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Geochemistry of the Adige river water from the Eastern Alps to the Adriatic Sea (Italy): evidences for distinct hydrological components and water-rock interactions --Manuscript Draft--

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Abstract:	<p>The Adige river flows from the Eastern Alps to the Adriatic Sea and the understanding of its fluvial dynamics can be improved by geochemical and O-H isotopic investigation. The most negative isotopic compositions are recorded close to the source ($\delta^{18}\text{O}$ between -14.1‰ and -13.8‰, δD between -100.3‰ and -97.0‰), and δD and $\delta^{18}\text{O}$ values generally increase downstream through the Upper Part (UP, the mountainous sector), stabilizing along the Lower Part (LP, the alluvial plain) of the river with $\delta^{18}\text{O}$ between -12.4‰ and -11.8‰, δD between -86.9‰ and -83.7‰. The isotopic variations along the stream path ($\delta^{18}\text{O}$-δD vs distance from the source) depict subparallel distributions for all the investigated periods, with less negative values recorded in winter. Total dissolved solids (TDS) concentration shows the lowest value (< 100 mg/l) at the river source, jumping to 310 mg/l at the Rio Ram inflow, then decreasing down to the Isarco river confluence; from here we observed an increase toward the river mouth, with different values in the distinct sampling periods. The lowest values (140-170 mg/l) were recorded during high discharge in spring, whereas higher TDS values (up to 250 mg/l) were recorded during winter low flow conditions. Extreme TDS values were observed in the estuarine samples (up to 450 mg/l), as result of mixing with sea water. The results allow for the identification of distinct water end-members: glacio-nival component(s) characterized by the most negative isotopic composition and extremely low TDS, a rainfall component characterized by intermediate isotopic and elemental composition and groundwater characterized by the less negative isotopic composition and comparatively higher TDS. An additional component is represented by sea-water, which is recorded at the lowest reach of the river during drought periods. These contributions variously mix along the stream path in the distinct hydrological periods, and the presented data are a snapshot of the current hydro-climatic conditions. Future investigations will evaluate possible hydrological variations related to meteo-climatic changes. Monitoring is fundamental for future water management to overcome the vanishing of a significant water end-member of the basin, i.e. the glacio-nival reservoir</p>	

	that is severely affected by the ongoing climatic changes.
Response to Reviewers:	<p>Our responses to the Reviewers' comments are in CAPITAL LETTERS.</p> <p>Reviewer #1: I think the Authors properly replied to my comments and that the submitted manuscript can be accepted in the present form.</p> <p>Reviewer #2: The revised manuscript is significantly improved following changes based on comments from all of the reviewers. In particular, the overall flow and the groundwork laid in the introduction make the objectives and methodology of the study much clearer, and it was a pleasure to read. My only hesitation in immediately recommending approval for publication is that it appears that the last page of comments in my review (#2) was not included in the revision. There are a few issues from these comments that I think still need to be addressed. First, please state whether water samples were filtered, and if so, how it was done. THIS DETAIL HAS BEEN INCLUDED</p> <p>This is especially important for trace elements. Second, how was HCO₃⁻ determined? There is no description of a dedicated sample collected for dissolved inorganic carbon or an alkalinity analysis. If DIC was calculated from alkalinity and pH, and HCO₃⁻ was assumed to be equal to either of these quantities, this needs to be stated. THIS DETAIL HAS BEEN INCLUDED</p> <p>Finally, the shaded areas of Fig. 7a are not explained anywhere. If these issues are addressed, I recommend publishing this manuscript and I don't need to review a revised version. A NEW SENTENCE HAS BEEN INCLUDED IN THE TEXT PROVIDING AN EXHAUSTIVE EXPLANATION OF FIG. 7.</p> <p>Reviewer #3: I thank the authors for considering the comments provided by the reviewers. The manuscript has improved significantly compared to the first version, especially in the introduction and the discussion part. Minor comments are reported in the attached pdf file. Furthermore, the manuscript would benefit from a careful proofreading and English should be checked by a native speaker. ALL THE LINGUISTIC IMPROVEMENTS SUGGESTED BY REVIEWER#3 HAVE BEEN INCLUDED IN THE NEW VERSION OF THE MANUSCRIPT. THE ADDITIONAL REFERENCE CARTURAN ET AL. (2015) REQUIRED BY THE REVIEWER HAS BEEN PROPERLY CITED.</p>
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Geochemistry of the Adige river water from the Eastern Alps to the Adriatic Sea (Italy): evidences for distinct hydrological components and water-rock interactions

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Abstract

The Adige river flows from the Eastern Alps to the Adriatic Sea and the understanding of its fluvial dynamics can be improved by geochemical and O-H isotopic investigation. The most negative isotopic compositions are recorded close to the source ($\delta^{18}\text{O}$ between -14.1‰ and -13.8‰, δD between -100.3‰ and -97.0‰), and δD and $\delta^{18}\text{O}$ values generally increase downstream through the Upper Part (UP, the mountainous sector), stabilizing along the Lower Part (LP, the alluvial plain) of the river with $\delta^{18}\text{O}$ between -12.4‰ and -11.8‰, δD between -86.9‰ and -83.7‰. The isotopic variations along the stream path ($\delta^{18}\text{O}$ - δD vs distance from the source) depict subparallel distributions for all the investigated periods, with less negative values recorded in winter. Total dissolved solids (TDS) concentration shows the lowest value (< 100 mg/l) at the river source, jumping to 310 mg/l at the Rio Ram inflow, then decreasing down to the Isarco river confluence; from here we observed an increase toward the river mouth, with different values in the distinct sampling periods. The lowest values (140-170 mg/l) were recorded during high discharge in spring, whereas higher TDS values (up to 250 mg/l) were recorded during winter low flow conditions. Extreme TDS values were observed in the estuarine samples (up to 450 mg/l), as result of mixing with sea water. The results allow identifying for the identification contribution of distinct water end-members: glacio-nival component(s) characterized by the most negative isotopic composition and extremely low TDS, a rainfall component characterized by intermediate isotopic and elemental composition and groundwater which is characterized by the less negative isotopic composition and comparatively higher TDS. An additional component is represented by sea-water, which is recorded at the lowest reach of the river during drought periods. These contributions variously mix along the stream path in the distinct hydrological periods, and the presented data are a snapshot of the current hydro-climatic conditions. Future investigations will evaluate possible hydrological variations related to meteo-climatic changes. Monitoring is fundamental for future water management to overcome the vanishing of a significant water end-member of the basin, i.e. the glacio-nival reservoir that is severely affected by the ongoing climatic changes.

Keywords: Adige river; water geochemistry; stable isotopes; hydrological components, water-rock interactions

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Introduction

Rivers have a key role in the water cycle as they return terrestrial precipitation back to the sea, ~~also~~ transporting the solutes produced by chemical weathering on the continents, as well as additional components potentially released by human activities. Their investigation is necessary for the understanding of the related ecosystems, which could be threatened by climatic changes and/or anthropogenic processes (Vörösmarty et al., 2013), and more in general are useful for a sustainable management of the water resources (Koundouri et al., 2016). In this framework, geochemical tracers are extremely useful to ~~complement~~ support hydrological studies, providing constraints ~~useful~~ for the understanding of the ongoing fluvial processes and to predict potential changes and future scenarios. Among the various tracers, hydrogen and oxygen isotopes in the water molecules are fractionated by temperature-related phase-transitions and provide clues on the origin of the river water that can be related to distinct meteoric contributions having different provenance, and/or occurring in distinct forms such as rainfall and (in alpine environments) snow/glacier melting (Chiogna et al., 2014; Penna et al., 2014; Engel et al., 2015; Fisher et al., 2015). Other tracers, such as the major dissolved components are intimately connected with the weathering processes of the outcropping lithologies, which in turn are influenced by climatic conditions that can promote the weathering efficiency.

For these reasons geochemical analyses of rivers can be considered as hydroarchives recording ongoing meteo-climatic processes. Systematic geochemical studies on creeks can provide tracer-based modelling that precisely evaluate the various water contributions, usually defined as end-members (e.g.: Chiogna et al., 2014; Penna et al., 2014; Engel et al., 2015), whereas studies of major rivers are more difficult to be parametrized, due to the difficulty of sampling systematically river lengths in the order of hundreds kilometers, and also because the contributing water end-members are multiple, often not sufficiently different from each other, and sometimes also variable in time. In spite of these limits, geochemical studies of major rivers have been widely taken into consideration (Gibbs 1970; Meybeck 1987; Gaillardet et al. 1999; Gaillardet 2014; Hartmann et al., 2014; Haldler et al., 2015) because they reflect processes at regional scale and their monitoring represents a snapshot of the existing conditions that, if compared with past and future investigation, allows for the prediction of evolutionary trends.

In this view, in northern Italy a recent geochemical investigation has been devoted to the Po river, which is the longest Italian river flowing from the northwestern Alps throughout the Padanian plain (Marchina et al., 2015; 2016), but not on the Adige river that is likewise important. The Adige is the second longest river and the third largest river basin in Italy, flowing for more than 400 km from the Eastern Alps to the Adriatic Sea, where its water budget (and the associated geochemical components) significantly influences the riparian and coastal ecosystems (Cozzi and Giani, 2011). Its hydrology is extremely complex due to an interplay between

1 natural (climatic) and anthropogenic factors (water withdrawal for energy production, irrigation and civil
2 uses) and understanding of the related fluvial processes is fundamental in order to face the increasing
3 demand of water resources.
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5 A recent review on the hydrological and chemical stressors in the Adige catchment was obtained integrating
6 local studies at sub-basin scale, highlighting that it is extremely important to unravel the distinct components
7 that contributes to the total water budget, as well as to identify the related water quality (Chiogna et al.,
8 2016). The same review emphasizes the lack of an integrated –systematic– hydrological characterization at a
9 basin scale, which would certainly improve the understanding of the river system and the predictive
10 capabilities of its hydrological behavior.
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15 The current contribution intends to fill this gap of knowledge and is inspired to recent studies of other
16 riverine systems (Mohammed et al., 2014; Campodonico et al., 2015; Harker et al., 2015). The goal can be
17 achieved combining classical hydrological approaches with a geochemical investigation at a basin scale that
18 is a powerful tool to identify the water provenance and origin, as well as to highlight local variations induced
19 by anthropogenic activities. For these reasons we present a comprehensive geochemical dataset (also
20 including oxygen and hydrogen isotopic data) of the Adige river water, systematically collected from the
21 mountainous upper part of the catchment down to the river mouth, in distinct seasons of the years 2013-
22 2015. The geochemical and hydrological data are also compared and discussed with literature data in order to
23 identify possible spatio-temporal variations occurred in the Adige river system in the last decennia, thus
24 providing proxies to evaluate ongoing and future (short- and long-term) changes in the water resource at a
25 basin scale. Specific objectives are: a) to determine the relation between oxygen and hydrogen isotopic
26 compositions for the Adige river waters and identify the main end-members to streamflow, define an updated
27 oxygen and hydrogen isotopic relation for the Adige water, thus obtaining a water meteoric isotopic
28 signature valid for the northeastern part of Italy, also recognizing the main water end members that occur
29 on it; b) to define assess the main hydrochemical facies of the Adige water defining backgrounds having
30 geogenic origin and anomalies related to anthropogenic activities; c) to define assess geochemical fluxes
31 transferred from the eastern Alps to the Adriatic sea; d) to compare the presented geochemical data set on the
32 Adige river with the analogous data-set obtained for river Po (Marchina et al., 2015; 2016) in order to
33 provide conclusions valid at regional scale for the whole northern part of the Italian Peninsula.
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51 **General outlines on the Adige river and its catchment**

