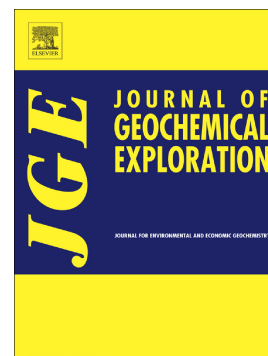


## Accepted Manuscript

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**Oxygen and hydrogen isotopic composition of waters in a past-mining area of southern Apuan Alps (Italy): hydrogeological characterization and implications on the fate of potentially toxic elements**

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**Abstract**

The oxygen and hydrogen isotopic composition of stream water, springs, groundwater tapped from irrigation wells and acid mine drainages were determined during two different surveys in 2015 in an area highly impacted by past-mining activity of Apuan Alps (Italy), as a guidance on good practices for water management. The isotopic local meteoric water line (LMWL) was built by monthly collecting rainwater between 2014 and 2018, given by  $\delta D = 7.02 \pm 0.35 \times \delta^{18}O + 8.54 \pm 2.89$ . The obtained results indicate that acid mine drainages (AMD) are supplied by freshwater from karst systems which flow throughout the post-mining workings. Such waters contaminate by interactions with sulfides (pyrite) that remained unmined in the ore-bodies. During rainstorms, infiltration rainwater displaces water ponding within mine, sharply increasing the outflow rate of highly-contaminated AMD. Acidic drippings in tunnels show an isotopic shift in both  $\delta^{18}O$  and  $\delta D$  values attributable to pyrite oxidation and Fe hydrolysis. The data reveal that karst-springs represents the primary supply for the stream. The isotopic data also reveal that waters flowing in the bedrock carbonate aquifer represent the main feeding component for the overlying alluvial aquifer tapped by wells. The prevailing transfer of clean freshwaters from the carbonate aquifer towards the alluvial aquifer system mitigates the possible influence of contaminated water from stream seepage. However, these observations require a monitoring program on water quality to be established.

**Keywords**

Oxygen and hydrogen isotopes; acid mine drainages; Apuan Alps meteoric water line; carbonate aquifers; groundwater

**1. Introduction**

In past mining areas, the major environmental impact is represented by potentially toxic elements (PTE) leaching and acid rock drainage (AMD) produced by sulfide oxidation and their by-products (Fields, 2003; Nordstrom, 2011, 2015). In these settings, the contaminant migration through the aqueous routes is a growing concern (Hajalilou et al, 2011; Sun et al., 2014; Ghezzi et al., 2019). The oxidative reaction pathways of sulfide minerals and the fate of PTE are impacted by the meteorological drivers governing the hydrological regime (Morton and Merkek, 1993; Schaidler et al., 2014) throughout variations in the infiltration rate of oxygenated meteoric waters and the dynamics of mine-tunnels flooding (e.g. Cidu et al., 2011). Indeed, within the hydrologic system of post-mining workings, AMDs are generated continuously during the groundwater flow in channels and open voids, and the quantity and quality of acid water that targets the aquatic environment is dependent on the recharge of

the aquifer that is hydrologically connected to the mine. In this scenario, the interconnections between acidic water outflows and the recharge of groundwater systems can represent a major environmental hazard.

Oxygen and hydrogen that form the water molecule have Damköhler number  $\ll 1$ , indicating negligible effects of fluid-rock interaction in most low-temperature environments (Blattner and Lassey, 1989). Indeed, the  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios in water, expressed through the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values (Clark and Fritz, 1997), generally act as conservative tracers. This implies that changes in stable oxygen and hydrogen isotopic abundances reflect the variation in time and space in precipitations at recharge areas and the physical processes that occur during the fluid flow (Gat, 2010). It has however to be noted that a study on AMD-impacted waters Sun et al. (2014) reported isotopic shifts in the  $\delta\text{D}$  of the water molecule due to pyrite oxidation and Fe hydrolysis.

The southern sector of the Apuan Alps chain (Tuscany Region, Italy) is characterized by the occurrence of sulfide-bearing mineral deposits (Lattanzi et al., 1994) since long exploited (the Valdicastello Carducci mining area). Mine closure occurred at the beginning of 1990's, leaving the legacy of abandoned tunnels and mine waste residuals that introduce a variety of PTE into the environment, in a densely-populated and high tourist vocation area (Perotti et al., 2017). Indeed, the acid mine drainages produced by the oxidation of the fine-grained pyrite and other base metal-sulfide minerals that characterize the mining area represent a source for As, Al, Fe, Ni, Zn, Cd, Sb, Tl released into the surface waters of the Baccatoio stream, crossing the mining area and the Valdicastello Carducci village. Previous studies (Perotti et al., 2017) showed highly variable concentration of PTE in the acidic plumes outflowing from tunnels and attenuation processes downstream. Flow rate measurements demonstrated that the outflow rate may change on order of magnitude and it is related to the rainfall amount (Giannecchini et al., 2016a). However, the interconnections between the water recharge, the mine tunnels flows, the groundwater-dependent ecosystem and the seepage infiltration from the Baccatoio stream are still unexplored.

To better understand some of the processes that take place in the Valdicastello Carducci mining area, and to ascertain how the hydrological regime behaves with time, oxygen and hydrogen isotopic data were obtained on acid effluents and acidic dripping waters inside tunnels, on stream water, springs and groundwater tapped from irrigation wells collected during different surveys in 2015. In addition, a local meteoric water line was built by collecting rainwater monthly between 2014 and 2018. Even if O-H stable isotopes represent a well-used tool in hydrology (Gat, 2010), these methods have been only occasionally applied to investigate mining areas (Seal II, 2003; Parizi and Samani, 2014).

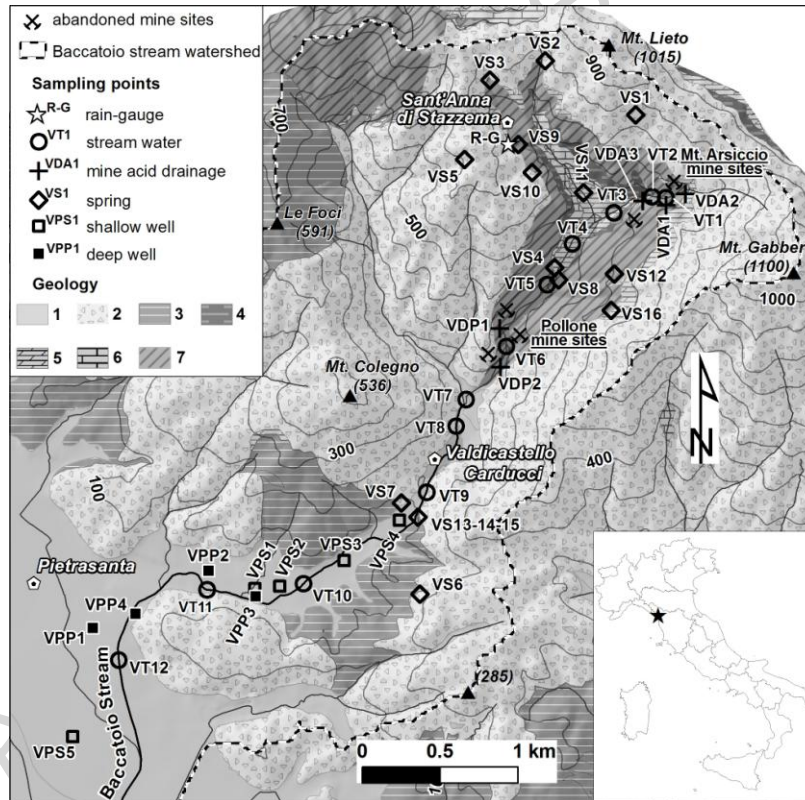
This approach assumes a particular interest in the study area, in view of the proximity of the mine site with springs providing drinking water supply and wells for domestic and irrigation uses.

