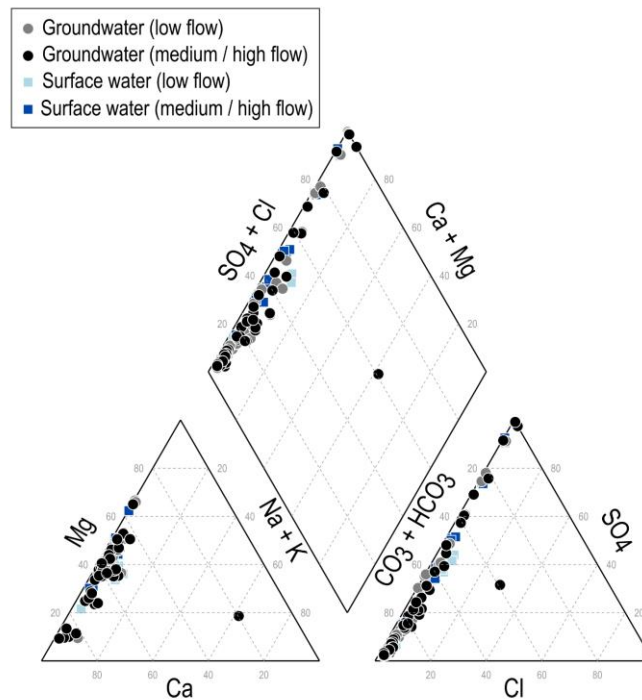
### 4.1. Major ion chemistry

215 A statistical summary of field parameters and selected dissolved constituents is presented in Table 1. Temperature ranged from 7.0 to 31.0 °C. Temperature values were strongly related to the sampling season in surface waters and showed a narrower range in groundwaters. Specific conductance and pH varied widely from 45 to 7800 μS/cm and from 2.01 to 9.62, respectively. The water samples were of Ca-Mg-HCO<sub>3</sub> to Mg-Ca-SO<sub>4</sub> types, with the exception of a spring draining the granitic rocks of the Pallières Horst which contained very low mineralized water of Na-Ca-HCO<sub>3</sub>-SO<sub>4</sub>-Cl composition (Fig. 4). Groundwaters  
 220 and surface waters showed similar water types, although surface waters were generally less mineralized than groundwaters, particularly during high flow conditions. Calcium and magnesium were the dominant cations in all samples with the exception of the granite spring water. Ca and Mg mainly originate from the dissolution of carbonate minerals, primarily calcite and dolomite. Sulfate concentrations were generally elevated, exceeding 50 mg/L in the majority of samples, and showed the greatest range in concentration among the major elements with concentrations ranging from 4.6 to 6679.5 mg/L (Table 1).  
 225 The concentrations of NO<sub>3</sub> and Cl were low, suggesting that water is not significantly affected by domestic sewage and/or agricultural runoff. The highest NO<sub>3</sub> concentration was measured in a groundwater sample collected in the vicinity of the abandoned Joseph Mine and is probably related to the use of nitrogen based explosives during mining operations (Gascoyne and Thomas, 1997; Hendry et al., 2018). Although the large majority of samples had near-neutral pH, acidic conditions with pH <6 were measured at seven sampling sites, three sites had pH below 3. Low pH values were generally associated with high  
 230 values of specific conductance, high SO<sub>4</sub> concentrations and elevated Mg and Ca concentrations (Mg-Ca-SO<sub>4</sub> water type). Acidic waters were collected from mine openings and near mine waste deposits, which indicates the occurrence of acid mine drainage. At these sites, SO<sub>4</sub> is derived from the oxidation of sulfide minerals and Mg and Ca occur at high concentrations as a result of further dissolution of calcite and dolomite under acidic conditions (Huang et al., 2019; Ren et al., 2021). In Triassic formations, sulfate may also be derived from the dissolution of gypsum and anhydrite in groundwater.