52 *Geography and hydrology*

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54 The Adige riverine system (Fig. 1) drains the Southern and Eastern Alps starting from the Italian-Swiss-
55 Austrian boundary and end into the Adriatic Sea, northward of the Po river delta (Marchina et al., 2015;
56 2016). ~~In fact,~~ The river rises at 1,586 m a.s.l., near Lake Resia, and after a course of 409 km reaches the sea
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1 near the village of Rosolina. On the basis of the morphological features, the river catchment has been
2 subdivided in an Upper Part (UP), corresponding to the mountainous sector, and a Lower Part (LP)
3 corresponding to the related alluvial plain. Its stream path crosses, at increasing distance from the source,
4 several important urban centers such as Bolzano (100 km, 237 m a.s.l.), Trento (150 Km, 193 m a.s.l.) and
5 Verona (250 km, 66 m a.s.l.). The Adige river catchment extends over an area of ca. 12.100 km² and is
6 commonly subdivided into seven major sub-basins in relation to its main tributaries: Adige–Passirio, 3,174
7 km², Isarco–Talvera-Rienza 4,210 km², Noce 1,386 km², Avisio 934 km², Adige-Fersina-Leno 1,007 km²
8 and Adige–Chiampo 1,464 km². Starting from the source, the Adige river flows generally E-W for ca. 70 km
9 in the Adige-Passirio sub-basin, and receives contributions from small mountainous sub-catchments
10 characterized by glaciated areas (Penna et al., 2013). After the confluence with the Passirio river, draining
11 the northernmost part of the basin, the Adige main stream turn toward N-S and after 30 km reaches the town
12 of Bolzano where it is characterized by a mean annual discharge of 50 m³/s. Few kilometers southward, the
13 Adige stream path meets the confluence with the Isarco river, which is one of the main tributaries (mean
14 annual discharge of 80 m³/s) draining about half (the whole N-E part) of the catchment (Isarco-Talvera-
15 Rienza sub-basins) characterized by a mean altitude of 1,750 m a.s.l. In the vicinity of Trento, Adige meets
16 the confluence with the Noce river (mean annual discharge of 35 m³/s), which drains an area characterized
17 by significant mean elevation (1,625 m a.s.l.) and by the presence of some important glaciers (Chiogna et al.,
18 2014); few kilometers southward the mainstream receives the Avisio and Fersina rivers (mean annual
19 discharge of 23.5 and 2.0 m³/s, respectively), both draining the central-eastern parts of the basin, having
20 mean altitude of 1660 and 1099 m a.s.l., respectively. Southward at ca. 220 km from the source, the Adige
21 stream path turns to E direction facing the alluvial plain deposits. Additional tributaries drain the Lessini
22 Mountains (Adige-Chiampo sub-basin) and reach the confluence with Adige river at ca. 280 km from the
23 source; afterwards the river does not receive any other superficial water income, and the riverbed confined
24 within continuous embankments on both sides progressively rises higher than the surrounding alluvial
25 plain. Therefore, most of the basin is located in Alpine morpho-climatic conditions (94.6 % of the basin area
26 is mountainous) that mainly contribute to the Adige river budget. In particular, the basin is characterized by
27 the presence of 185 glaciers covering about 212 km² that represent an important water supply for the Adige
28 river discharge, especially during warmer periods (Milner et al., 2009). Accordingly, the mean annual
29 discharge measured at the Trento S. Lorenzo station (185 m³/s), i.e. at the closure of mountainous part of the
30 catchment, is comparable with that observed at the lowest reach station of Boara Pisani (202 m³/s) located 60
31 km upstream from the estuarine mouth (Adige River Basin Authority, Autorità di Bacino del fiume Adige,
32 2008).

33 *Meteo-climatic characteristics of the catchment*

34 The study area is thoroughly monitored by meteorological stations which record time series of precipitation
35 and temperature and the data are available at the following websites: <http://www.meteotrentino.it>;
36 <http://www.provincia.bz.it/meteo/home.as>; <http://www.arpa.veneto.it>. The general climatic conditions of the
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1 Adige river catchment are characterized by continental climate, with a precipitation regime that is influenced
2 by western Atlantic airflows and southern circulation patterns (Norbiato et al., 2009). It mainly results in
3 relatively dry winters with maximum of precipitations recorded during springs and falls. A significant
4 amount of the water budget is accumulated at higher elevations during winter in the form of snow, which
5 undergoes melting starting from spring time. This results in a “nival” hydrological regime of the catchment,
6 which is characterized by general water availability in the warm seasons and low discharge in winter. The
7 mean annual precipitation in the distinct sub-basins is highly variable depending on catchments elevation,
8 valleys orientation and distance from orographic barriers: it varies from a minimum of 400-500 mm/y in Val
9 Venosta (UP) to a maximum of 1600 mm/y at higher elevations and in the valleys opened toward the
10 floodplain (LP). In general, all the stations record a notable minimum of precipitations during winter due to
11 the dominance of the Russian-Siberian anticyclone over the entire alpine region (data from
12 <http://www.bacino-adige.it>). Consequently, streamflow shows a typical Alpine regime with two peaks: one
13 in spring due to snow melt and one in autumn due to cyclonic storms, which are the main causes of flooding
14 events.
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25 *Water use*

26 The Adige river water (and that of its alpine tributaries) is intensively conveyed into reservoirs and used for
27 hydropower production, with intermittent water uptake and downflow release. Withdrawals are widespread
28 in the mountainous part of the basin, providing water to 34 large hydropower plants that produce a total
29 effective power of 650 MW (Chiogna et al., 2016 and references therein). Smaller withdrawals are devoted
30 to a variety of agricultural, civil and industrial water uses. Licensed water uptakes for agricultural uses are
31 remarkable (up to 50 m³/s) especially in the provinces of Bolzano in the upper part, and of Verona in the
32 lower part of the catchment. Supplies for drinking use are also widespread within the basin but usually lower
33 than 20 m³/s (Provincia Autonoma di Trento, 2006; Provincia Autonoma di Bolzano, 2010; Chiogna et al.,
34 2016).
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43 *Geology and lithologies*

44 Geological information is also important because water chemistry is strictly related to the outcropping
45 lithologies that have distinct mineralogical composition, peculiar weathering rates and distinct release of
46 chemical components in the interacting waters. The Adige river drains various lithologies along the
47 mountainous path (Fig. 1): from the rise to Merano (70 km, Venosta Valley) it crosses the quartz-feldspathic
48 metamorphic rocks of the Austroalpine domain, downflow to Ora (110 km from the source) the rhyolitic
49 rocks of the Atesian volcanic complex, and then the carbonate units of the Southalpine domain (Lagarina
50 Valley) that outcrop down to the town of Affi (220 km from the source) where the river is embedded in the
51 alluvial plain deposits (Möller et al., 2003).
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60 **Sampling and analytical methods**

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In this study 65 samples of Adige river water have been collected in distinct seasonal periods that include variable hydrological conditions representative of the biennia 2013-2015. The first two sampling campaigns (15 samples each) have been conducted in August 2013 and May 2014 from the site of Andriano downstream to the river mouth at Rosolina Mare. In March and May 2015 the Adige river has been sampled from the outlet of the lake of S. Valentino alla Muta to the river mouth in order to investigate the whole stream path (18 and 17 samples, respectively; Table 1 and Fig. 1). The summer hydrological regime (August 2013) ~~recorded~~ **was characterized by** relatively high flow in the UP (ca. 200 m³/s after the Isarco confluence) and low discharge in the LP (average of ca. 175 m³/s). The winter hydrological condition (March 2015) showed the lowest discharge both in the UP (55 m³/s after the Isarco confluence) and in the LP, the latter being characterized by a peculiar downstream increase (from 95 to 172 m³/s). The spring hydrological conditions (May 2014 and 2015) were characterized by intermediate to high flow both in the UP (from 190 to 300 m³/s after the Isarco confluence) and in the LP (up to 410 m³/s in May 2014). The rationale behind the selection of sampling locations was to monitor the water geochemistry along the river profile, before/after the confluence of important tributaries, settlements, and/or zones of important productive activities, but logistical criteria (i.e., easy site accessibility) were also taken into consideration. Each sampling location was geo-referenced by a portable global positioning system (GPS), to locate the points and to set up future field surveys. Surface water was collected at 40–50-cm depth using a bucket, possibly far from the shore (using piers or sampling above bridges). Electrical conductivity (EC), pH, and temperature were directly measured in the field using a handheld probe (HI9813-5, ~~by~~ Hanna Instruments; Table 1), then water samples were stored in 100-mL bottles. Laboratory analyses were carried out **on filtered water samples (by 0.45- μ m Minisart® NML syringe cellulose acetate filters)** at the Department of Physics and Earth Sciences of the University of Ferrara. Hydrogen and oxygen isotope ratios were determined **injecting water samples into a** ~~using the~~ CRDS Los Gatos LWIA 24-d isotopic analyzer and reported in Table 2. The isotopic ratios of ²H/¹H and ¹⁸O/¹⁶O are expressed as δ notation [$\delta=(R_{\text{sample}}/R_{\text{standard}}-1)\times 1000$] with respect to the Vienna Standard Mean Ocean Water (V-SMOW) international standard. **The isotopic composition of the samples values have been** ~~was~~ **obtained through by six analyses-injections; discarding the first two injections were discarded to minimize** ~~potentially affected by~~ **memory effects (Penna et al. 2012), while the isotopic values of the last four injections were and averaged** ~~ing the remaining four~~. Four bracketing standards that cover the whole range of isotopic values of the Adige river water were run throughout the analytical sessions. These standards, obtained from the Los Gatos Research Company, were calibrated with international standards such as V-SMOW and SLAP (Standard Light Antarctic Precipitation). **The typical instrumental** ~~Analytical~~ **precision and accuracy were** ~~was~~ **better than 0.3 and 1.0 ‰ for $\delta^{18}\text{O}$ and δD , respectively.** Cations and trace elements have been measured by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo-Scientific X Series instrument on samples previously diluted 1:10 by deionized Milli-Q water (resistivity of ca. 18.2 M Ω ×cm), also introducing known amount of Re and Rh as internal standard; in each analytical session, the analysis of samples was verified with that of the reference materials EU-L-1 and ES-L1 provided by SCP-Science (www.scpscience.com). The major anions were determined by ion chromatography using a

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Dionex ICS-1000 calibrated using solutions obtained by different dilutions of the Dionex “7-ion standard.” Accuracy and precision, based on the repeated analyses of samples and standards, were better than 10 % for all the considered parameters. Alkalinity was determined by titration using the HI-3811 alkalinity test kit (Hanna Instruments), and for the observed pH range reflects the HCO_3^- content (Ryan, 2014). The mentioned analyses are reported in Table 3. The coherence of chemical data has been verified checking the ionic balance, as the sum of cations (expressed in meq/L) approaches that of anions with relative error $[(\Sigma_{\text{cations}} - \Sigma_{\text{anions}})/(\Sigma_{\text{cations}} + \Sigma_{\text{anions}})] \times 100$, which is generally minor than 5%.