## 2. Mine location, geological and hydrogeological outlines

The study mining area is located in the southern part of the Apuan Alps chain (Tuscany Region, Italy), in the Baccatoio stream catchment, a stream having its headwater in the Mt. Gabberi and Mt. Lieto reliefs (Figure 1). The Baccatoio stream receives the AMD-impacted effluents from the mining districts of Mt. Arsiccio and Pollone (Figure 1). The amount of AMD, averaged on annual basis, outflowing from Mt. Arsiccio and Pollone mine sites ranges between 0.3 to 3.0 L/s and 0.3 to 1.0 L/s (Giannecchini et al., 2016a), respectively, showing a strong dependence on the amount of precipitation, mostly releasing Fe (about 61 tons/year), Zn (about 1.1 ton/year), Al (about 800 kg/year), As (about 110 kg/year), Cu (about 40 kg/year), Tl (about 25 kg/year), Sb (about 10 kg/year), in addition to Pb, Cd, Ni, Ba (total amount about 25 kg/year) (Perotti et al., 2017). The stream crosses the Valdicastello Carducci village and reaches the Ligurian Sea in the Versilia coastline, an area densely populated and of strong touristic vocation. The exposed rocks in the basin include a metamorphic complex of the Paleozoic basement (mostly formed by phyllite, quartzite and metarhyolite) and carbonatic rocks of the Apuan Alps Unit (metadolostones and limestones of the Grezzoni and Marmi Fms.). They are unconformably covered by the non-metamorphic units of the Tuscan Nappe, mainly constituted by limestones and cataclastic breccias (Calcare Cavernoso and Breccie Poligeniche Fm.) (Molli and Meccheri, 2012). Pyrite  $\pm$  baryte  $\pm$  iron oxide  $\pm$  (Pb-Zn-Ag) orebodies form lenses and/or small bodies generally associated with the basement rocks, usually close to the contact with the metadolostones. In particular, the fine-grained pyrite is characterized by high levels of PTE, including thallium that reaches about 1 g/kg (D'Orazio et al., 2017).

In agreement with the overall hydrogeology of Apuan Alps (Doveri et al., 2019 and references therein), the main aquifer system in the study area is hosted in the metamorphic carbonate sequence (Grezzoni and Marmi Fms.), and it is structurally included between the mostly impermeable phyllites belonging to the Apuan Unit (Figure 1). Within such carbonate complexes, a low fracture development at depth promoted a low-density network of well-developed karst shapes, thus enhancing a strong inhomogeneity of groundwater circulation (Doveri et al., 2013). A second carbonate aquifer system is present in the Baccatoio stream basin, consisting in the non-metamorphic limestone-cataclastic breccia of the Calcare Cavernoso and Breccie Poligeniche Fm.

The average amount of precipitation in the area exceeds 2000 mm/year (Giannecchini et al., 2016b) and high rates of rainfall infiltration through fractures and cavities characterize carbonate aquifer systems, which originate several springs. Some of these springs are tapped and are strategic for drinkable water and human consumption, and are especially vulnerable to contamination (Ghezzi et al., 2019). In the lower part of the catchment a third aquifer system extends within the intravalley and fan alluvial deposits, formed by coarse-grained sediments, prevalently gravel and sand. The system is mainly unconfined, and it is fed by direct recharge from rainwater, seepage from Baccatoio stream water and likely underground water transfer from the underlying karstified carbonatic rocks. This alluvial aquifer has a remarkable capacity for water storage and in the Valdicastello Carducci village area it is tapped by many private wells used for irrigation purposes.



**Figure 1.** Sketch-map of the study area containing a simplified geology and the sampling points distribution (1: Alluvial sediments; 2: Limestone and cataclastic breccia of the Calcare Cavernoso and Breccie Poligeniche Fms./Tuscan Nappe Unit; 3: Phyllite, quartzite and meta-conglomerate/Massa Unit; 4: Meta-sandstone and phyllite of the Pseudomacigno Fm./Apuan Alps Unit; 5: Meta-limestone of the Marmi Fm./Apuan Alps Unit; 6: Meta-dolonstone of the Grezzoni Fm./Apuan Alps Unit; 7: Phyllite, quartzite and meta-rhyolite of the Paleozoic basement/Apuan Alps Unit) (geological data source from <http://www.lamma.rete.toscana.it/territorio/geologia>).

### 3. Materials and methods

Rain water was collected monthly from 2014 to 2018 using a sampling device and prescriptions as specified by IAEA (IAEA/GNIP precipitation sampling guide V2.02, 2014). The rain collector is designed with an anti-evaporation system as described in Gröning et al. (2012). It consists of a narrow polypropylene flexible tube, connecting the outlet of a 20 cm $\varnothing$  polyethylene funnel to the bottom of a high quality high-density polyethylene (HDPE) reservoir tank of 10 L, a size suggested for rainy regions. This equipment minimizes the exposure of the collected water to the outside air. The rain collector was placed at about 660 m a.s.l. (Sant'Anna di Stazzema, Figure 1), an altitude close to the average elevation of the middle-high sector of the Baccatoio stream catchment, paying attention to minimize the influence of nearby objects. The amount of precipitation was also recorded monthly.

A rainfall event (33 mm rainwater) occurred in the same day of the April 2015 survey and heavy showers characterized the three days immediately before the October 2015 survey (87 mm rainwater): these single rainfalls were collected through runoff on hillslopes, with the assumption that the isotopic signature of rainfall is transmitted without discriminant to the overland flow.

Superficial waters from the Baccatoio stream in different stations from the headwater downstream (24 samples, labelled VT); springs representing waters hosted in the two different fractured aquifers of the basin (30 samples, labelled VS); groundwater from shallow (depth < 15 m, 10 samples, labelled VPS) and deep (depth > 30 m, 8 samples, labelled VPP) wells, were collected during two different surveys on April and October 2015 (labelled with -1 and -2, respectively). Most wells are in the alluvial cover, and only VPP2 and VPP3 reach the aquifer hosted in carbonates. Acid mine drainages (pH in the range between 1.9 and 2.4) from both Mt. Arsiccio and Pollone mine sites (labelled VDA and VDP, respectively) were collected in May, 2015, April, 2015 and October, 2015 (10 samples, labelled with -0, -1 and -2, respectively). In addition, highly acidic water (pH=1.2) drippings from tunnel ceilings characterized by reactive-pyrite to iron-hydroxysulphate and iron-oxides, were collected in the same period from both Mt. Arsiccio and Pollone (2 samples).

All waters were collected in clean, dry high-density polyethylene bottles capping without head space. The sampling locations are shown in Figure 1.