**Table 1.** Statistical summary of physico-chemical parameters and selected dissolved constituents.

Parameters	Minimum	Median	90th percentile	Maximum	MAD	n	% <DL	EU standards
T (°C)	7.00	13.60	18.40	31.00	1.80	118	0	
pH	2.01	7.63	8.40	9.62	0.48	119	0	
SC (µS/cm)	45.00	620.00	1,508.00	7,800.00	200.00	119	0	2,500*
HCO <sub>3</sub> (mg/L)	0.0	265.3	475.6	585.7	117.1	120	0	
SO <sub>4</sub> (mg/L)	4.6	57.0	628.7	6,679.5	40.0	120	0	250*
Cl (mg/L)	1.1	6.4	10.0	25.9	1.4	120	0	250*
NO <sub>3</sub> (mg/L)	0.1	0.7	4.3	16.1	0.3	91	38.5	50
Ca (mg/L)	1.4	76.2	179.6	531.8	24.5	120	0	
Mg (mg/L)	0.0	34.1	75.3	648.8	14.3	120	0	
Na (mg/L)	2.0	4.2	7.0	16.0	0.8	120	0	200*
K (mg/L)	0.2	1.2	3.0	10.3	0.5	113	0	
Fe (µg/L)	0.003	3.337	509.000	588,724.016	2.745	121	23.1	200*
Mn (µg/L)	0.000	3.157	312.000	4,659.170	3.107	119	2.5	50*
Ba (µg/L)	1.960	21.000	70.333	200.000	14.600	121	0	
Al (µg/L)	0.266	4.013	80.000	52,647.662	3.320	121	32.2	200*
As (µg/L)	0.031	1.000	7.900	40.000	0.800	121	2.5	10
Cd (µg/L)	0.000	0.019	9.200	202.000	0.017	119	18.5	5
Cr (µg/L)	0.000	0.083	0.224	45.424	0.059	118	38.1	50
Cu (µg/L)	0.018	0.559	11.896	1,520.152	0.483	121	14.9	2,000
Ni (µg/L)	0.017	0.661	13.000	150.182	0.475	121	24	20
Pb (µg/L)	0.000	0.097	4.849	1,610.000	0.093	118	23.7	10
Sb (µg/L)	0.008	0.216	1.103	26.444	0.136	99	17.2	5
Zn (µg/L)	0.132	12.342	2,005.719	36,500.000	11.433	121	13.2	

\* indicator parameters



**Fig. 4.** Piper diagram showing groundwater samples collected during low flow conditions (n = 22) and medium / high flow conditions (n = 53), and surface water samples collected during low flow conditions (n = 11) and medium / high flow conditions (n = 15). Only samples with charge balance error within 15 % are presented (n = 101).

235 4.2. Dissolved metal(loid) concentrations

Dissolved metal(loid)s showed a wide range of concentrations in water samples. Dissolved Fe, Mn and Zn ranged from below 1 µg/L to maximum concentrations of 588.7, 4.6 and 36.5 mg/L, respectively, and occurred at elevated concentrations in a significant proportion of samples (Table 1). The maximum concentrations of Al, Cu and Pb were as high as 52.6, 1.5 and 1.6 mg/L, but these elements were present at high concentrations in a limited number of samples. More than 18 % of the 240 sampling sites exceeded the EU drinking water standards for at least one trace metals (Table 1). Dissolved Pb concentrations exceeded the EU limit of 10 µg/L at 8 sampling sites including three mine openings, three waste deposits (leachate samples) and two intermittent streams located in the vicinity of abandoned mine sites. Dissolved As concentrations ranged from less than 0.1 to 40 µg/L and exceeded the permissible limit of 10 µg/L at 11 sampling points including four mine openings, four 245 springs, one borehole, one intermittent stream and one perennial river. Dissolved Cd reached a maximum concentration of 202 µg/L and was above the EU standard of 5 µg/L at 10 sampling sites including five mine openings, three waste deposits and two intermittent streams. Dissolved Ni concentrations ranged from less than 0.1 to 150 µg/L, exceeding the limit of 20 µg/L in water samples obtained from four mine openings, one waste deposit and one intermittent stream. The dissolved concentrations of Sb were generally low, exceeding the EU standard of 5 µg/L in only two samples obtained from a mine opening and a karst borehole. Similarly, Cr concentrations exceeded the limit of 25 µg/L at only two sampling points located 250 near mine wastes.

A PCA was performed to explore the relationships between trace metal concentrations and other chemical parameters. A compositional biplot of clr-transformed data is shown in Fig. 5 (a classical non-compositional biplot is provided in Fig. S2 for comparison). The two principal components explain more than 50 % of the total data variance. The clr-biplot shows a clear association between two groups of variables:

- 255
- 1) Ca, Na, Cl, HCO<sub>3</sub> and Mg; which are associated with karst and surface waters ;
  - 2) SO<sub>4</sub>, Mn, Fe, Ni, Al, Zn, Cd, Cu, Pb; which are typical of waters affected by mining pollution.