14 Results

15 *pH, temperature, and conductivity of Adige river waters*

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Physico-chemical parameters measured in situ such as pH, temperature, and conductivity of Adige river water have been reported in Table 1. In order to appreciate physico-chemical changes along the flow path, the sample population has been geographically subdivided in two subsets corresponding to increasing distance from the river source, defined as UP (upper part), LP (lower part), and the related variability has been also evaluated in order to delineate spatial-temporal changes. pH does not show any systematic variation along the stream path in the distinct periods and displayed higher values during the drought season (August 2013, March 2015); it showed the highest values at Spondigna (UP) and Zevio (LP) where it reached the maximum value of 8.6 in August 2013. The lowest pH value (7.7) was recorded at the end of UP (Andriano) in May 2014. On the other hand, the water temperature showed increasing values from the source to the mouth with the lowest variation recorded in the colder (10.0-16.0°C, March 2015) and the highest in the warmer (13.9-21.5°C August 2013) sampling periods. Electrical conductivity showed the highest variation in the UP with a sudden increase (up to 300 $\mu\text{S}/\text{cm}$) just after the confluence with Rio Ram (Spondigna) followed by a variable decrease down to the confluence with the Isarco river, where the lowest EC value (140 $\mu\text{S}/\text{cm}$, Vadena Nuova) was recorded in May 2015. Downstream this confluence, EC generally increased down to the river mouth indicating progressively higher amounts of dissolved components moving from the UP, to the LP catchment areas. The average EC value was lower in May 2015 (190 $\mu\text{S}/\text{cm}$) with respect to that recorded in other sampling periods (250-260 $\mu\text{S}/\text{cm}$), whereas slightly higher EC average values was recorded in March 2015 (300 $\mu\text{S}/\text{cm}$). This means that, although it is not possible to delineate a clear correlation between EC and discharge, the highest EC values occur during the winter low discharge, whereas lower EC values occur during higher flow regime occurring in spring, plausibly in relation to dilution effects. Higher electrical conductivity has been observed in the estuarine samples (L10), with values of 500 and 690 $\mu\text{S}/\text{cm}$ recorded in March 2015 and August 2013, corresponding to the lowest discharge periods. These anomalously high EC values obviously reflect interaction with sea water.

It is important to note that an abrupt change of the physico-chemical parameters of the Adige river is recorded after the confluence with Isarco river. This is in accordance with the values measured in the Isarco

1 waters in May 2015, which demonstrated the capability of this tributary to deeply modify the Adige river
2 water values by mixing, in agreement with the relative water discharge (Data from Provincia Autonoma di
3 Bolzano), as already described by Leibundgut et al., 2009.

4 5 *Isotopic composition of Adige river waters*

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8 The variation of δD and $\delta^{18}O$ isotopic ratios of Adige river waters in the distinct sampling periods is reported
9 in Table 2 and Fig. 2a, the relation between the water isotopic composition and the sampling elevation (m
10 a.s.l.) is highlighted in Fig. 2b, and the isotopic variation along the stream path is reported in Fig. 3. In Fig.
11 2a, it can be observed that the recorded isotopic compositions of the Adige river waters mainly lie between
12 the Global Meteoric Water Line (GMWL; Craig, 1961) and the Local Meteoric Water Line (LMWL) defined
13 for Northern Italy by Longinelli and Selmo (2003). The same diagram reports for comparison the isotopic
14 composition of rainfalls and melt waters from snow and glaciers of an alpine sub-basin located near the river
15 source (Penna et al., 2013, 2014), which suggests that the Adige river waters reflect –in addition to rainfall–
16 significant contribution from snow and glacier melting in the distinct seasons. From Fig. 2b, where δD is
17 plotted vs the sampling elevation it ~~is evident~~ can be observed that the altitude effect is evident in all the
18 investigated hydrological periods. The most negative isotopic compositions are recorded in the first 20 km
19 from the source where $\delta^{18}O$ ranges between -14.1‰ and -13.8‰, δD between -100.3‰ and -97.0‰. In this
20 sector of the river, the discharge is still low and therefore the incoming tributaries influence the isotopic
21 composition of the main stream, as observed for Saldur which induces a notable shift toward more negative
22 values in the main stream at its confluence (Fig. 3). δD and $\delta^{18}O$ values generally increase downstream from
23 the source through the UP, whereas they tend to stabilize along the LP down to river mouth. The isotopic
24 trends along the stream path are subparallel for all the investigated periods, with distinctly less negative
25 values observed in March 2015 which shows, except for the first 20 km after the source, a mean shift of
26 +0.9‰ $\delta^{18}O$ (SD 0.2‰) and +7.3‰ δD (SD 3.5‰) with respect to the averaged data of the other seasons. On
27 the whole, isotopic composition doesn't not show dependence with respect to the relative water discharge
28 and, with the exception of March 2015, is comparable in the distinct investigated periods, especially for LP.
29 In UP, slight but consistent differences are observed in the average isotopic compositions, with August 2013
30 showing the most negative value, possibly due to an higher glacier melt contribution, as commonly observed
31 in alpine catchments located in the Eastern Alps (Penna et al., 2014; Engel et al., 2015). Slight differences
32 exist between the isotopic composition recorded in May 2014 and May 2015, the latter being generally
33 characterized by more negative values; ~~this is possibly due to the involvement of snow/glacier melting in~~
34 ~~response of the anomalously high temperature occurred in spring 2015.~~ **this is possibly due to higher spring temperatures in 2015 with**
35 **respect to 2014 (<http://www.provincia.bz.it/meteo/climareport.asp>) leading to an earlier snowmelt period,**
36 **especially in high-elevation sub-catchments.** On the other hand, samples collected
37 during the drought of March 2015 systematically display a difference -with isotopic values distinctively less
38 negative- which becomes progressively more marked in the LP. In this season, we observed the least
39 negative values ($\delta^{18}O$ -10.8‰, δD -73.0‰) at Brentino Belluno (205 km from the source), in
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correspondence of a meandering sector of the river where channel sinuosity plausibly favor hyporheic exchanges (Buss et al., 2009).

It is interesting to note the different isotopic gradients along the river profile that depend on the specific orographic features of the basin (UP vs LP) and on the seasonal variations. The strongest isotopic variation characterizes UP and is more marked in drought seasons, resulting in a notable isotopic gradient in August 2013 ($\delta^{18}\text{O}$ 0.02‰/km, δD 0.18‰/km) and March 2015 ($\delta^{18}\text{O}$ 0.02‰/km, δD 0.13‰/km). On the other hand, the Adige river waters in LP are characterized by a very weak isotopic variation for all the investigated sampling periods (average of $\delta^{18}\text{O}$ 0.001‰/km and δD 0.02‰/km). These gradients are very similar to that observed for the LP of the Po river (Marchina et al., 2015), possibly reflecting common hydrological conditions for rivers flowing in the Padanian Plain.

In Table 2, the deuterium excess calculated as: $d\text{-exc}=\delta\text{D}-8\times\delta^{18}\text{O}$ on the basis of the global meteoric water line as defined by Dansgaard (1964) is also reported. Average d-exc for each sampling season has been calculated for UP where more of the river recharge is concentrated: it varies between 10.1 (March 2015) and 13.1 (May 2015). In general it can be observed that the d-exc average values recorded in warm periods (spring and summer) are higher than those recorded in the conditions recorded in March.

Dissolved components

The total dissolved solid (TDS), calculated as a sum of the major chemical species (Table 3), shows marked variation along the stream path. The lowest value (< 100 mg/l) was measured at the outlet of the Lake of San Valentino alla Muta (source) in May 2015. A sharp TDS increase was recorded after few kilometers as a result of the confluence of Rio Ram, which is responsible for TDS up to 310 mg/l in the site of Spondigna; from here the TDS decreased downstream for 70-80 km to the Isarco river confluence (Bolzano) and subsequently generally increased to the river mouth (Rosolina Mare), with average values significantly different in the distinct sampling periods. The lowest values (140-170 mg/l) were recorded during high discharge in spring (May 2014 and 2015), whereas higher TDS were recorded during low flow conditions in August 2013 (190 mg/l) and in March 2015 (250 mg/l). Higher TDS values were observed during low discharge periods in the estuarine samples (up to 450 mg/l), which result from mixing with sea water during momentary high-tide influence.

The TDS of Adige is also plotted against the $[\text{Na}^+(\text{Na}^++\text{Ca}^{2+})]$ in the Gibbs diagram (Fig. 4a) which is widely used to describe the composition of river waters, and compared with Po river waters (the longest Italian river; Marchina et al., 2015). It can be observed that most compositions cluster in the central part of the diagram, as also observed for Po river waters. This chemical fingerprint appears predominant in most riverine systems in northern Italy (Donnini et al., 2016) and worldwide, irrespective to significant differences in the lithologies outcropping in their catchments, due to the preferential weathering of carbonate respect to the silicate rocks (Gibbs 1970). Coherently, analogies between the Adige and the Po waters are also envisaged in the Piper diagram, which displays a common Ca-HCO_3 hydrochemical facies (Fig. 4b).

1 Significant differences between the waters of these two important rivers are observed only in the terminal
2 part, characterized by the appearance of Na-Cl hydrochemical facies, where Po river waters show a more
3 marked (and widespread) salinization, in contrast to those of Adige that are affected by mixing with sea
4 water only near the mouth (Rosolina Mare).
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7 More detailed insights on the Adige river water evolution can be obtained investigating the variation along
8 the streamflow of single parameters in the distinct seasons. For example, in Fig. 5 it is reported the variation
9 of Na⁺ and Ca²⁺: very low concentrations have been measured at the outlet of the Lake of San Valentino alla
10 Muta in May 2015, but marked variations suddenly appear at the confluence of Rio Ram which, having a
11 notable discharge and a peculiar chemical composition (it drains Triassic dolomitic rocks), deeply modifies
12 the geochemical budget of the Adige river. The following tributaries are represented by creeks draining
13 resistant metamorphic rocks that are scarcely weatherable thus providing water characterized by low TDS
14 and, in particular, extremely low calcium content. This “dilution” trend is maintained down to the confluence
15 of Isarco river, from which we observed a reversal of the Ca²⁺ trend that starts to increase downstream as a
16 result of contribution from water that interacted with sedimentary lithologies (see geology in Fig. 1). As
17 concerns seasonal variations, higher concentrations have been observed in the low discharge periods of
18 August 2013 and March 2015 which also show the more scattered distribution, probably in relation to local
19 effects. In particular, remarkable concentrations of both calcium and sodium (up to 50 and 9.5 mg/l,
20 respectively) are recorded between 200 and 250 km from the source in the lowest flow sampling campaign
21 (March 2015). This part of Adige corresponds to a meandering sector of the river located at the end of the
22 mountainous part of the catchment. In our view, as already highlighted by isotopic analyses, this reflects an
23 interaction with groundwater of the connected phreatic aquifer that contributes to the river flow, especially
24 during low discharge hydrological periods. Trace element concentrations can be even more useful to
25 highlight river contributions and dynamics. For example, the Rb and Sr covariation reported in Fig. 6
26 highlights that samples collected during the drought of March 2015 have different composition
27 (comparatively enriched in Sr) with respect to those of the other seasons thus corroborating a significantly
28 higher groundwater contribution in the river flow during this period. Insights can be raised also by the Rb
29 and Li covariation showing that samples collected during the drought of March 2015 ($R^2 > 0.75$) have
30 different composition (comparatively enriched in Li) respect to those of May of the years 2014 and 2015 (R^2
31 > 0.85). This suggests that in these hydrological periods, although variable, trace element contents reflect a
32 geogenic signature. On the other hand, samples collected in August 2013 show anomalous Li distribution,
33 which is uncorrelated with Rb (R^2 ca. 0.1), and strongly correlated ($R^2 = 0.87$) with B (an element that is
34 often below the detection limit in other periods), suggesting possible contamination. Further investigation
35 will be necessary to verify the possible recurrence and origin of these anomalies.
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58 Discussion

59 *Influence of catchment elevation and nature of meteoric components*

1 At any point along a river reach water is derived from precipitation falling within upstream catchment
2 sectors, and therefore river water isotopic composition is related to that of precipitation (Peng et al., 2015),
3 which in turn changes seasonally, depends on elevation, and is also event specific (Chiogna et al., 2014). The
4 seasonal isotopic variability of precipitation is attenuated in rivers (and springs) due to the delayed signal of
5 snow (Penna et al., 2014; Carturan et al., 2015; Engel et al., 2015) and also as result of storage/mixing
6 favored by groundwater and lakes (Marchina et al., 2015). These inferences on the oscillation of river
7 isotopic signature with respect to the input meteoric signal have been conceptualized by catchment
8 functioning in small mountain creeks (e.g. Chiogna et al., 2014) and confirmed by systematic observation of
9 major rivers world-wide (Haldler et al., 2015).