Oxygen and hydrogen isotopic compositions were determined at the Ca' Foscari University of Venice following the CO<sub>2</sub>/H<sub>2</sub> water equilibration technique (Horita et al., 1989) using a HDO equilibration device on line with a Thermo Fisher Delta Plus Advantage mass spectrometer equipped with a dual-inlet, which allows for high precision measurements. The O-H isotope data are expressed by using the conventional delta notation ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ), which represents the ‰ deviation with respect to the V-

SMOW standard ( $\delta = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$  (‰)), where R represents the  $^{18}\text{O}/^{16}\text{O}$  or D/H isotope ratio). In each analysis run two internal standards, periodically calibrated against the IAEA international standards V-SMOW2 and SLAP2, are analysed along with the samples, and used for building a calibration curve. The analytical uncertainty for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  was  $\pm 0.05\%$  ( $1\sigma$ ) and  $\pm 0.7\%$  ( $1\sigma$ ), respectively.

The chloride and sodium contents on springs were determined at the Earth Science Department (University of Pisa) by ion-chromatography using a Thermo ICS 900 instrument equipped with Dionex IonPack AS-23 and CS-10 columns, respectively. Uncertainty is within 5%.

#### 4. Results

The O-H isotopic composition and deuterium excess (d-excess ‰ =  $\delta\text{D} - 8 \cdot \delta^{18}\text{O}$ , Dansgaard, 1964 referred to the Global Meteoric Water Line GMWL:  $\delta\text{D} = 8 \cdot \delta^{18}\text{O} + 10$ , Craig, 1961) in precipitations are given in Table 1. Precipitations show quite large isotopic fluctuations, in the range from  $-10.11\%$  to  $-2.01\%$  and from  $-64.15\%$  to  $-11.99\%$  for  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , respectively. The volume-weighted average annual isotopic composition of rain is: 2014:  $\delta^{18}\text{O} = -7.31 \pm 0.69\%$ ,  $\delta\text{D} = -45.73 \pm 4.50\%$ , d-excess =  $12.79 \pm 1.05\%$ ; 2015:  $\delta^{18}\text{O} = -6.92 \pm 0.71\%$ ,  $\delta\text{D} = -42.91 \pm 4.46\%$ , d-excess =  $12.49 \pm 1.26\%$ ; 2016:  $\delta^{18}\text{O} = -6.53 \pm 0.42\%$ ,  $\delta\text{D} = -40.89 \pm 1.90\%$ , d-excess =  $11.45 \pm 0.40\%$ ; 2017:  $\delta^{18}\text{O} = -5.54 \pm 0.49\%$ ,  $\delta\text{D} = -30.72 \pm 2.84\%$ , d-excess =  $13.59 \pm 1.15\%$ ; 2018:  $\delta^{18}\text{O} = -6.21 \pm 0.37\%$ ,  $\delta\text{D} = -36.86 \pm 2.37\%$ , d-excess =  $12.81 \pm 0.87\%$ . This variability reflects the expected seasonal cycle with more negative values in winter and less negative values in summer, although deviations from this general rule are observed, for example in December 2015 and in July 2014 (Table 1). The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values measured on July 2016 ( $+0.61\%$  and  $-0.64\%$ , respectively) refer to a very small volume of rainwater (0.08 L, Table 1), close to the minimum amount indicated for the representativeness of the sample by IAEA/GNIP. The negative d-excess ( $-5.5\%$ ) suggests that this samples was exposed to evaporation altering the original isotopic composition and for this reason it was excluded. The precipitation  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values are related to the local site temperature (Dansgaard, 1964) but are also influenced by the history of the air mass, which contain information on the moisture source regions (relative humidity and sea surface temperature) as well as on the trajectory followed by the air mass. The single rain events collected through runoff on April and October 2015 are characterized by markedly different  $\delta^{18}\text{O}$  and  $\delta\text{D}$  from the corresponding monthly sampling (Rindsberger et al., 1990; Liotta et al., 2008) (Table 1).

The d-excess values in precipitations show a wide variability between  $+3.24\%$  and  $+22.28\%$  (Table 1).



The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in spring waters (Table 2) collected during the April 2015 survey range between -5.73‰ and -7.03‰ and between -33.31‰ and -40.46‰, respectively. In October 2015,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  range respectively between -5.96‰ and -6.92‰ and between -34.45‰ and -38.77‰.

The O-H isotopic composition on acid mine drainages and tunnel dripping waters, on stream waters and wells are reported in Table 3. The chloride and sodium content are also reported on the same Table. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in acid mine drainages from Mt. Arsiccio are in the relatively narrow ranges between -6.15‰ and -6.37‰ and between -35.13‰ and -36.69‰, respectively. Mine drainages from Pollone are systematically shifted towards an isotopically heavier signature, in the range between -5.50‰ and -5.71‰ for  $\delta^{18}\text{O}$  and -29.47‰ and -33.07‰ for  $\delta\text{D}$ . Acid mine drainages from both mine sites do not show significant isotopic variations in the different sampling periods. The dripping acidic water from Mt. Arsiccio shows a markedly heavier isotopic composition compared with AMD outflows ( $\delta^{18}\text{O}$  and  $\delta\text{D}$  of -5.75 ‰ and -30.60 ‰); a similar isotopic range characterizes acidic drippings from Pollone mine site ( $\delta^{18}\text{O}$  and  $\delta\text{D}$  of -5.27 ‰ and -29.47 ‰).

Waters from the Baccatoio stream collected during April 2015 are characterized by  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values ranging between -4.50‰ and -5.98‰ and -23.57‰ and -34.28‰, respectively. During the October 2015 survey, the isotopic data significantly changed, the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values range between -6.04‰ and -6.41‰ and -35.19‰ and -37.35‰, respectively.

The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values in waters from wells in the alluvial deposits collected on April 2015 range between -5.59‰ and -6.08‰, and between -30.65‰ and -35.40‰, respectively. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values in October 2015 range between -5.80‰ and -6.15‰, and between -33.66‰ and -34.96‰, respectively. No isotopic differences are observed between wells tapping waters from the phreatic and the deeper aquifer hosted in carbonates.

## 5. Discussion

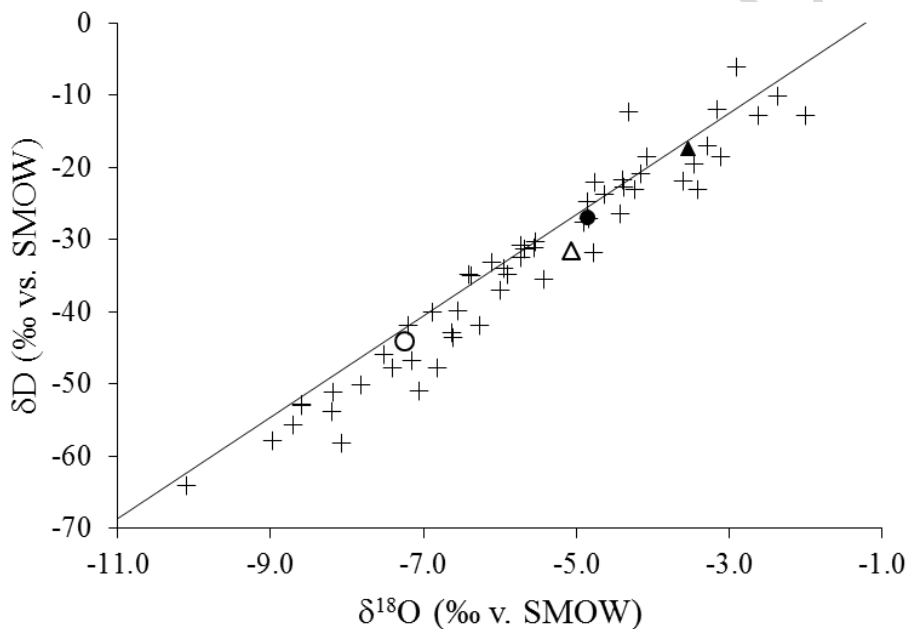
### 5.1 Oxygen and hydrogen isotopic data of precipitation and the LMWL