In addition, there is a strong correlation between Zn, Cd, Cu and Pb in the mine impacted waters. These elements are likely derived from the same source, i.e. from mine waste material enriched in galena and sphalerite. Zn can be considered as the best indicator of mining influence because it showed a strong negative correlation with the characteristic elements of 260 uncontaminated waters (HCO<sub>3</sub>, Ca, Na, Cl; Fig. 5 and Fig. S3), in addition of being detected in almost all water samples. Al and Ni were closely associated due to their common occurrence at high concentrations in acid mine waters. A strong positive correlation was also observed between Fe, Mn and SO<sub>4</sub>. Fe and Mn have similar geochemical behavior in waters and are likely derived predominantly from the alteration of pyrite. The presence of As in mine impacted waters is also thought to originate

265 from the alteration of arsenian pyrite, in which As substitutes for S ( $\text{Fe}(\text{S}, \text{As})_2$ ). However, elevated As concentrations were also present in the surface waters of the Gardon River, which explains the poor correlation of As with Fe, Mn and  $\text{SO}_4$  (Fig. 5). Unlike metal cations, arsenic oxyanions tend to remain in solution at near-neutral pH away from the source of pollution. Similarly, Mg showed a moderate correlation with Ca, Na and Cl (Fig. 5). Mg is mainly associated with karst waters but the highest concentrations occurred in mine impacted waters, probably due to the increased dissolution of dolomite under acidic conditions.

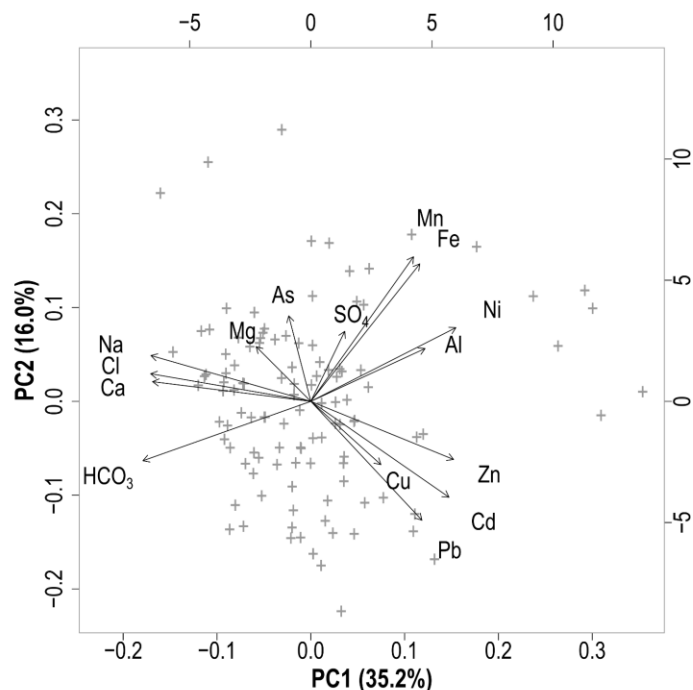


Fig. 5. clr-biplot for the dataset.

270 4.3. Spatial distribution of dissolved metal(loid)s

Geochemical mapping was used to explore the spatial distribution of dissolved Zn and As concentrations in the study area (Fig. 6). Zn and As provide a comprehensive view of mining pollution, as such trace metals are derived from different mineralogical sources and have different chemical behavior in waters. From the map in Fig. 6A, it can be seen that high Zn concentrations were spatially associated with abandoned mine sites. Dissolved Zn concentrations exceeding 0.5 mg/L were observed in water samples collected from mine openings and near mine wastes (Pallières Mine, Durfort Mine, Pradinas Mine, Joseph Mine and Le Serre Mine). The high Zn concentrations measured upstream of Naville Stream and in the La Baraque borehole appears to be derived from contaminated mine wastes. Moreover, two springs contained more than 0.5 mg/L Zn and significant concentrations of Mn, As and Ni typical of neutral mine drainage: the Bijournet Spring and the Valat de Serre Spring. Formed by a mine opening, the intermittent Valat de Serre Spring is expected to be an overflow spring of the aquifer developed in the mine workings of the abandoned Joseph Mine. The major outflow from this mine aquifer occurs at the base