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16 In this framework, the hydrogen and oxygen isotopic composition of the Adige river water shows a
17 systematic variation in all the investigated periods, characterized by a strong enrichment in heavy isotopes
18 (^{18}O and ^2H) from the source to ca. 130 km downstream (UP), followed by a very slight increase of $\delta^{18}\text{O}$ and
19 δD values all along the LP down to the river mouth. This general variation mainly reflects the
20 morphoclimatic features of the basin which can be subdivided in a northern mountainous UP characterized
21 by high average elevations (with steep slopes) and a by a southern LP which varies from the foothill to the
22 floodplain with limited altitude/slope gradients (Fig. 1c). The comparison with data provided by Fuganti et
23 al. (2005) highlights that the southern UP (stations of Zambana Nuova and Mattarello) maintained very
24 similar water isotopic values, as well as and the observed average LP composition ($\delta^{18}\text{O} = -12.0\text{‰}$) is very
25 similar to that recorded at the hydrometric station of Boara Pisani (60 km upstream from the mouth) by
26 Zuppi and Bortolami (1982). The systematic isotopic characterization along the river stream in distinct
27 seasons allows recognizing for the identification of the spatio-temporal contribution of distinct water end-
28 members to the Adige river flow. The river water budget is strongly influenced by snow (and glacier)
29 melting in late spring and summer, which confers relatively light isotopic composition, whereas a trend
30 toward less negative compositions is observed in March soon downstream the river source. This trend
31 observed during the low discharge conditions of March is attributed to a greater contribution of rainfall
32 components which are conveyed to the river by surface runoff and (especially in LP) by groundwater of
33 unconfined aquifers, which are typically characterized by relatively heavy isotopic composition (Zuppi and
34 Bortolami, 1982; Fuganti et al., 2005). Coherently, the groundwater outflows and its contribution to the river
35 is magnified during the drought season and locally marked by anomalies (less negative isotopic values) in
36 the $\delta^{18}\text{O}$ -distance from the source diagram of Fig. 3. This allows to identifying suitable sectors of the river
37 for future “hydrograph separation” studies (Klaus and McDonnell, 2013) useful to distinguish the
38 glacier/snow melt and groundwater contributions to the streamflow.

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55 The mean UP gradient (0.2‰ $\delta^{18}\text{O}$ and 1.5‰ δD per 10 km) can be referred to altitude variation of the
56 meteoric recharge along the river course, as the water budget along the profile progressively integrates
57 meteoric contributions related to lower altitudes. In fact, according to our data the altitude effect on the
58 whole Adige catchment is in the order of -2.0 for δD and -0.3 for $\delta^{18}\text{O}$ per 100m rise of elevation and the

1 same gradients are obtained for the UP. These values are similar ~~with respect~~ to those observed by Penna et
2 al. (2014) in the more elevated mountainous sub-basins of the Adige UP, where -1.6‰ for δD and -0.23‰
3 for $\delta^{18}O$ per 100 m rise of elevation have been recorded in the years 2012 and 2013, but lower than that
4 observed for the Po river catchment ($\delta^{18}O$ ca. -0.5 per 100 m rise; Marchina et al., 2015). The observed
5 isotopic variation can be related to the elevation of precipitation and the application of equation 5 provided
6 by Engel et al. (2015) reveals that $\delta^{18}O$ values between 12 and 12.5 ‰ (typical of the UP) conform to a
7 catchment elevation of ca. 1800 m a.s.l., which is slightly higher than the average topographic elevation of
8 the Adige basin (1675 m a.s.l., Donnini et al., 2016).

13 Taking into consideration the strict relation between the isotopic composition of river water and that of
14 precipitation within the relative catchment, the presented δD - $\delta^{18}O$ data on the whole provide the following
15 River Water Line (RWL):

$$16 \delta D = 8.1\delta^{18}O + 12.3 \quad (n = 65, R^2 = 0.95) \quad (1)$$

22 that is similar to the local meteoric water line (LMWL) defined for a mountainous sub-catchment belonging
23 to UP ($\delta D = 8.1\delta^{18}O + 10.3$; Penna et al., 2014).

27 Note that the difference between LMWL and RWL may reflect the contribution of snow/ice melting which
28 characterizes the river water budget; the involvement of glacier melting is effective as shown by the d-exc
29 values that, during the warm periods, conform to those measured in rivulets outflowing from alpine glaciers
30 located in the Adige UP (d-exc up to 13; Penna et al., 2014). The RWL therefore appears more sensitive than
31 the LMWL to monitor ongoing climatic changes and, according to recent studies, glacier melting should
32 involve significant isotopic fractionation, in turn resulting in distinct regression lines and d-exc (Penna et al.,
33 2014; Engel et al., 2015; Zhou et al. 2014). Therefore, the presented isotopic values, integrated with those
34 existent in the literature (Chiogna et al., 2014; Penna et al., 2014) for the highest part of the basin, could be
35 useful to provide a snapshot of the current climatic condition in the eastern Alps. The same data, if merged
36 with those provided for the Po river basin could be useful to enlarge the survey, providing a snapshot valid
37 for the whole northern Italy. In this view, we merged the isotopic data presented in this paper with those
38 provided by Marchina et al. (2015) and Donnini et al. (2016), obtaining the following RWL regression:

$$39 \delta D = 7.9 \delta^{18}O + 9.5 \quad (n = 156, R^2 = 0.96) \quad (2)$$

45 that can therefore reflect the meteo-climatic conditions valid at a regional scale for Northern Italy in the
46 years 2011-2015.

47 *Origin of the dissolved components*

51 ~~An understanding~~ **The comprehension** of the processes controlling the water chemistry of a river is useful to
52 define geochemical cycles within a given catchment (Mohammed et al., 2014; Campodonico et al., 2015;

1 Harker et al., 2015). Although natural studies of riverine chemistry at the global scale have been widely
2 discussed (Gibbs 1970; Meybeck 1987; Gaillardet et al. 1999; Gaillardet 2014; Viers et al. 2014), specific
3 regional researches performed on the Adige river catchment are incomplete (i.e. considering only few
4 parameters) and never available for the whole stream path (Chiogna et al., 2016).
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7 In theory, the amount of the dissolved species is related to the nature of lithologies outcropping in the
8 catchment and the weathering processes typically occurring in the region (Voss et al. 2014 and references
9 therein), but anthropogenic contribution related to human activities cannot a priori be neglected. Taking into
10 consideration the chemical analyses of the major cations and anions (Table 3), water composition is
11 invariably dominated by Ca-HCO₃ hydrochemical facies with the exception of the estuarine samples
12 collected during drought season, which are affected by sea water interaction and characterized a Na-Cl
13 hydrochemical facies. It is interesting to note that the predominant Ca-HCO₃ hydrochemical facies persisted
14 in the river water at least for the last 40 years (Fossato, 1971; Fuganti et al., 2005) and that the unique
15 parameter that significantly increased is the nitrate, plausibly related to anthropogenic pollution, similarly to
16 what observed in the Po river water where a drastic increase of nitrate has been related to agricultural and
17 zootechnical activities (Marchina et al., 2016). Additional anthropogenic trace element input could be
18 represented by the occasional observation (August 2013) of anomalous Li and B contents, often referred as
19 proxies of pollution related to human activities (Kszos and Steward, 2003). Further, anthropogenic anomalies
20 affecting the Adige river water composition have been recorded by Möller et al. (2003) ~~that analyzing trace~~
21 ~~elements~~ that emphasized high gadolinium concentration with respect to other Rare Earth Elements (REE).
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33 The spatio-temporal distribution of the chemical species is regulated by the hydrological regime, with
34 general increase in concentration during the low discharge periods. This phenomenon, also observed in the
35 past (Fossato, 1971), cannot only be related to dilution/concentration processes, but necessarily requires the
36 involvement of groundwater contributions (Fig. 7), which variously mix within the river in specific sites
37 mainly located in the hinge zone between UP and LP. UP waters (identified by fields in Fig. 7a) are
38 generally characterized by TDS decreasing from the Rio Ram (draining sedimentary rocks) confluence
39 downstream to the LP, resulting from a subsequent income of water draining “unweatherable” metamorphic
40 rocks, which induces a dilution effect. TDS progressively increase in LP waters due to the presence of more
41 weatherable lithologies and to the contribution of groundwater, which become significant at 200-300 km
42 from the source during the drought period of March 2015 (Fig 7b). In particular, hyporheic exchange seems
43 to be very effective in a meandering sector of the river, in accordance with numerical flow models
44 suggesting that surface- groundwater interaction is strongly tied to river morphology, and that any
45 irregularity in an otherwise straight river induces localized hyporheic exchange (Buss et al., 2009). In fact,
46 in this sector of the river we observed a sudden increase of Ca²⁺ (and more in general TDS) which is coupled
47 with marked trace element variations (low Rb/Sr) and an isotopic shift toward less negative compositions.
48 This trend is induced by rainwater infiltrated in the foothill alluvial fans constituted of coarse to medium
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1 grained (mainly carbonatic) high-permeability sediments, which represent the phreatic reservoirs of the area
2 (Castagna et al., 2015).
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6 **Conclusions**