The local meteoric water line (LMWL) is an important reference line for the quantitative understanding of hydrologic systems that are fed by meteoric water, as in the case of Baccatoio catchment response. In the present study, different regression techniques have been applied to the oxygen and hydrogen isotope composition of rain, including ordinary least squares regression (OLSR), reduced major axis regression (RMA; IAEA, 1992), major axis least squares (MA) and precipitation weighted regressions (PWLSR, PWRMA, PWMA; Crawford et al, 2014). Precipitation weighted regressions better account

for possible re-evaporation processes beneath the cloud (Gat, 2000; Peng et al., 2007) and/or errors in sample collection when dealing with small precipitation amounts that may mask the original isotope content of air masses.

Precipitation data in the  $\delta$ -space (Figure 2) show a quite poor correlation, likely reflecting kinetic fractionation that results in significant different slopes for the different regression methods. Differences in slopes due to large scatter generally characterize precipitations in coastal areas (Gat, 2005), in particular in Mediterranean (Liotta et al., 2008). The root mean of sum of squared errors ( $\text{rmSSE}_{\text{av}}$ , Crawford et al., 2014) is a parameter that determines the goodness of fit, which is better when  $\text{rmSSE}_{\text{av}}$  equals 1.00. The calculated values of  $\text{rmSSE}_{\text{av}}$  for the different regressions indicate that PWLSR is the most suitable model in fitting precipitation data for the Baccatoio stream catchment ( $\text{rmSSE}_{\text{av}} = 1.01$ ). The preferred LMWL equations is:

$$\delta\text{D} = 7.02 \pm 0.35 \times \delta^{18}\text{O} + 8.54 \pm 2.89$$



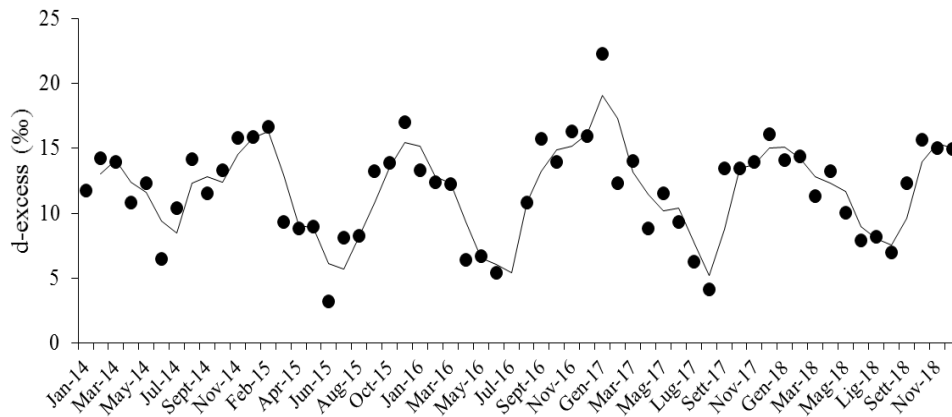
**Figure 2.**  $\delta^{18}\text{O}/\delta\text{D}$  diagram reporting the monthly isotopic values of precipitation (60 total samples) at Sant'Anna di Stazzema station (see Figure 1 for location). Solid and open triangles represent the April, 2015 single rain event and April, 2015 monthly value, respectively. Solid and open circles represent the October 2015 single rain event and October, 2015 monthly value. The LMWL obtained by PWLSR regression is shown ( $\delta\text{D} = 7.02 \pm 0.35 \times \delta^{18}\text{O} + 8.54 \pm 2.89$  solid line). See text for explanations.

The slope of the obtained LMWL overlaps with the meteoric water line reported by Mussi et al. (1998) ( $\delta\text{D} = 7.14 \times \delta^{18}\text{O} + 6.77$ ) and with the central Italy meteoric water line reported by Longinelli and Selmo (2003) ( $\delta\text{D} = 7.05 \times \delta^{18}\text{O} + 5.61$ ) and Giustini et al. (2016) ( $\delta\text{D} = 7.46 \pm 0.32 \times \delta^{18}\text{O} + 8.29 \pm 2.33$ ), showing a somewhat lower slope with respect to the Global Meteoric Water Line (GMWL slope  $\delta\text{D} / \delta^{18}\text{O} \approx 8$ ,

Craig, 1961; Rozanski et al., 1993). The obtained lower slope compared with the GMWL indicates less humid conditions and the possible partial evaporation of falling droplets (Dandgaard, 1964; Gonfiantini, 1986).

The O-H isotopic data and pattern on precipitations represent the basis to know the source and origin of mine waters, the hydrodynamic behaviour of groundwater and the interactions between groundwater and surface waters.