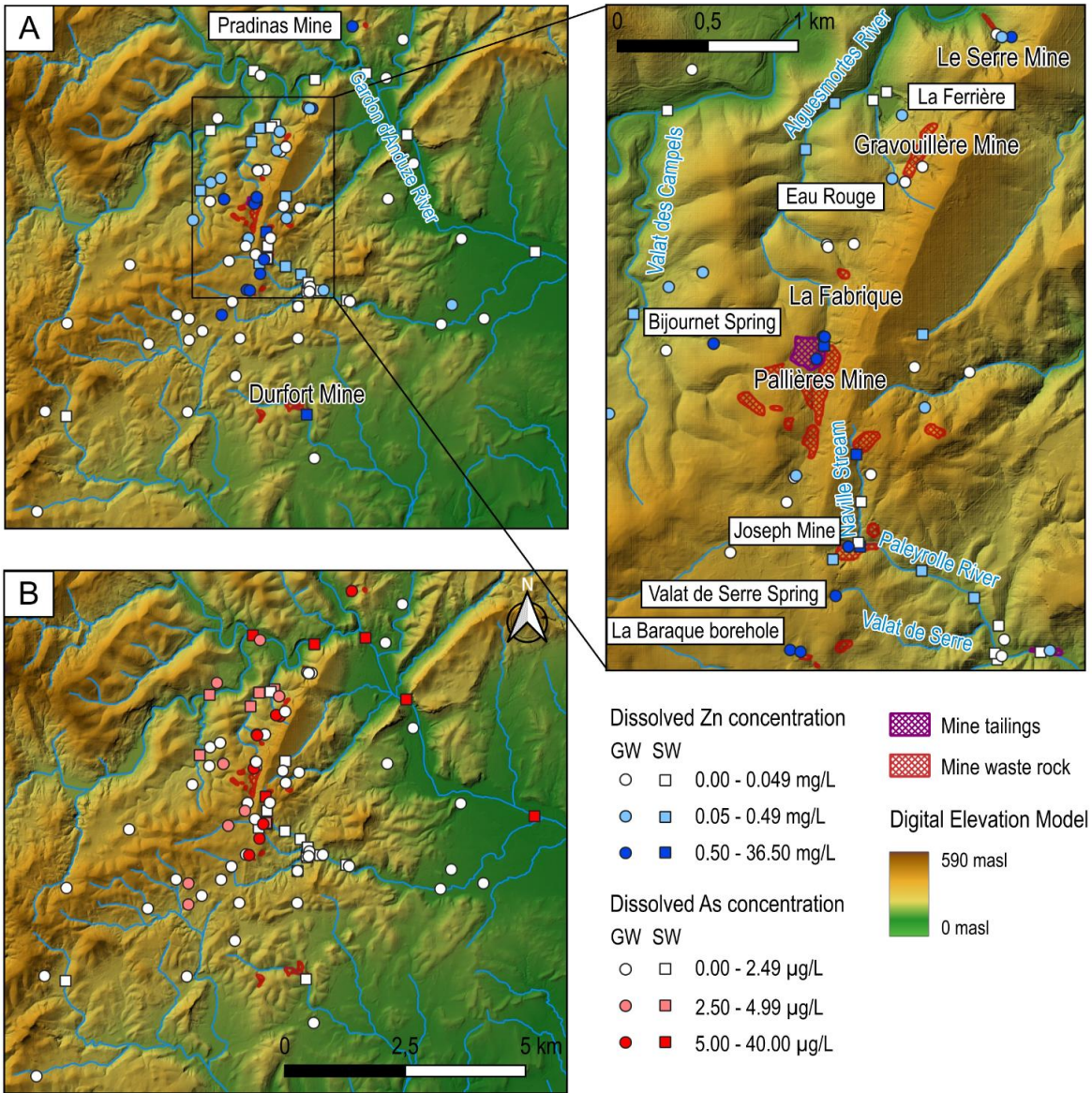
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of the waste pile into the Paleyrolle River and is characterized by acidic waters. On the other hand, the Bijournet Spring is a perennial karst spring located in the vicinity of the Pallières Mine (Fig. 2B). The elevated metal(loid) concentrations strongly suggest that the spring is affected by mine drainage from the tailings deposits and/or the mine workings of the abandoned Pallières Mine. Dissolved Zn concentrations between 0.05 and 0.5 mg/L were observed at greater distances from abandoned mine sites in groundwater and river water samples (Paleyrolle River, Ayguesmortes River, Valat de Campels) (Fig. 6). In areas where no mining has occurred, dissolved Zn concentrations were below 0.05 mg/L with the exception of one borehole completed in alluvial deposits, in which Zn could be related to corrosion of the casing and/or agricultural activities.