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9 The Adige river waters investigated along the whole stream path in distinct seasonal periods give insights on
10 the current hydrological regime and on natural and anthropogenic components from local to basin scale. The
11 spatio-temporal distribution of some geochemical tracers help identify the relative contribution of distinct
12 water end-members: a glacio-nival component characterized by the most negative isotopic composition (δD
13 down to -120 ‰, Penna et al., 2014) and extremely low TDS, a rainfall component characterized by
14 intermediate isotopic and elemental composition and groundwater from phreatic aquifers which is
15 characterized by the less negative isotopic composition (δD up to -59 ‰, Fuganti et al., 2005) and
16 comparatively higher TDS mainly represented by elements released by carbonate-bearing lithologies
17 (relatively high Ca and Sr). An additional component is represented by sea-water, which is recorded at the
18 lowest reach of the river during drought periods. These contributions variously mix along the stream path in
19 the distinct hydrological periods, and the presented data reflect, as a snapshot, the current hydroclimatic
20 conditions. Systematic future investigations will ~~therefore~~ help evaluate hydrological variations, in turn
21 related to meteo-climatic changes. This is of fundamental importance for the future water management
22 policy, which will tackle and try to overcome the vanishing of a significant water end-member of the basin.
23 **Particular attention has to be devoted to ~~the~~ the glacio-nival reservoir, nowadays regulating the hydrological**
24 **regime and providing the water especially in the warmer and drought period (Huss, 2011). Note that, in case**
25 **of significantly high glacier melting as a consequence of climatic warming, a response is expected on the**
26 **future parameters of the δD - $\delta^{18}O$ RWL (Zhou et al., 2014). Moreover, the presented results provide insights**
27 **into the seasonal hydrological budget that can improve the understanding of relationships between the river**
28 **and the connected aquifers, thus improving the groundwater management at a local scale (e.g. Castagna et**
29 **al., 2015).**
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45 Most of the dissolved components reflect a natural (geogenic) signature, which is related to the weathering
46 processes of the rocks existing in the basin and sharp geochemical variations reflect confluences of
47 tributaries having peculiar lithologies in the sub-basins (e.g. Rio Ram), and/or remarkable discharge (e.g.
48 Isarco); additional geochemical variations are locally induced by significant contribution from groundwater,
49 a process that is particularly highlighted in the hinge zone between UP and LP. The recorded hydrochemical
50 facies remained constant over the last decades, **and only nitrogen compounds showed temporal variations.**
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56 On the whole, considering an average annual water volume of ca. 8 km^3 of the Adige river (period 2013-
57 2015), the observed TDS implies a solute flux in the order of $1,371 \cdot 10^3 \text{ t/y}$ transferred from the river toward
58 the Adriatic Sea, a value that is intimately related to the weathering processes occurring in the basin. These
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1 weathering processes are in turn intrinsically related to annual temperature, meteoric precipitations, and CO₂
2 activity (Viers et al. 2014; Donnini et al., 2016).
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4 Although the measured concentrations of dissolved components are below the thresholds indicated by the
5 environmental legislations for drinking purposes, ~~an~~ the historical trend of nitrate increase clearly reflects the
6 growing of anthropogenic inputs occurred in the last decades at a basin scale. Accordingly, the nitrate
7 distribution doesn't correlate with the hydrological regime, but is deeply influenced by the agricultural cycles
8 and during the drought seasons reflects local effects. The average dissolved nitrate delineates a river load of
9 ca 32.9 10³ t/y, which represents a significant portion of the nitrogen budget transferred to the Adriatic Sea,
10 together with the nitrogen fraction associated to the suspended particulate matter (Corazzari et al. 2016). The
11 data can therefore be useful to refine estimates of the geochemical fluxes conveyed toward the sea, which are
12 mainly based on data relative to the Po river (Pettine et al., 1998; Naldi et al., 2010; Cozzi and Giani, 2011;
13 Marchina et al., 2015; 2016; Corazzari et al., 2016) and have to be taken into account by scientists that
14 evaluate the processes occurring in the sensitive costal ecosystems (Viaroli et al., 2015).
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33 **Conflict of interest**

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35 The authors declare that they have no conflict of interest.
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52 **Table captions**

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55 **Table 1** - Sampling locations (expressed with geographic coordinates, name of the locality and abbreviation of the
56 province - capital letters in brackets) and physico-chemical parameters measured in the Adige river waters sampled in
57 distinct hydrological periods from August 2013 to May 2015.
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1 **Table 2** - Hydrogen (δD) and oxygen ($\delta^{18}O$) isotope ratios recorded in the Adige river waters sampled in distinct
2 hydrological periods from August 2013 to May 2015.

3 **Table 3** - Chemical composition of Adige river waters sampled in distinct hydrological periods from August 2013 to
4 May 2015. bdl = below detection limit.
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10 **Figure captions**

11 **Figure 1** – (a) Simplified geological setting of northern Italy and stream path location of the Adige river (frame). (b)
12 Hillshade of the Adige river catchment with sampling locations. (c) Elevation profile of the Adige river from the source
13 to the mouth with sampling locations. For interpretation, refer to the colored web version of the paper.
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17 **Figure 2** – (a) Hydrogen (δD) and oxygen ($\delta^{18}O$) isotope ratios of the Adige river waters in distinct seasons of the
18 biennia 2013-2015. Isotopic composition of rainfalls (light gray field) and snow-~~and~~/glacier melts (dark gray field)
19 from the Saldur creek catchment (UP of the Adige river) are reported for comparison (data from Figs 3 and 4 in Penna
20 et al., 2014, excluding extreme compositions). Global Meteoric Water Line - GMWL from Craig (1971). Local
21 Meteoric Water Line - LMWL (Northern Italy, dashed line) from Longinelli and Selmo (2003); (b) $\delta^{18}O$ value of the
22 Adige river waters vs sampling elevation. The isotopic composition of the Isarco river sampled in May 2015 (sample
23 IS) and of the Saldur creek sampled in August 2013 (Penna et al., 2014) and March 2015 (sample S) are also reported.
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29 **Figure 3** – (a) Oxygen ($\delta^{18}O$) and (b) hydrogen (δD) isotopic variation along the stream path of Adige river waters
30 sampled in distinct hydrological periods from August 2013 to May 2015. The isotopic composition of the Isarco river
31 sampled in May 2015 (sample IS) and of the Saldur creek sampled in August 2013 (Penna et al., 2014) and March 2015
32 (sample S) are also reported. (c) Adige river average daily discharge recorded at the hydrometric stations of Spondigna,
33 Tel, Ponte Adige, Bronzolo, Trento S. Lorenzo, Villa Lagarina, Boara Pisani during the distinct sampling periods (data
34 from Provincia autonoma di Bolzano, Meteotrentino, Autorità di Bacino del fiume Adige, ARPA Veneto). The location
35 of the confluence of some tributaries along the main streamflow is also indicated .
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41 **Figure 4** – (a) Gibbs - TDS vs $[Na+/(Na^{+}+Ca^{2+})]$ - and (b) Piper classification diagrams of Adige river waters sampled
42 in distinct hydrological periods from August 2013 to May 2015. Waters from the Isarco river (sample IS) sampled in
43 May 2015 and of the Saldur creek (sample S) sampled in and March 2015– are also reported. The Po river water
44 compositional variation (Marchina et al., 2015) is also reported for comparison (gray fields).
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48 **Figure 5** – Na^{+} (a) and Ca^{2+} (b) variation along the stream path of the Adige river waters sampled in distinct
49 hydrological periods from August 2013 to May 2015. The main lithologies outcropping along the river profile are also
50 reported.
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53 **Figure 6** – Rb vs Sr binary diagram of the Adige river waters sampled in distinct hydrological periods from August
54 2013 to May 2015. Composition of Po river water (gray field) is also reported for comparison (data from Marchina et
55 al., 2015)
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58 **Figure 7** – (a) TDS vs $\delta^{18}O$ binary diagram of the Adige river waters sampled in distinct hydrological periods from
59 August 2013 to May 2015. Fields represent the UP samples. (b) TDS variation along the stream path of Adige river
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waters. The isotopic composition of the Isarco river sampled in May 2015 (sample IS) and of the Saldur creek sampled March 2015 (sample S) are also reported. **Groundw. Int. stands for samples recording groundwater interaction.** See text for further details.

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Geochemistry of the Adige river water from the Eastern Alps to the Adriatic Sea (Italy): evidences for distinct hydrological components and water-rock interactions

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Abstract

The Adige river flows from the Eastern Alps to the Adriatic Sea and the understanding of its fluvial dynamics can be improved by geochemical and O-H isotopic investigation. The most negative isotopic compositions are recorded close to the source ($\delta^{18}\text{O}$ between -14.1‰ and -13.8‰, δD between -100.3‰ and -97.0‰), and δD and $\delta^{18}\text{O}$ values generally increase downstream through the Upper Part (UP, the mountainous sector), stabilizing along the Lower Part (LP, the alluvial plain) of the river with $\delta^{18}\text{O}$ between -12.4‰ and -11.8‰, δD between -86.9‰ and -83.7‰. The isotopic variations along the stream path ($\delta^{18}\text{O}$ - δD vs distance from the source) depict subparallel distributions for all the investigated periods, with less negative values recorded in winter. Total dissolved solids (TDS) concentration shows the lowest value (< 100 mg/l) at the river source, jumping to 310 mg/l at the Rio Ram inflow, then decreasing down to the Isarco river confluence; from here we observed an increase toward the river mouth, with different values in the distinct sampling periods. The lowest values (140-170 mg/l) were recorded during high discharge in spring, whereas higher TDS values (up to 250 mg/l) were recorded during winter low flow conditions. Extreme TDS values were observed in the estuarine samples (up to 450 mg/l), as result of mixing with sea water. The results allow for the identification of distinct water end-members: glacio-nival component(s) characterized by the most negative isotopic composition and extremely low TDS, a rainfall component characterized by intermediate isotopic and elemental composition and groundwater characterized by the less negative isotopic composition and comparatively higher TDS. An additional component is represented by sea-water, which is recorded at the lowest reach of the river during drought periods. These contributions variously mix along the stream path in the distinct hydrological periods, and the presented data are a snapshot of the current hydro-climatic conditions. Future investigations will evaluate possible hydrological variations related to meteorological changes. Monitoring is fundamental for future water management to overcome the vanishing of a significant water end-member of the basin, i.e. the glacio-nival reservoir that is severely affected by the ongoing climatic changes.

Keywords: Adige river; water geochemistry; stable isotopes; hydrological components, water-rock interactions

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Introduction

Rivers have a key role in the water cycle as they return terrestrial precipitation back to the sea, transport the solutes produced by chemical weathering on the continents, as well as additional components potentially released by human activities. Their investigation is necessary for the understanding of the related ecosystems, which could be threatened by climatic changes and/or anthropogenic processes (Vörösmarty et al., 2013), and more in general are useful for a sustainable management of the water resources (Koundouri et al., 2016). In this framework, geochemical tracers are extremely useful to support hydrological studies, providing constraints for the understanding of the ongoing fluvial processes and to predict potential changes and future scenarios. Among the various tracers, hydrogen and oxygen isotopes in the water molecules are fractionated by temperature-related phase-transitions and provide clues on the origin of the river water that can be related to distinct meteoric contributions having different provenance, and/or occurring in distinct forms such as rainfall and (in alpine environments) snow/glacier melting (Chiogna et al., 2014; Penna et al., 2014; Engel et al., 2015; Fisher et al., 2015). Other tracers, such as the major dissolved components are intimately connected with the weathering processes of the outcropping lithologies, which in turn are influenced by climatic conditions that can promote the weathering efficiency.