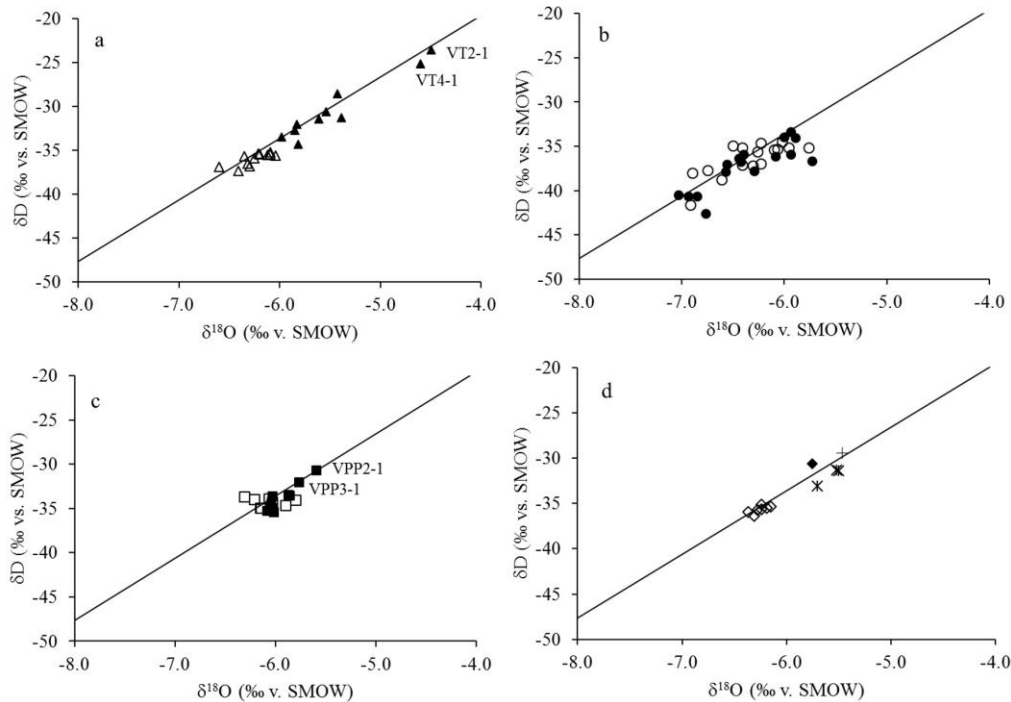
The seasonal pattern of d-excess in precipitation (Figure 3) is characterized by maximum during winter and minimum in summer as expected in the northern hemisphere (Rozanski et al., 1993; Pfahl and Sodemann, 2014). In winter, the source vapour underwent greater non-equilibrium fractionation effects due to more dry conditions yielding a high value of d-excess in the evaporating moisture (He and Smith, 1999; Uemura et al., 2008; Pfahl and Sodemann, 2014). It is worth to note that the highest d-excess reflects the specific conditions of the vapour formation over the eastern Mediterranean areas, while d-excess values approximately in the range between 8 ‰ and 11 ‰ possibly reflect oceanic and northern Europe origin (Rozanski et al., 1993). High d-excess values hence indicate vapour that formed under low relative humidity conditions, while d-values lower than 10 ‰ may reflect secondary evaporation processes such as evaporation of falling raindrops (Craig and Gordon, 1965). In the study area, the measured d-excess fluctuation in rainwater from the same month in different years indicate that precipitation events are more variable than expected based on this simplified seasonal model. This likely reflects changes in rainfall intensity and in general the complex meteorological history of the air masses, also considering that convective clouds are generally characterized by precipitation with higher  $\delta$ -values compared with stratiform clouds, in coastal areas.



**Figure 3.** Seasonal cycle of d-excess of the monthly composite rainfall samples at the Sant'Anna di Stazzema station (see Figure 1)

## 5.2 Oxygen and hydrogen isotopic data in stream waters, springs, wells and acid mine drainages

Isotopic data on stream, springs, wells and AMD are shown in Figure 4. It is observed that waters are mostly aligned along the LMWL, even if deviations from a strict adherence occur (Figure 4a-d).



**Figure 4.**  $\delta^{18}\text{O}/\delta\text{D}$  diagram. a) stream waters (samples VT2-1 and VT4-1 are labelled); b) spring waters; c) wells (samples VPP2-1 and VPP3-1 are labelled). Filled and open symbols refer to the April, 2015 and October, 2015 surveys, respectively. d) AMD, including drainages outflowing from Mt. Arsiccio mining area (open diamond) and drippings inside tunnels (filled diamond) and drainages outflowing from Pollone mining area (star) and drippings inside tunnels (cross). The LMWL is also superimposed.

A positive shift is observed in stream waters during the April 2015 survey (Figure 4a) compared to October 2015. This indicates the contribution of the single rainfall event that occurred while sampling, suggesting that drains over the surface were beyond the infiltration capacity. This is mostly evident in the upstream stations (VT2-1 and VT4-1), possibly due to the surface morphology that allows runoff to increase locally. Some spring waters plot below the LMWL (Figure 4b) and in general springs show a higher scatter respect to LMWL. Most wells (Figure 4c) tapping the alluvial aquifer show isotopic values similar to springs outflowing from the carbonate outcrops bordering the alluvial fan (spring samples VS6, VS7, VS13-15), downstream in the basin. This suggests that waters flowing in the bedrock carbonate aquifer represent the main feeding component for the overlying alluvial aquifer. The prevailing transfer of clean freshwaters from the carbonate aquifer towards the alluvial aquifer system dilutes the influence of contaminated water from stream seepage. Furthermore, the supply of

oxygenated waters at circum-neutral pH can promote PTE scavenging by sorption processes on precipitating hydrous-ferric oxides and other sorbing surfaces within the alluvial aquifer, thus enhancing the positive effects in terms of groundwater quality. This is also confirmed by invariably low PTE contents in waters tapped by wells in the alluvial aquifer (Giannecchini et al., 2016a). However, waters from two deep wells drilled nearby the stream and collected on April, 2015 (VPP2 and VPP3, Figure 4c) show an isotopic shift which is congruent with a possible water component infiltrated through the Baccatoio streambed. This might reflect leaks in the well casing (e.g. by corrosion), allowing contaminants and pollutants more easily enter the well. Alternatively, direct rainwater infiltration might be invoked. These hypothesis require additional investigations.

Figure 4d shows the  $\delta D$  and  $\delta^{18}O$  relation in acid drainages and dripping waters, together with the LMWL. The  $\delta^{18}O$  and  $\delta D$  values of AMD highlight that waters from the effluents in the Mt. Arsiccio and Pollone mine sites are isotopically different, indicating distinct meteoric water feeding systems. In particular, the O-H isotopic feature of Pollone acid drainages might be related to a lower mean altitude of the infiltration area compared with Mt. Arsiccio. In addition, the former lies below the LMWL, possibly reflecting the isotopic fractionations that accompany re-evaporation.

It is worth to note that dripping waters are shifted towards an isotopically heavier signature with respect to drainages, in particular for Mt. Arsiccio, and mostly for heavier  $\delta D$  with respect to  $\delta^{18}O$ . These data might reflect fractionation during pyrite oxidation and Fe hydrolysis. Indeed, pyrite oxidation processes are well documented in the studied area. In particular, fine-granular pyrite ( $FeS_2$ ) containing high content of PTE is the most abundant sulphide mineral which is exposed to weathering in the Mt. Arsiccio and Pollone tunnels and in outcrops. As already stated, the conversion of pyrite to AMD products through oxidative dissolution (yielding the precipitation of ferric iron hydroxides), represents the major environmental impact in the Baccatoio basin (Perotti et al., 2017; Ghezzi et al., 2019).

It has been demonstrated that during pyrite oxidation the oxygen present in the sulfate that forms mostly comes from water molecule and not from dissolved molecular oxygen (e.g. Dos Santos et al., 2016) and that oxygen isotopic fractionation occurs between  $H_2O$ ,  $O_2$  and  $SO_4^{2-}$  during both abiotic and biotic pyrite oxidation through the incorporation of  $^{18}O$  in the sulfate and iron hydrolysis products (Balci et al., 2007; Brunner et al., 2008). Sun et al. (2014) in a study of the hydrogen and oxygen isotopic composition of karst waters impacted by AMD claimed that during Fe hydrolysis and pyrite oxidation the remaining water is enriched in heavy isotopes. In particular, Sun et al. (2014) observed a heavier  $\delta D_{H_2O}$  signature in AMD-impacted waters while  $\delta^{18}O_{H_2O}$  remained similar to non-AMD-impacted. In the present study, the isotopic data indicate that acid runoff outflowing from tunnels is

mostly formed by groundwater hosted in the karst aquifer systems and not by the water ponding that form due to the diffuse acid dripping in the tunnel environment. Furthermore, the almost negligible isotopic variability of the AMD suggests a well organized groundwater flow path system, which is able to obliterate the isotopic variability of the infiltration waters. It can be supposed that shortly after heavy rain events the infiltrating rainwater is routed to recharge the carbonate aquifer systems, allowing the displacement of water bodies mainly by piston-flow (Ghezzi et al., 2019) and supplying the mines through the fractures network, as well as increasing the outflow rates of AMD from tunnels. The latter process may also mobilize the highly contaminated waters flooding mine tunnels, accounting for the PTE concentration changes recorded in the mine drainages (Perotti et al., 2017).