The spatial distribution of As concentrations in water samples is shown in Fig. 6B. Dissolved As concentrations above 5 µg/L were found in two distinct environments: 1) the river waters of the Gardon d'Anduze watershed, and 2) the groundwaters affected by mining pollution in the vicinity of abandoned mine sites. In the Gardon d'Anduze watershed, elevated As concentrations have been mainly attributed to upstream pollution from past mining activities as well as elevated geochemical background (Resongles et al., 2015, 2014; Ebengue Atega et al., 2022). Elevated geochemical background refers to the presence of naturally elevated concentrations of metal(loid)s in some areas, in the absence of mining impacts (i.e. positive geochemical anomalies). In the study area, As concentrations above 5 µg/L occurred at sampling sites affected by mine drainage including the Pradinas Mine, Joseph Mine (Valat de Serre Spring and Joseph Mine outflow), upstream Naville Stream, La Baraque borehole and Bijournet Spring. In addition, similar As concentrations occurred in spring waters in the vicinity of the Gravouillère Mine and La Fabrique area, where the ore was processed in the early 19th century. The Gravouillère Mine was mainly worked for pyrite in the 19th-early 20th centuries and As concentrations of 260-2800 ppm have been measured by pXRF in the waste deposits. Similar As contents have been measured at La Fabrique area, with As ranging from 100 to 2450 ppm (GEODERIS, 2019).

Therefore, the spatial distribution of Zn and As indicated that water contamination is mainly related to past mining in the area. Although a minor contribution from the natural background is likely, there is no evidence of elevated metal(loid) concentrations that are exclusively of natural origin. The geochemical maps show that the extent of the contamination is limited to the vicinity of abandoned mine sites. This suggests that trace metals are rapidly immobilized in surface waters and groundwaters, although contaminant transport can occur in various forms according to flow conditions.



**Fig. 6.** Geochemical maps showing A) dissolved Zn concentrations and B) dissolved As concentrations in the study area. Maximum concentration is displayed at sites where multiple samples were collected. Sampling sites are labeled in a white frame. GW = groundwater, SW = surface water.

#### 4.4. Seasonal variability of metal(loid) concentrations

Unfiltered and filtered concentrations of Fe, Mn, Zn, As, Ni and Cd measured at selected groundwater sampling sites under different flow conditions are presented in Fig. 7. Fe, Mn, Zn, As, Ni and Cd were selected because their concentrations generally exceeded detection limits in waters affected by both acid and neutral mine drainage, in contrast to other metal contaminants such as Al, Pb, and Cu.

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*Bijournet Spring.* Groundwater samples were collected at a perennial spring that drains a karst aquifer adjacent to the Pallières Mine. Fig. 7 shows that Fe, As and Cd concentrations were slightly higher during high flow conditions, whereas Mn,

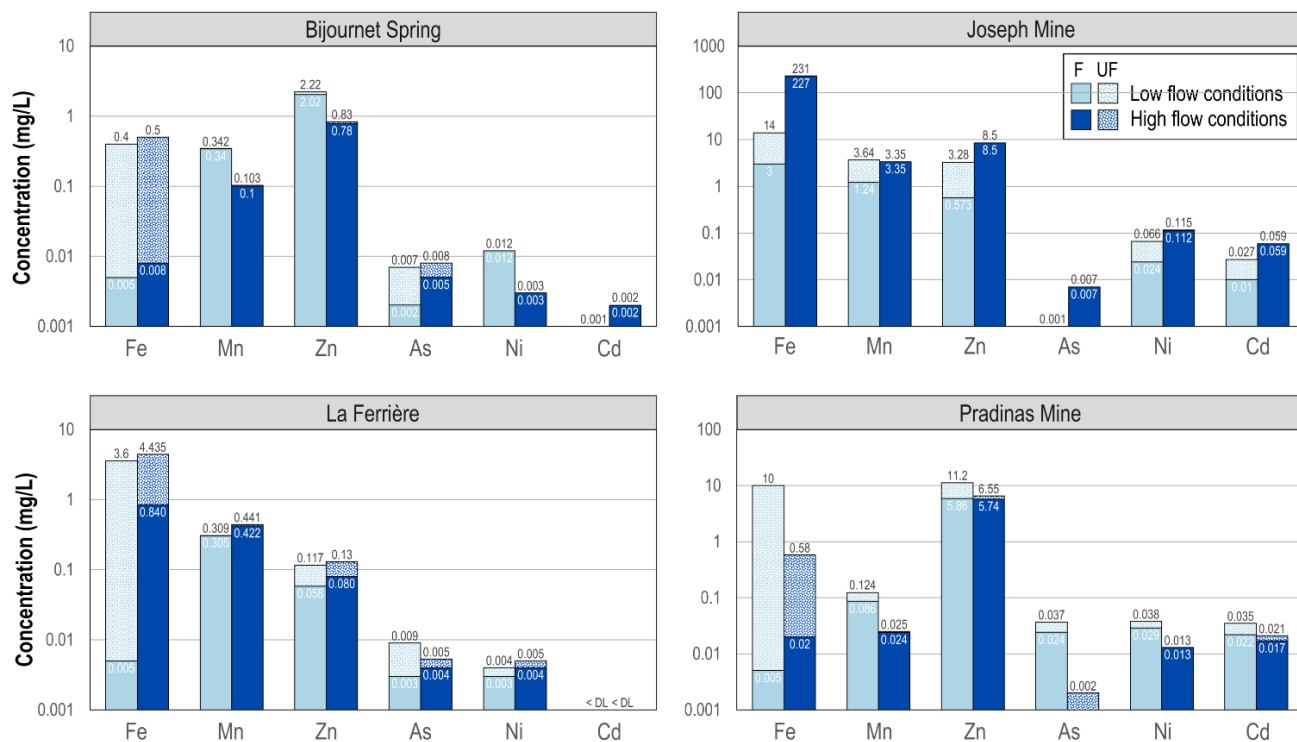
Zn and Ni concentrations significantly decreased. Mn, Zn and Ni were mainly present in dissolved form under low and high flow conditions. Their noticeable decrease in concentration under high flow likely results from dilution by uncontaminated karst waters. In contrast, Fe occurred predominantly in acid-extractable form under low and high flow, most likely as oxyhydroxide particles (Cholet et al., 2019; Vesper, 2019). This suggests that the geochemical conditions in the karst aquifer are favorable for the precipitation of Fe, which is much more rapidly oxidized than other trace metals especially Mn. Rapid precipitation of Fe-oxyhydroxides is supported by the presence of reddish-brown precipitate in the spring sediments. Hence, the slight increase in Fe concentrations despite dilution with uncontaminated recharge water during high flow might be related to the remobilization of particulate Fe in the cave sediments (White, 2018). Arsenic was mainly found in acid-extractable form likely due to adsorption onto Fe-oxyhydroxides. The different behavior of Fe and As on the one hand, and Mn, Zn and Ni on the other hand is in agreement with the results obtained during the 2016 sampling campaign under low and medium flow conditions (Fig S4).