For these reasons geochemical analyses of rivers can be considered as hydroarchives recording ongoing meteo-climatic processes. Systematic geochemical studies on creeks can provide tracer-based modelling that precisely evaluate the various water contributions, usually defined as end-members (*e.g.*: Chiogna et al., 2014; Penna et al., 2014; Engel et al., 2015), whereas studies of major rivers are more difficult to be parametrized, due to the difficulty of sampling systematically river lengths in the order of hundreds kilometers, and also because the contributing water end-members are multiple, often not sufficiently different from each other, and sometimes also variable in time. In spite of these limits, geochemical studies of major rivers have been widely taken into consideration (Gibbs 1970; Meybeck 1987; Gaillardet et al. 1999; Gaillardet 2014; Hartmann et al., 2014; Haldler et al., 2015) because they reflect processes at regional scale and their monitoring represents a snapshot of the existing conditions that, if compared with past and future investigation, allows for the prediction of evolutionary trends.

In this view, in northern Italy a recent geochemical investigation has been devoted to the Po river, which is the longest Italian river flowing from the northwestern Alps throughout the Padanian plain (Marchina et al., 2015; 2016), but not on the Adige river that is likewise important. The Adige is the second longest river and the third largest river basin in Italy, flowing for more than 400 km from the Eastern Alps to the Adriatic Sea, where its water budget (and the associated geochemical components) significantly influences the riparian and coastal ecosystems (Cozzi and Giani, 2011). Its hydrology is extremely complex due to an interplay between natural (climatic) and anthropogenic factors (water withdrawal for energy production, irrigation and civil

1 uses) and understanding of the related fluvial processes is fundamental in order to face the increasing
2 demand of water resources.

3
4 A recent review on the hydrological and chemical stressors in the Adige catchment was obtained integrating
5 local studies at sub-basin scale, highlighting that it is extremely important to unravel the distinct components
6 that contributes to the total water budget, as well as to identify the related water quality (Chiogna et al.,
7 2016). The same review emphasizes the lack of an integrated –systematic– hydrological characterization at a
8 basin scale, which would certainly improve the understanding of the river system and the predictive
9 capabilities of its hydrological behavior.

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14 The current contribution intends to fill this gap of knowledge and is inspired to recent studies of other
15 riverine systems (Mohammed et al., 2014; Campodonico et al., 2015; Harker et al., 2015). The goal can be
16 achieved combining classical hydrological approaches with a geochemical investigation at a basin scale that
17 is a powerful tool to identify the water provenance and origin, as well as to highlight local variations induced
18 by anthropogenic activities. For these reasons we present a comprehensive geochemical dataset (also
19 including oxygen and hydrogen isotopic data) of the Adige river water, systematically collected from the
20 mountainous upper part of the catchment down to the river mouth, in distinct seasons of the years 2013-
21 2015. The geochemical and hydrological data are also compared and discussed with literature data in order to
22 identify possible spatio-temporal variations occurred in the Adige river system in the last decennia, thus
23 providing proxies to evaluate ongoing and future (short- and long-term) changes in the water resource at a
24 basin scale. Specific objectives are: a) to determine the relation between oxygen and hydrogen isotopic
25 compositions for the Adige river waters and identify the main end-members to streamflow, obtaining a water
26 meteoric isotopic signature valid for the northeastern part of Italy; b) to assess the main hydrochemical facies
27 of the Adige water defining backgrounds having geogenic origin and anomalies related to anthropogenic
28 activities; c) to assess geochemical fluxes transferred from the eastern Alps to the Adriatic sea; d) to compare
29 the presented geochemical data set on the Adige river with the analogous data-set obtained for river Po
30 (Marchina et al., 2015; 2016) in order to provide conclusions valid at regional scale for the whole northern
31 part of the Italian Peninsula.

32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 **General outlines on the Adige river and its catchment**

49 50 51 *Geography and hydrology*

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53 The Adige riverine system (Fig. 1) drains the Southern and Eastern Alps starting from the Italian-Swiss-
54 Austrian boundary and end into the Adriatic Sea, northward of the Po river delta (Marchina et al., 2015;
55 2016). The river rises at 1,586 m a.s.l., near Lake Resia, and after a course of 409 km reaches the sea near the
56 village of Rosolina. On the basis of the morphological features, the river catchment has been subdivided in
57 an Upper Part (UP), corresponding to the mountainous sector, and a Lower Part (LP) corresponding to the
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1 related alluvial plain. Its stream path crosses, at increasing distance from the source, several important urban
2 centers such as Bolzano (100 km, 237 m a.s.l.), Trento (150 Km, 193 m a.s.l.) and Verona (250 km, 66 m
3 a.s.l.). The Adige river catchment extends over an area of ca. 12.100 km² and is commonly subdivided into
4 seven major sub-basins in relation to its main tributaries: Adige–Passirio, 3,174 km², Isarco–Talvera–Rienza
5 4,210 km², Noce 1,386 km², Avisio 934 km², Adige-Fersina-Leno 1,007 km² and Adige–Chiampo 1,464
6 km². Starting from the source, the Adige river flows generally E-W for ca. 70 km in the Adige-Passirio sub-
7 basin, and receives contributions from small mountainous sub-catchments characterized by glaciated areas
8 (Penna et al., 2013). After the confluence with the Passirio river, draining the northernmost part of the basin,
9 the Adige main stream turn toward N-S and after 30 km reaches the town of Bolzano where it is
10 characterized by a mean annual discharge of 50 m³/s. Few kilometers southward, the Adige stream path
11 meets the confluence with the Isarco river, which is one of the main tributaries (mean annual discharge of 80
12 m³/s) draining about half (the whole N-E part) of the catchment (Isarco-Talvera-Rienza sub-basins)
13 characterized by a mean altitude of 1,750 m a.s.l. In the vicinity of Trento, Adige meets the confluence with
14 the Noce river (mean annual discharge of 35 m³/s), which drains an area characterized by significant mean
15 elevation (1,625 m a.s.l.) and by the presence of some important glaciers (Chiogna et al., 2014); few
16 kilometers southward the mainstream receives the Avisio and Fersina rivers (mean annual discharge of 23.5
17 and 2.0 m³/s, respectively), both draining the central-eastern parts of the basin, having mean altitude of 1660
18 and 1099 m a.s.l., respectively. Southward at ca. 220 km from the source, the Adige stream path turns to E
19 direction facing the alluvial plain deposits. Additional tributaries drain the Lessini Mountains (Adige-
20 Chiampo sub-basin) and reach the confluence with Adige river at ca. 280 km from the source; afterwards the
21 river does not receive any other superficial water income, and the riverbed confined within continuous
22 embankments on both sides progressively rises higher than the surrounding alluvial plain. Therefore, most of
23 the basin is located in Alpine morpho-climatic conditions (94.6 % of the basin area is mountainous) that
24 mainly contribute to the Adige river budget. In particular, the basin is characterized by the presence of 185
25 glaciers covering about 212 km² that represent an important water supply for the Adige river discharge,
26 especially during warmer periods (Milner et al., 2009). Accordingly, the mean annual discharge measured at
27 the Trento S. Lorenzo station (185 m³/s), i.e. at the closure of mountainous part of the catchment, is
28 comparable with that observed at the lowest reach station of Boara Pisani (202 m³/s) located 60 km upstream
29 from the estuarine mouth (Adige River Basin Authority, Autorità di Bacino del fiume Adige, 2008).

30 *Meteo-climatic characteristics of the catchment*

31 The study area is thoroughly monitored by meteorological stations which record time series of precipitation
32 and temperature and the data are available at the following websites: <http://www.meteotrentino.it>;
33 <http://www.provincia.bz.it/meteo/home.as>; <http://www.arpa.veneto.it>. The general climatic conditions of the
34 Adige river catchment are characterized by continental climate, with a precipitation regime that is influenced
35 by western Atlantic airflows and southern circulation patterns (Norbiato et al., 2009). It mainly results in
36 relatively dry winters with maximum of precipitations recorded during springs and falls. A significant

1 amount of the water budget is accumulated at higher elevations during winter in the form of snow, which
2 undergoes melting starting from spring time. This results in a “nival” hydrological regime of the catchment,
3 which is characterized by general water availability in the warm seasons and low discharge in winter. The
4 mean annual precipitation in the distinct sub-basins is highly variable depending on catchments elevation,
5 valleys orientation and distance from orographic barriers: it varies from a minimum of 400-500 mm/y in Val
6 Venosta (UP) to a maximum of 1600 mm/y at higher elevations and in the valleys opened toward the
7 floodplain (LP). In general, all the stations record a notable minimum of precipitations during winter due to
8 the dominance of the Russian-Siberian anticyclone over the entire alpine region (data from
9 <http://www.bacino-adige.it>). Consequently, streamflow shows a typical Alpine regime with two peaks: one
10 in spring due to snow melt and one in autumn due to cyclonic storms, which are the main causes of flooding
11 events.
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20 *Water use*

21 The Adige river water (and that of its alpine tributaries) is intensively conveyed into reservoirs and used for
22 hydropower production, with intermittent water uptake and downflow release. Withdrawals are widespread
23 in the mountainous part of the basin, providing water to 34 large hydropower plants that produce a total
24 effective power of 650 MW (Chiogna et al., 2016 and references therein). Smaller withdrawals are devoted
25 to a variety of agricultural, civil and industrial water uses. Licensed water uptakes for agricultural uses are
26 remarkable (up to 50 m³/s) especially in the provinces of Bolzano in the upper part, and of Verona in the
27 lower part of the catchment. Supplies for drinking use are also widespread within the basin but usually lower
28 than 20 m³/s (Provincia Autonoma di Trento, 2006; Provincia Autonoma di Bolzano, 2010; Chiogna et al.,
29 2016).
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38 *Geology and lithologies*

39 Geological information is also important because water chemistry is strictly related to the outcropping
40 lithologies that have distinct mineralogical composition, peculiar weathering rates and distinct release of
41 chemical components in the interacting waters. The Adige river drains various lithologies along the
42 mountainous path (Fig. 1): from the rise to Merano (70 km, Venosta Valley) it crosses the quartz-feldspathic
43 metamorphic rocks of the Austroalpine domain, downflow to Ora (110 km from the source) the rhyolitic
44 rocks of the Atesian volcanic complex, and then the carbonate units of the Southalpine domain (Lagarina
45 Valley) that outcrop down to the town of Affi (220 km from the source) where the river is embedded in the
46 alluvial plain deposits (Möller et al., 2003).
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55 **Sampling and analytical methods**