### 5.3 Spring recharge

In the previous section it has been highlighted that groundwater from the karst system, discharged through springs, and AMD have a hydraulic connectivity. Spring waters collected during the April 2015 and October 2015 surveys show changes in the d-excess parameter (Figure 5).

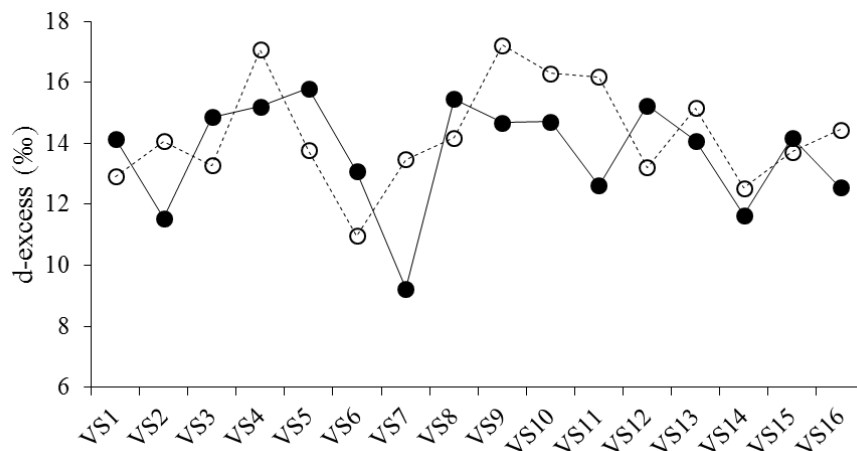
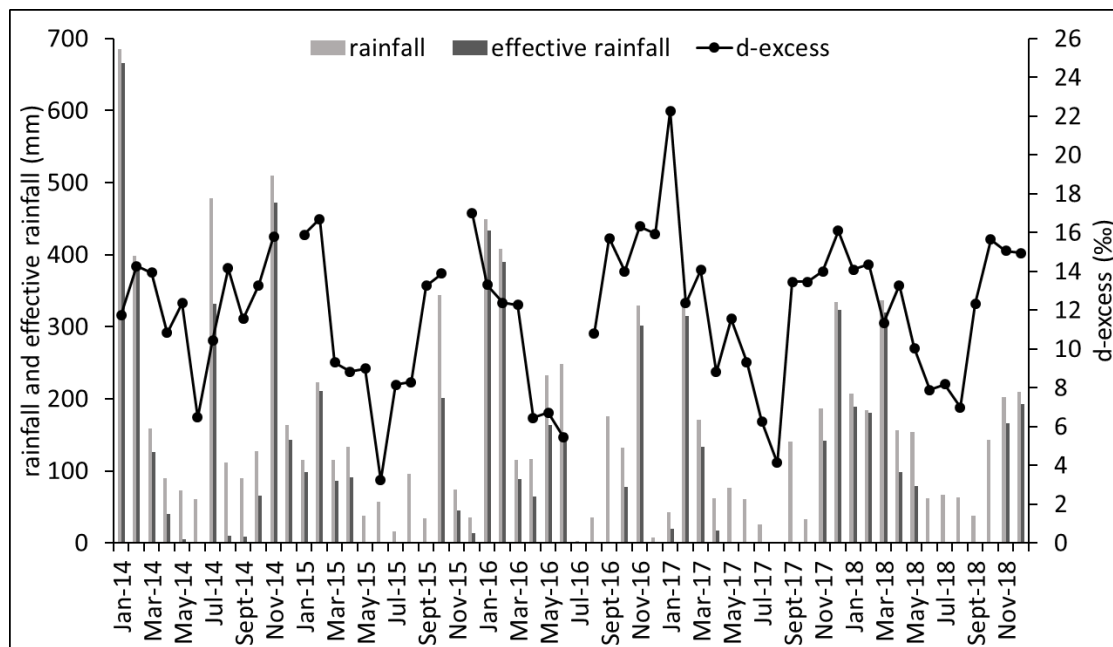


Figure 5. d-excess patterns in spring waters during the April, 2015 (filled circle) and October, 2015 (open circle) surveys

This behavior is related to the relative rapid transfer of groundwater that are drained by such springs in karst environment and that reflect the high seasonal variability of d-excess in the effective rainfall (Figure 6). The diagram of Figure 6 shows that when significant effective rainfalls are available, d-excess varies in the range 10-16 %. This variability can affect the karst-spring discharge rate depending on the development of the karst character in the fractures network.

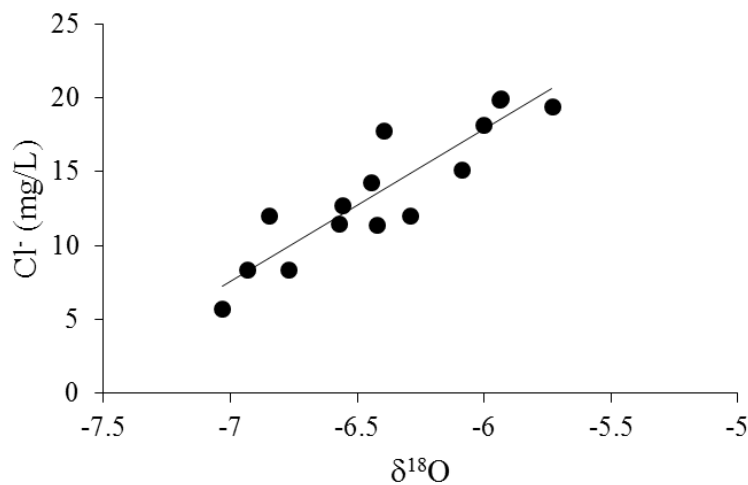


**Figure 6.** Rainfall d-excess compared with total and effective monthly rainfall. The effective rainfall was estimated according to the Thornthwaite and Mather (1957) approach.

The comparison of the isotope content of springs and Baccatoio stream waters (Figure 4a-b) indicates that the stream baseflow is represented in most part by the groundwater discharge, and that the response during the rainy season to single rain event by direct runoff is episodic.

Due to the exposure of the mine basin, facing the seacoast, it is expected that both wet and dry deposition of maritime sea salts occur varying both temporally and spatially. In particular, the dense vegetation canopy that characterizes the Baccatoio upstream catchment can enhance the dry atmospheric deposition during rain-free periods. The Na/Cl molar ratio of most spring waters collected during the October and April surveys is shown in Table 2, ranging from 0.79 to 1.46 and from 0.50 to 1.17 respectively. The Na/Cl molar ratio hence approaches to 1, even if most samples show a Na/Cl molar ratio <1. Due to the lack of evaporite (halite) deposits and coal-bearing formations, this reflects the dissolution of sea salts deposited on the soil and canopy and excludes a significant role of anthropogenic sources of chloride. Assuming that chloride behaves conservatively in the water phase, a Na/Cl molar ratio <1 could be attributable to sodium loss. Since both atmospheric wet and dry deposition quantify the diffuse recharge of groundwater through the soil profile, the data suggest the non-conservative behaviour of Na ions during the solute transport in soil possibly due to absorption to soil particles through ion exchange (Kumar et al., 2009), and the different contribution to the total recharge for some spring.