*Joseph Mine.* The samples were collected at a perennial groundwater flow that drains waste materials and that is thought to be fed by the mine aquifer. Metal(loid) concentrations were significantly higher during high flow conditions, with the exception of Mn (Fig. 7). The dissolved fraction of trace metals also increased and trace metals were almost entirely dissolved under high flow. The water sample collected during high flow was characterized by lower pH values (2.35 vs. 3.4) and higher SO<sub>4</sub> concentrations (3830 vs. 2040 mg/L). Such changes in water chemistry likely result from 1) the increased leaching and sulfide oxidation in waste rock, and/or 2) the flushing of highly contaminated waters from mine workings. The occurrence of highly acidic conditions also contributes to the persistence of dissolved metal(oid)s in water.

*La Ferrière.* The samples were obtained from a mine opening located in a quarry adjacent to the abandoned Gravouillère Mine. Fe and Mn concentrations were higher during high flow conditions, while Zn and Ni did not show significant variations (Fig. 7). The dissolved metal(loid) fraction tended to increase under high flow, except for Mn that was mainly dissolved under low and high flow conditions. The dissolved fraction of Fe showed the most obvious increase, suggesting a flushing of more reducing groundwater during high flow. In contrast to low flow, it is likely that Fe<sup>2+</sup> did not have time to be completely oxidized under high flow. Similarly to the Bijournet Spring, the precipitation of Fe is attested by the presence of reddish-brown coating on the rock surface. The dissolved fraction of As increased under high flow, despite a decrease in unfiltered As concentrations, which is consistent with the potential flushing of more reducing groundwater during high flow. These results are in agreement with those presented in Fig S4 for the Bijournet Spring and Eau Rouge during low and medium flow conditions (2016 sampling campaign).

*Pradinas Mine.* The water samples were collected from a mine adit. As shown in Fig. 7, unfiltered metal(loid) concentrations decreased during high flow, likely as a result of dilution with uncontaminated recharge water. Similarly to the

other sampling sites, the dissolved fraction of trace metals increased during high flow, except for As which was entirely associated with the acid-extractable fraction at high flow.



**Fig. 7.** Unfiltered (black font) and filtered (white font) concentrations of Fe, Mn, Zn, As, Ni and Cd under low and high flow conditions, in October 2017 and Marsh 2018 respectively, for a selection of sampling sites. F = filtered concentration, UF = unfiltered concentration.