56 In this study 65 samples of Adige river water have been collected in distinct seasonal periods that include
57 variable hydrological conditions representative of the biennia 2013-2015. The first two sampling campaigns
58 (15 samples each) have been conducted in August 2013 and May 2014 from the site of Andriano
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1 downstream to the river mouth at Rosolina Mare. In March and May 2015 the Adige river has been sampled
2 from the outlet of the lake of S. Valentino alla Muta to the river mouth in order to investigate the whole
3 stream path (18 and 17 samples, respectively; Table 1 and Fig. 1). The summer hydrological regime (August
4 2013) was characterized by relatively high flow in the UP (ca. 200 m³/s after the Isarco confluence) and low
5 discharge in the LP (average of ca. 175 m³/s). The winter hydrological condition (March 2015) showed the
6 lowest discharge both in the UP (55 m³/s after the Isarco confluence) and in the LP, the latter being
7 characterized by a peculiar downstream increase (from 95 to 172 m³/s). The spring hydrological conditions
8 (May 2014 and 2015) were characterized by intermediate to high flow both in the UP (from 190 to 300 m³/s
9 after the Isarco confluence) and in the LP (up to 410 m³/s in May 2014). The rationale behind the selection of
10 sampling locations was to monitor the water geochemistry along the river profile, before/after the confluence
11 of important tributaries, settlements, and/or zones of important productive activities, but logistical criteria
12 (i.e., easy site accessibility) were also taken into consideration. Each sampling location was geo-referenced
13 by a portable global positioning system (GPS), to locate the points and to set up future field surveys. Surface
14 water was collected at 40–50-cm depth using a bucket, possibly far from the shore (using piers or sampling
15 above bridges). Electrical conductivity (EC), pH, and temperature were directly measured in the field using a
16 handheld probe (HI9813-5, Hanna Instruments; Table 1), then water samples were stored in 100-mL bottles.
17 Laboratory analyses were carried out on filtered water samples (by 0.45- μ m Minisart® NML syringe
18 cellulose acetate filters) at the Department of Physics and Earth Sciences of the University of Ferrara.
19 Hydrogen and oxygen isotope ratios were determined injecting water samples into a CRDS Los Gatos LWIA
20 24-d isotopic analyzer and reported in Table 2. The isotopic ratios of ²H/¹H and ¹⁸O/¹⁶O are expressed as δ
21 notation [$\delta=(R_{\text{sample}}/R_{\text{standard}}-1)\times 1000$] with respect to the Vienna Standard Mean Ocean Water (V-SMOW)
22 international standard. The isotopic composition of the samples was obtained by six injections; the first two
23 injections were discarded to minimize potential-memory effects (Penna et al. 2012), while the isotopic values
24 of the last four injections were averaged. Four bracketing standards that cover the whole range of isotopic
25 values of the Adige river water were run throughout the analytical sessions. These standards, obtained from
26 the Los Gatos Research Company, were calibrated with international standards such as V-SMOW and SLAP
27 (Standard Light Antarctic Precipitation). The typical instrumental precision was better than 0.3 and 1.0 ‰
28 for $\delta^{18}\text{O}$ and δD , respectively. Cations and trace elements have been measured by inductively coupled
29 plasma mass spectrometry (ICP-MS) using a Thermo-Scientific X Series instrument on samples previously
30 diluted 1:10 by deionized Milli-Q water (resistivity of ca. 18.2 M Ω ×cm), also introducing known amount of
31 Re and Rh as internal standard; in each analytical session, the analysis of samples was verified with that of
32 the reference materials EU-L-1 and ES-L1 provided by SCP-Science (www.scpscience.com). The major
33 anions were determined by ion chromatography using a Dionex ICS-1000 calibrated using solutions obtained
34 by different dilutions of the Dionex “7-ion standard.” Accuracy and precision, based on the repeated analyses
35 of samples and standards, were better than 10 % for all the considered parameters. Alkalinity was determined
36 by titration using the HI-3811 alkalinity test kit (Hanna Instruments), and for the observed pH range reflects
37 the HCO₃⁻ content (Ryan, 2014). The mentioned analyses are reported in Table 3. The coherence of chemical
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1 data has been verified checking the ionic balance, as the sum of cations (expressed in meq/L) approaches that
2 of anions with relative error $[(\sum_{\text{cations}} - \sum_{\text{anions}})/(\sum_{\text{cations}} + \sum_{\text{anions}})] \times 100$, which is generally minor than 5%.

3 4 5 **Results**

6 *pH, temperature, and conductivity of Adige river waters*

7 Physico-chemical parameters measured in situ such as pH, temperature, and conductivity of Adige river
8 water have been reported in Table 1. In order to appreciate physico-chemical changes along the flow path,
9 the sample population has been geographically subdivided in two subsets corresponding to increasing
10 distance from the river source, defined as UP (upper part), LP (lower part), and the related variability has
11 been also evaluated in order to delineate spatial-temporal changes. pH does not show any systematic
12 variation along the stream path in the distinct periods and displayed higher values during the drought season
13 (August 2013, March 2015); it showed the highest values at Spondigna (UP) and Zevio (LP) where it
14 reached the maximum value of 8.6 in August 2013. The lowest pH value (7.7) was recorded at the end of UP
15 (Andriano) in May 2014. On the other hand, the water temperature showed increasing values from the source
16 to the mouth with the lowest variation recorded in the colder (10.0-16.0°C, March 2015) and the highest in
17 the warmer (13.9-21.5°C August 2013) sampling periods. Electrical conductivity showed the highest
18 variation in the UP with a sudden increase (up to 300 $\mu\text{S}/\text{cm}$) just after the confluence with Rio Ram
19 (Spondigna) followed by a variable decrease down to the confluence with the Isarco river, where the lowest
20 EC value (140 $\mu\text{S}/\text{cm}$, Vadena Nuova) was recorded in May 2015. Downstream this confluence, EC
21 generally increased down to the river mouth indicating progressively higher amounts of dissolved
22 components moving from the UP, to the LP catchment areas. The average EC value was lower in May 2015
23 (190 $\mu\text{S}/\text{cm}$) with respect to that recorded in other sampling periods (250-260 $\mu\text{S}/\text{cm}$), whereas slightly
24 higher EC average values was recorded in March 2015 (300 $\mu\text{S}/\text{cm}$). This means that, although it is not
25 possible to delineate a clear correlation between EC and discharge, the highest EC values occur during the
26 winter low discharge, whereas lower EC values occur during higher flow regime occurring in spring,
27 plausibly in relation to dilution effects. Higher electrical conductivity has been observed in the estuarine
28 samples (L10), with values of 500 and 690 $\mu\text{S}/\text{cm}$ recorded in March 2015 and August 2013, corresponding
29 to the lowest discharge periods. These anomalously high EC values obviously reflect interaction with sea
30 water.
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49 It is important to note that an abrupt change of the physico-chemical parameters of the Adige river is
50 recorded after the confluence with Isarco river. This is in accordance with the values measured in the Isarco
51 waters in May 2015, which demonstrated the capability of this tributary to deeply modify the Adige river
52 water values by mixing, in agreement with the relative water discharge (Data from Provincia Autonoma di
53 Bolzano), as already described by Leibundgut et al. (2009).
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59 *Isotopic composition of Adige river waters*

1 The variation of δD and $\delta^{18}O$ isotopic ratios of Adige river waters in the distinct sampling periods is reported
2 in Table 2 and Fig. 2a, the relation between the water isotopic composition and the sampling elevation (m
3 a.s.l.) is highlighted in Fig. 2b, and the isotopic variation along the stream path is reported in Fig. 3. In Fig.
4 2a, it can be observed that the recorded isotopic compositions of the Adige river waters mainly lie between
5 the Global Meteoric Water Line (GMWL; Craig, 1961) and the Local Meteoric Water Line (LMWL) defined
6 for Northern Italy by Longinelli and Selmo (2003). The same diagram reports for comparison the isotopic
7 composition of rainfalls and melt waters from snow and glaciers of an alpine sub-basin located near the river
8 source (Penna et al., 2013, 2014), which suggests that the Adige river waters reflect –in addition to rainfall–
9 significant contribution from snow and glacier melting in the distinct seasons. From Fig. 2b, where δD is
10 plotted vs the sampling elevation it can be observed that the altitude effect is evident in all the investigated
11 hydrological periods. The most negative isotopic compositions are recorded in the first 20 km from the
12 source where $\delta^{18}O$ ranges between -14.1‰ and -13.8‰, δD between -100.3‰ and -97.0‰. In this sector of
13 the river, the discharge is still low and therefore the incoming tributaries influence the isotopic composition
14 of the main stream, as observed for Saldur which induces a notable shift toward more negative values in the
15 main stream at its confluence (Fig. 3). δD and $\delta^{18}O$ values generally increase downstream from the source
16 through the UP, whereas they tend to stabilize along the LP down to river mouth. The isotopic trends along
17 the stream path are subparallel for all the investigated periods, with distinctly less negative values observed
18 in March 2015 which shows, except for the first 20 km after the source, a mean shift of +0.9‰ $\delta^{18}O$ (SD
19 0.2‰) and +7.3‰ δD (SD 3.5‰) with respect to the averaged data of the other seasons. On the whole,
20 isotopic composition does not show dependence with respect to the relative water discharge and, with the
21 exception of March 2015, is comparable in the distinct investigated periods, especially for LP. In UP, slight
22 but consistent differences are observed in the average isotopic compositions, with August 2013 showing the
23 most negative value, possibly due to an higher glacier melt contribution, as commonly observed in alpine
24 catchments located in the Eastern Alps (Penna et al., 2014; Engel et al., 2015). Slight differences exist
25 between the isotopic composition recorded in May 2014 and May 2015, the latter being generally
26 characterized by more negative values; this is possibly due to higher spring temperatures in 2015 with
27 respect to 2014 (<http://www.provincia.bz.it/meteo/climareport.asp>) leading to an earlier snowmelt period,
28 especially in high-elevation sub-catchments. On the other hand, samples collected during the drought of
29 March 2015 systematically display a difference -with isotopic values distinctively less negative- which
30 becomes progressively more marked in the LP. In this season, we observed the least negative values ($\delta^{18}O$ -
31 10.8‰, δD -73.0‰) at Brentino Belluno (205 km from the source), in correspondence of a meandering
32 sector of the river where channel sinuosity plausibly favor hyporheic exchanges (Buss et al., 2009).
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53 It is interesting to note the different isotopic gradients along the river profile that depend on the specific
54 orographic features of the basin (UP vs LP) and on the seasonal variations. The strongest isotopic variation
55 characterizes UP and is more marked in drought seasons, resulting in a notable isotopic gradient in August
56 2013 ($\delta^{18}O$ 0.02‰/km, δD 0.18‰/km) and March 2015 ($\delta^{18}O$ 0.02‰/km, δD 0.13‰/km). On the other
57 hand, the Adige river waters in LP are characterized by a very weak isotopic variation for all the investigated
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sampling periods (average of $\delta^{18}\text{O}$ 0.001‰/km and δD 0.02‰/km). These gradients are very similar to that observed for the LP of the Po river (Marchina et al., 2015), possibly reflecting common hydrological conditions for rivers flowing in the Padanian Plain.

In Table 2, the deuterium excess calculated as: $d\text{-exc}=\delta\text{D}-8\times\delta^{18}\text{O}$ on the basis of the global meteoric water line as defined by Dansgaard (1964) is also reported. Average d-exc for each sampling season has been calculated for UP where more of the river recharge is concentrated: it varies between 10.1 (March 2015) and 13.1 (May 2015). In general it can be observed that the d-exc average values recorded in warm periods (spring and summer) are higher than those recorded in the conditions recorded in March.

Dissolved components

The total dissolved solid (TDS), calculated as a sum of the major chemical species (Table 3), shows marked variation along the stream path. The lowest value (< 100 mg/l) was measured at the outlet of the Lake of San Valentino alla Muta (source) in May 2015. A sharp TDS increase was recorded after few kilometers as a result of the confluence of Rio Ram, which is responsible for TDS up to 310 mg/l in the site of Spondigna; from here the TDS decreased downstream for 70-80 km to the Isarco river confluence (Bolzano) and subsequently generally increased to the river mouth (Rosolina Mare), with average values significantly different in the distinct sampling periods. The lowest values (140-170 mg/l) were recorded during high discharge in spring (May 2014 and 2015), whereas higher TDS were recorded during low flow conditions in August 2013 (190 mg/l) and in March 2015 (250 mg/l). Higher TDS values were observed during low discharge periods in the estuarine samples (up to 450 mg/l), which result from mixing with sea water during momentary high-tide influence.