Assuming that the atmospheric input is the only chloride source and that this element behaves conservatively in the water phase in the subsurface, the chloride content may be coupled with  $\delta^{18}\text{O}$  as an additional environmental tracer for groundwater recharge (Guan et al., 2010). A positive linear correlation ( $R^2=0.82$ ) is observed between the chloride content and  $\delta^{18}\text{O}$  for spring waters collected on April, 2015, with the chloride content increasing with  $\delta^{18}\text{O}$  values (Figure 7). A similar trend, even if with a smaller data-set, have been presented by Mussi et al. (1998) who hypothesized a sea spray origin for the chloride in spring waters. A more scattered distribution ( $R^2=0.67$ ) is observed in October (not shown).



**Figure 7** Chloride (mg/L) vs.  $\delta^{18}\text{O}$  correlation in spring waters.

Dry deposition of sea salt is expected to decrease from coast to inland (e.g. Ten Harkel, 1997). Even if several factors may control the chloride deposition yielding a strong spatial variability in coastal areas, the  $\text{Cl}^-$  concentration vs.  $\delta^{18}\text{O}$  isotopic data correlation indicates a lower chloride deposition as increasing the catchment average recharge altitude and distance from the coastline (Gustafsson and Franzen, 1996). This observation suggests that in the studied area the elevation has a primary effect on water isotope signature, thus confirming the powerfulness of the isotopic approach to estimate catchment groundwater recharge in the hydrogeologically-complex region of the Apuan Alps.

## 6. Conclusions

The karst aquifers in the Apuan Alps host a large portion of the freshwater reservoirs which are strategic for regional water availability. The Baccatoio stream catchment, in the southern sector of the



Apuan Alps chain, is characterized by carbonate-hosted mineralizations that were extensively mined in the past. The mining practice promotes the pervasive flow of waters through the amount of pyrite that remained unmined in the ore-bodies, providing the conditions for pyrite oxidation and the release of AMD. In this setting, the principal control on AMD transport and mitigation strategies being used is through the understanding of the major hydrologic processes.

The  $\delta D$  and  $\delta^{18}O$  data obtained in this study suggest that the acid mine effluents are mostly supplied by groundwater locally recharged and stored in the carbonate aquifers, which flow in the post-mining workings. Such waters contaminate by interactions with the exposed mineralization in the tunnels. During large recharge events, following rainstorms, infiltration water displaces the water ponding within mine sharply increasing the outflow rate of AMD. During this phenomenon the remobilization of highly contaminated waters may occur yielding transients of high PTE concentration in drainages. Acidic drippings in tunnels reveal an isotopic shift in both  $d18O$  and  $dD$  values towards heavier compositions, preliminary attributable to pyrite oxidation and Fe hydrolysis.

The isotopic data indicate that outflows from springs are the primary supply for the Baccatoio stream and that the contribution of runoff vanishes shortly after rain storm events. The admixing of freshwater from the karst aquifer to the stream water allows the fast precipitation of iron oxyhydroxides, scavenging most of EPT.

Observations show that the Baccatoio stream water leaks into the groundwater system via the streambed, and in summer time the entire stream may disappears into the alluvial fan. This poses a potential threat for contamination of the aquifer tapped by domestic wells. Nevertheless, the isotopic data indicate that waters flowing in the bedrock carbonate aquifer represent the main feeding component for the overlying alluvial aquifer. The prevailing transfer of clean freshwaters from the carbonate aquifer towards the alluvial aquifer system dilutes the influence of contaminated water from stream seepage.

These results represent a basis for planning the best practices in the management of this heavily impacted ecosystem.

**Table 1.** Meteoric water. O-H isotope-ratio, d-excess (d-ex, ‰) and rain amount (mm)

	$\delta^{18}\text{O}$	$\delta\text{D}$	d-ex	Rain		$\delta^{18}\text{O}$	$\delta\text{D}$	d-ex	Rain		$\delta^{18}\text{O}$	$\delta\text{D}$	d-ex	Rain
<b>Year 2014</b>					<b>Year 2015</b>					<b>Year 2016</b>				
January	-8.20	-53.85	11.75	685	January	-8.6	-52.9	15.88	115	January	-5.73	-32.5	13.30	449
February	-7.52	-45.89	14.27	398	February	-10.11	-64.15	16.70	223	February	-6.54	-40.0	12.39	408
March	-8.70	-55.66	13.94	159	March	-6.61	-43.58	9.31	115	March	-7.81	-50.2	12.28	115
April	-5.99	-37.08	10.84	89	April	-5.06	-31.66	8.83	134	April	-8.08	-58.2	6.45	116
May	-5.90	-34.84	12.36	73	May	-4.42	-26.37	8.98	38	May	-6.82	-47.8	6.71	232
June	-4.78	-31.76	6.48	61	June	-2.01	-12.84	3.24	57	June	-7.05	-51.0	5.44	248
July	-7.15	-46.76	10.44	478	July	-2.62	-12.79	8.15	16	July	0.61	-0.64	-5.52	3
August	-4.08	-18.48	14.16	111	August	-6.27	-41.88	8.28	96	August	-4.24	-23.1	10.80	35
September	-4.90	-27.66	11.54	89	September	-4.63	-23.78	13.26	34	September	-7.20	-41.9	15.71	175
October	-3.16	-11.99	13.29	127	October	-7.25	-44.12	13.88	344	October	-5.53	-30.2	14.00	132
November	-8.59	-52.92	15.80	510	December	-2.90	-6.20	17	35	November	-6.40	-34.9	16.31	330
										December	-4.76	-22.2	15.93	8
	$\delta^{18}\text{O}$	$\delta\text{D}$	d-ex	Rain		$\delta^{18}\text{O}$	$\delta\text{D}$	d-ex	Rain					
<b>Year 2017</b>					<b>Year 2018</b>					<b>Runoff</b>				
January	-4.32	-12.29	22.28	42	January	-4.86	-24.80	14.08	207	April 2015	-3.54	-17.44	10.91	
February	-4.16	-20.93	12.35	334	February	-8.18	-51.08	14.36	185	October 2015	-4.85	-26.90	11.90	
March	-5.68	-31.37	14.07	170	March	-7.40	-47.86	11.34	337					
April	-2.37	-10.15	8.81	62	April	-5.55	-31.12	13.28	156					
May	-4.84	-27.17	11.55	77	May	-6.63	-42.99	10.05	154					
June	-3.29	-16.99	9.33	61	June	-5.43	-35.56	7.88	62					
July	-3.11	-18.62	6.26	25	July	-3.46	-19.51	8.17	67					
August	-3.41	-23.15	4.13	2	August	-3.61	-21.90	6.98	64					
September	-5.94	-34.07	13.45	140	September	-4.38	-22.71	12.33	37					
October	-4.39	-21.66	13.46	33	October	-6.11	-33.23	15.65	143					
November	-8.98	-57.85	13.99	186	Novembre	-6.88	-39.98	15.06	203					
December	-6.38	-34.96	16.08	334	December	-5.72	-30.81	14.95	210					