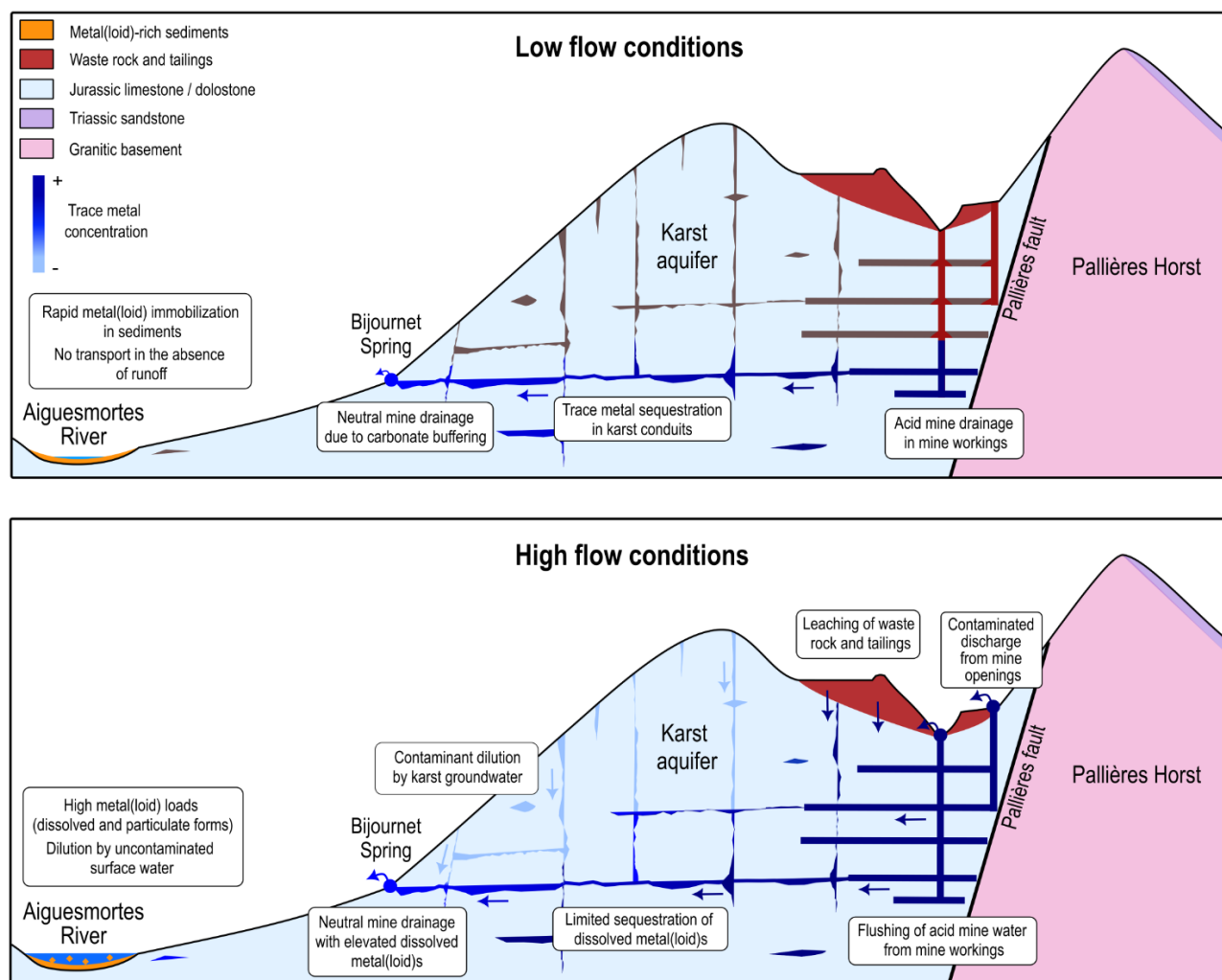
#### 345 4.5. Conceptual model of metal(loid) mobilization and transport in karst water systems

A conceptual model describing the mobilisation and transport of metal(loid)s at and around the abandoned Pallières Mine is presented in Fig. 8. Most of the processes included in this model are applicable to other abandoned mine sites in the study area.

350 During low flow periods, acid mine drainage is produced at depth in mine workings by the oxidation of sulfide minerals mainly present in underground waste rocks. Acid mine waters contain very high concentrations of SO<sub>4</sub> and metal(loid)s, particularly Fe, Mn, Al, Pb and Zn. On the other hand, sulfide oxidation is probably limited by water availability in waste rock and tailings stored at the surface. The slow groundwater flow and extensive interaction of water with carbonate minerals rapidly neutralize the acidity (Cidu et al., 2009; Qin et al., 2019). Metallic cations are largely immobilized under near-neutral conditions, especially Fe, Al, Pb and Cu. In particular, the formation of metal carbonates such as rhodochrosite (MnCO<sub>3</sub>),  
 355 cerrusite (PbCO<sub>3</sub>) or smithsonite (ZnCO<sub>3</sub>) may be an important sink for trace metals (Cidu et al., 2009; Valencia-Avellan et al., 2017; White, 2018). Moreover, the contaminated karst groundwater becomes increasingly oxidizing along the flow path in absence of sulfide oxidation. Under near-neutral and oxidizing conditions, secondary Fe-oxyhydroxides such as ferrihydrite