**Table 2.** Spring water. O-H isotope-ratio, d-excess (d-ex, ‰), temperature (T °C), Cl<sup>-</sup> and Na<sup>+</sup> content (mg/L) and Na/Cl molar ratio

Sample name	$\delta^{18}\text{O}$ (‰)	$\delta\text{D}$ (‰)	d-ex	Cl <sup>-</sup>	Na <sup>+</sup>	Na/Cl	T (°C)
<b>April, 2015</b>							
VS1-1	-6.85	-40.62	14.16	12.00	4.09	0.52	10.8
VS2-1	-6.77	-42.63	11.54	8.40	4.58	0.84	10.7
VS3-1	-6.94	-40.62	14.87	8.36	4.84	0.89	10.7
VS4-1	-6.44	-36.35	15.21	14.30	10.29	1.11	12.7
VS5-1	-7.03	-40.46	15.81	5.70	4.03	1.09	11.0
VS6-1	-5.89	-34.03	13.09	22.80	17.30	1.17	13.8
VS7-1	-5.73	-36.63	9.23	19.40	8.52	0.68	15.9
VS8-1	-6.56	-37.01	15.46	12.70	4.60	0.56	12.0
VS9-1	-6.42	-36.70	14.69	11.40	7.50	1.01	12.2
VS10-1	-6.57	-37.88	14.71	11.50	6.35	0.85	11.9
VS11-1	-6.09	-36.10	12.63	15.16	6.00	0.61	12.7
VS12-1	-6.40	-35.94	15.24	17.80	5.73	0.50	12.1
VS13-1	-6.00	-33.94	14.10	18.20	8.64	0.73	16.3
VS14-1	-5.94	-35.88	11.64	19.87	9.12	0.71	14.5
VS14-1	-5.94	-33.31	14.18	19.99	9.47	0.73	14.6
VS16-1	-6.29	-37.80	12.55	12.00	5.27	0.68	12.3
<b>October, 2015</b>							
VS1-2	-6.23	-36.96	12.92	10.64	5.44	0.79	12.5
VS2-2	-6.61	-38.77	14.07	8.77	5.12	0.90	10.9
VS3-2	-6.31	-37.18	13.28	10.98	5.82	0.82	12.6
VS4-2	-6.50	-34.90	17.08	12.14	7.91	1.00	13.8
VS5-2	-6.92	-41.59	13.78	5.40	5.13	1.46	12.6
VS6-2	-5.76	-35.15	10.96	19.17	15.76	1.27	16.2
VS7-2	-6.10	-35.35	13.48	18.92	11.29	0.92	16.2
VS8-2	-6.41	-37.11	14.19	9.69	5.82	0.92	13.2
VS9-2	-6.90	-37.98	17.23	10.66	6.89	0.99	11.6
VS10-2	-6.75	-37.68	16.31	10.09	6.24	0.95	11.2
VS11-2	-6.41	-35.14	16.18	12.92	8.06	0.96	11.8
VS12-2	-6.07	-35.31	13.21	13.52	7.42	0.84	11.5
VS13-2	-6.23	-34.63	15.17	14.20	10.17	1.10	15.7
VS14-2	-5.96	-35.18	12.54	14.53	8.59	0.91	14.7
VS15-2	-6.02	-34.45	13.72	14.54	8.64	0.91	14.8
VS16-2	-6.26	-35.60	14.46	12.81	6.60	0.79	11.4

**Table3.** Stream, wells and AMD. O-H isotope-ratio, d-excess (d-ex, ‰), temperature (T °C).

Sample name	$\delta^{18}\text{O}$ (‰)	$\delta\text{D}$ (‰)	d-ex	T (°C)
<b>Stream</b>				
April, 2015				
VT1-1	-5.43	-28.56	14.88	11.6
VT2-1	-4.5	-23.57	12.43	12.3
VT4-1	-4.6	-25.15	11.65	12.2
VT6-1	-5.61	-31.46	13.44	13.7
VT7-1	-5.54	-30.55	13.75	13.9
VT8-1	-5.98	-33.49	14.39	14.1
VT9-1	-5.83	-32.03	14.61	14.7
VT10-1	-5.85	-32.75	14.05	15.2
VT11-1	-5.39	-31.27	11.81	15.4
VT12-1	-5.82	-34.28	12.24	15.3
October, 2015				
VT1-2	-6.21	-35.37	14.31	8.9
VT2-2	-6.2	-35.43	14.17	8.3
VT3-2	-6.12	-35.53	13.43	10.9
VT4-2	-6.04	-35.57	12.75	10.6
VT5-2	-6.6	-36.88	15.94	12.3
VT6-2	-6.41	-37.35	13.93	11.4
VT7-2	-6.32	-36.51	14.05	12.4
VT8-2	-6.3	-36.8	13.6	10.4
VT9-2	-6.25	-35.88	14.12	14.7
VT10-2	-6.09	-35.41	13.31	15.6
VT11-2	-6.35	-35.69	15.08	
VT12-2	-6.09	-35.19	13.53	11.0
<b>Wells</b>				
April, 2015				
VPP1-1	-6.03	-33.58	14.69	16.0
VPP2-1	-5.59	-30.65	14.10	16.8
VPP3-1	-5.77	-31.98	14.15	16.3
VPP4-1	-6.04	-34.60	13.72	21.1
VPS1-1	-6.02	-35.40	12.72	15.2
VPS2-1	-6.08	-35.27	13.38	14.8
VPS3-1	-5.86	-33.55	13.32	16.4
VPS4-1	-6.04	-34.48	13.88	16.5
VPS5-1	-5.87	-33.41	13.56	16.8
October, 2015				
VPP1-2	-6.15	-34.96	14.21	15.7
VPP2-2	-5.80	-34.06	12.37	16.7
VPP3-2	-5.90	-34.65	12.58	16.5
VPP4-2	-6.21	-33.96	15.70	17.9
VPS1-2	-6.04	-35.01	13.31	20.1
VPS2-2	-6.31	-33.66	16.85	18.0

VPS3-2	-6.03	-34.23	14.02	16.7
VPS4-2	-6.14	-34.94	14.14	17.2
VPS5-2	-6.06	-33.89	14.58	20.7

**AMD**

May, 2015

VDA1-0	-6.24	-35.61	14.31	12.5
VDA3-0	-6.31	-36.39	14.09	13.8
VDP2-0	-5.71	-33.07	12.57	12.4
VDP3-0	-5.50	-31.35	12.65	13.1

April, 2015

VDA1-1	-6.24	-35.13	14.79	12.0
VDA2-1	-6.28	-35.73	14.50	11.2

October, 2015

VDA1-2	-6.15	-35.38	13.82	11.2
VDA2-2	-6.37	-35.94	15.02	14.1
VDA3-2	-6.19	-35.50	14.02	12.5
VDP3-2	-5.52	-31.32	12.84	13.1

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**Highlights**

The oxygen and hydrogen isotopic signature of rainwater traces groundwater recharge.

Acid mine drainage impacted waters show hydrogen isotopic fractionation.

O-H isotopes allow interconnections between groundwater pathways to be established.

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