(Fe(OH)<sub>3</sub>) and goethite (FeOOH) may precipitate as coatings on cave walls and sediment grains (Friedrich et al., 2011; Vesper, 2019). Such Fe-oxyhydroxide phases are likely to sorb significant quantities of other trace metals. Nevertheless, karst groundwater may still contain elevated concentrations of metal(loid)s typical of neutral mine drainage such as Mn, Zn, As, Ni and Cd (Fig. 7). The neutral drainage observed at the Bijournet Spring discharges into the Aiguesmortes River if there is sufficient flow. No transport of metal(loid)s occurs in intermittent rivers during periods of no flow, especially in summer. During low flow, metal(loid) concentrations continue to decrease along the river flow due to sequestration in sediments (Casiot et al., 2009; Resongles et al., 2015).

365 During high flow conditions, groundwater discharges from multiple karst springs and mine openings in intermittent rivers, which are also fed by surface runoff. Groundwater discharging from mine openings may contain very high metal(loid)s concentrations and show evidence of acid mine drainage. These high metal(loid) concentrations are thought to be derived from sulfide oxidation caused by the leaching of waste rock and tailings as well as from the flushing of contaminated groundwater in the mine workings. The dissolution of efflorescent sulfate salts formed during low flow may be an important source of metal(loid)s during high flow (Cidu et al., 2011). As a result, dissolved metal(loid) concentrations in groundwater affected by mine drainage may remain elevated despite dilution by uncontaminated recharge water through the karst network (Du Preez et al., 2016; Qin et al., 2019). Our results suggest that metal(loid)s are primarily transported in dissolved form in karst groundwater under high flow conditions. However, metal(loid) transport on suspended sediments might occur under higher flow velocities during the flood peak or during larger storm events (Vesper and White, 2003). In surface waters, 375 metal(loid) concentrations at high flow are further diluted by rainwater and uncontaminated tributaries although surface leaching of mine wastes and washing out of sediments may constitute an additional source of metal(loid)s.



**Fig. 8.** Conceptual model of metal(loid) mobilization and transport in karst groundwater and surface water near the abandoned Pallières Mine.

## 5. Conclusion

The sampling and analysis of groundwater and surface water in a karst area showed that water quality is affected by contamination from past mining more than 50 years after mining activities have ceased. Acid mine drainage with very high concentrations of Fe, Mn, Al, Pb and Zn occurred occasionally in the immediate vicinity of mine openings and waste dumps. However, neutral drainage with elevated concentrations of Mn, Zn, As, Ni and Cd is generally observed at contaminated sites due to buffering by carbonate dissolution. The extent of the contamination is spatially limited around abandoned mine sites due to metal(loid) sequestration in secondary phases under the near-neutral and oxidizing conditions that prevail in karst water and surface water. During low flow conditions, metal(loid)s are likely to be rapidly sequestered in metal carbonates and Fe-oxyhydroxides and contaminant transport is limited in surface water due to low or no surface runoff in intermittent rivers. In contrast, trace metal transport can be important under high flow conditions, particularly in dissolved form. Dissolved

metal(loid) concentrations remain elevated at high flow despite dilution by uncontaminated recharge water as a result of higher leaching of mine wastes and flushing of contaminated waters from mine workings. In addition, trace metals are less likely to be sequestered in secondary minerals under high flow velocities. This work shows that metal(loid) contamination from past mining activities is a great environmental concern in karst water systems which are highly vulnerable to pollution. Abandoned mines may be significant sources of metal(loid)s in karst watersheds, especially during high flow periods.

This research provides valuable information on the hydrological and geochemical processes that control the concentrations of metal(loid)s in karst groundwater and downstream surface waters. Our study highlights the importance of considering the temporal variability of trace metal concentrations and partitioning to evaluate the processes controlling their fate and transport in natural water. Considering the rapid response of the karst system to rainfall and the high level of contamination, future work should include high-frequency monitoring of water quality during high flow events. Although it requires significant resources, monitoring efforts are needed to improve understanding of temporally variable processes in karst aquifers (Vesper and White, 2003). Finally, this study provides a baseline for assessing future changes in water quality. For example, the comparison of our data with future data could be used to evaluate the efficiency of rehabilitation works or the potential impacts of mine reopening on water quality.

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