The TDS of Adige is also plotted against the $[\text{Na}^+(\text{Na}^++\text{Ca}^{2+})]$ in the Gibbs diagram (Fig. 4a) which is widely used to describe the composition of river waters, and compared with Po river waters (the longest Italian river; Marchina et al., 2015). It can be observed that most compositions cluster in the central part of the diagram, as also observed for Po river waters. This chemical fingerprint appears predominant in most riverine systems in northern Italy (Donnini et al., 2016) and worldwide, irrespective to significant differences in the lithologies outcropping in their catchments, due to the preferential weathering of carbonate respect to the silicate rocks (Gibbs 1970). Coherently, analogies between the Adige and the Po waters are also envisaged in the Piper diagram, which displays a common Ca- HCO_3 hydrochemical facies (Fig. 4b). Significant differences between the waters of these two important rivers are observed only in the terminal part, characterized by the appearance of Na-Cl hydrochemical facies, where Po river waters show a more marked (and widespread) salinization, in contrast to those of Adige that are affected by mixing with sea water only near the mouth (Rosolina Mare).

More detailed insights on the Adige river water evolution can be obtained investigating the variation along the streamflow of single parameters in the distinct seasons. For example, in Fig. 5 it is reported the variation of Na^+ and Ca^{2+} : very low concentrations have been measured at the outlet of the Lake of San Valentino alla

1 Muta in May 2015, but marked variations suddenly appear at the confluence of Rio Ram which, having a
2 notable discharge and a peculiar chemical composition (it drains Triassic dolomitic rocks), deeply modifies
3 the geochemical budget of the Adige river. The following tributaries are represented by creeks draining
4 resistant metamorphic rocks that are scarcely weatherable thus providing water characterized by low TDS
5 and, in particular, extremely low calcium content. This “dilution” trend is maintained down to the confluence
6 of Isarco river, from which we observed a reversal of the Ca^{2+} trend that starts to increase downstream as a
7 result of contribution from water that interacted with sedimentary lithologies (see geology in Fig. 1). As
8 concerns seasonal variations, higher concentrations have been observed in the low discharge periods of
9 August 2013 and March 2015 which also show the more scattered distribution, probably in relation to local
10 effects. In particular, remarkable concentrations of both calcium and sodium (up to 50 and 9.5 mg/l,
11 respectively) are recorded between 200 and 250 km from the source in the lowest flow sampling campaign
12 (March 2015). This part of Adige corresponds to a meandering sector of the river located at the end of the
13 mountainous part of the catchment. In our view, as already highlighted by isotopic analyses, this reflects an
14 interaction with groundwater of the connected phreatic aquifer that contributes to the river flow, especially
15 during low discharge hydrological periods. Trace element concentrations can be even more useful to
16 highlight river contributions and dynamics. For example, the Rb and Sr covariation reported in Fig. 6
17 highlights that samples collected during the drought of March 2015 have different composition
18 (comparatively enriched in Sr) with respect to those of the other seasons thus corroborating a significantly
19 higher groundwater contribution in the river flow during this period. Insights can be raised also by the Rb
20 and Li covariation showing that samples collected during the drought of March 2015 ($R^2 > 0.75$) have
21 different composition (comparatively enriched in Li) respect to those of May of the years 2014 and 2015 (R^2
22 > 0.85). This suggests that in these hydrological periods, although variable, trace element contents reflect a
23 geogenic signature. On the other hand, samples collected in August 2013 show anomalous Li distribution,
24 which is uncorrelated with Rb (R^2 ca. 0.1), and strongly correlated ($R^2 = 0.87$) with B (an element that is
25 often below the detection limit in other periods), suggesting possible contamination. Further investigation
26 will be necessary to verify the possible recurrence and origin of these anomalies.
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45 **Discussion**

46 *Influence of catchment elevation and nature of meteoric components*

47 At any point along a river reach water is derived from precipitation falling within upstream catchment
48 sectors, and therefore river water isotopic composition is related to that of precipitation (Peng et al., 2015),
49 which in turn changes seasonally, depends on elevation, and is also event specific (Chiogna et al., 2014). The
50 seasonal isotopic variability of precipitation is attenuated in rivers (and springs) due to the delayed signal of
51 snow (Penna et al., 2014; Carturan et al., 2015; Engel et al., 2015) and also as result of storage/mixing
52 favored by groundwater and lakes (Marchina et al., 2015). These inferences on the oscillation of river
53 isotopic signature with respect to the input meteoric signal have been conceptualized by catchment
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1 functioning in small mountain creeks (*e.g.* Chiogna et al., 2014) and confirmed by systematic observation of
2 major rivers world-wide (Haldler et al., 2015).
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4 In this framework, the hydrogen and oxygen isotopic composition of the Adige river water shows a
5 systematic variation in all the investigated periods, characterized by a strong enrichment in heavy isotopes
6 (^{18}O and ^2H) from the source to ca. 130 km downstream (UP), followed by a very slight increase of $\delta^{18}\text{O}$ and
7 δD values all along the LP down to the river mouth. This general variation mainly reflects the
8 morphoclimatic features of the basin which can be subdivided in a northern mountainous UP characterized
9 by high average elevations (with steep slopes) and a by a southern LP which varies from the foothill to the
10 floodplain with limited altitude/slope gradients (Fig. 1c). The comparison with data provided by Fuganti et
11 al. (2005) highlights that the southern UP (stations of Zambana Nuova and Mattarello) maintained very
12 similar water isotopic values, and the observed average LP composition ($\delta^{18}\text{O} = -12.0\text{‰}$) is very similar to
13 that recorded at the hydrometric station of Boara Pisani (60 km upstream from the mouth) by Zuppi and
14 Bortolami (1982). The systematic isotopic characterization along the river stream in distinct seasons allows
15 for the identification of the spatio-temporal contribution of distinct water end-members to the Adige river
16 flow. The river water budget is strongly influenced by snow (and glacier) melting in late spring and summer,
17 which confers relatively light isotopic composition, whereas a trend toward less negative compositions is
18 observed in March soon downstream the river source. This trend observed during the low discharge
19 conditions of March is attributed to a greater contribution of rainfall components which are conveyed to the
20 river by surface runoff and (especially in LP) by groundwater of unconfined aquifers, which are typically
21 characterized by relatively heavy isotopic composition (Zuppi and Bortolami, 1982; Fuganti et al., 2005).
22 Coherently, the groundwater contribution to the river is magnified during the drought season and locally
23 marked by anomalies (less negative isotopic values) in the $\delta^{18}\text{O}$ -distance from the source diagram of Fig. 3.
24 This allows to identify suitable sectors of the river for future “hydrograph separation” studies (Klaus and
25 McDonnell, 2013) useful to distinguish the glacier/snow melt and groundwater contributions to the
26 streamflow.
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28 The mean UP gradient (0.2‰ $\delta^{18}\text{O}$ and 1.5‰ δD per 10 km) can be referred to altitude variation of the
29 meteoric recharge along the river course, as the water budget along the profile progressively integrates
30 meteoric contributions related to lower altitudes. In fact, according to our data the altitude effect on the
31 whole Adige catchment is in the order of -2.0 for δD and -0.3 for $\delta^{18}\text{O}$ per 100m rise of elevation and the
32 same gradients are obtained for the UP. These values are similar to those observed by Penna et al. (2014) in
33 the more elevated mountainous sub-basins of the Adige UP, where -1.6‰ for δD and -0.23‰ for $\delta^{18}\text{O}$ per
34 100 m rise of elevation have been recorded in the years 2012 and 2013, but lower than that observed for the
35 Po river catchment ($\delta^{18}\text{O}$ ca. -0.5 per 100 m rise; Marchina et al., 2015). The observed isotopic variation can
36 be related to the elevation of precipitation and the application of equation 5 provided by Engel et al. (2015)
37 reveals that $\delta^{18}\text{O}$ values between 12 and 12.5 ‰ (typical of the UP) conform to a catchment elevation of ca.
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1800 m a.s.l., which is slightly higher than the average topographic elevation of the Adige basin (1675 m a.s.l., Donnini et al., 2016).

Taking into consideration the strict relation between the isotopic composition of river water and that of precipitation within the relative catchment, the presented δD - $\delta^{18}O$ data on the whole provide the following River Water Line (RWL):

$$\delta D = 8.1\delta^{18}O + 12.3 \quad (n = 65, R^2 = 0.95) \quad (1)$$

that is similar to the local meteoric water line (LMWL) defined for a mountainous sub-catchment belonging to UP ($\delta D = 8.1\delta^{18}O + 10.3$; Penna et al., 2014).

Note that the difference between LMWL and RWL may reflect the contribution of snow/ice melting which characterizes the river water budget; the involvement of glacier melting is effective as shown by the d-exc values that, during the warm periods, conform to those measured in rivulets outflowing from alpine glaciers located in the Adige UP (d-exc up to 13; Penna et al., 2014). The RWL therefore appears more sensitive than the LMWL to monitor ongoing climatic changes and, according to recent studies, glacier melting should involve significant isotopic fractionation, in turn resulting in distinct regression lines and d-exc (Penna et al., 2014; Engel et al., 2015; Zhou et al. 2014). Therefore, the presented isotopic values, integrated with those existent in the literature (Chiogna et al., 2014; Penna et al., 2014) for the highest part of the basin, could be useful to provide a snapshot of the current climatic condition in the eastern Alps. The same data, if merged with those provided for the Po river basin could be useful to enlarge the survey, providing a snapshot valid for the whole northern Italy. In this view, we merged the isotopic data presented in this paper with those provided by Marchina et al. (2015) and Donnini et al. (2016), obtaining the following RWL regression:

$$\delta D = 7.9 \delta^{18}O + 9.5 \quad (n = 156, R^2 = 0.96) \quad (2)$$

that can therefore reflect the meteo-climatic conditions valid at a regional scale for Northern Italy in the years 2011-2015.

Origin of the dissolved components

The comprehension of the processes controlling the water chemistry of a river is useful to define geochemical cycles within a given catchment (Mohammed et al., 2014; Campodonico et al., 2015; Harker et al., 2015). Although natural studies of riverine chemistry at the global scale have been widely discussed (Gibbs 1970; Meybeck 1987; Gaillardet et al. 1999; Gaillardet 2014; Viers et al. 2014), specific regional researches performed on the Adige river catchment are incomplete (i.e. considering only few parameters) and never available for the whole stream path (Chiogna et al., 2016).

In theory, the amount of the dissolved species is related to the nature of lithologies outcropping in the catchment and the weathering processes typically occurring in the region (Voss et al. 2014 and references

1 therein), but anthropogenic contribution related to human activities cannot a priori be neglected. Taking into
2 consideration the chemical analyses of the major cations and anions (Table 3), water composition is
3 invariably dominated by Ca-HCO₃ hydrochemical facies with the exception of the estuarine samples
4 collected during drought season, which are affected by sea water interaction and characterized a Na-Cl
5 hydrochemical facies. It is interesting to note that the predominant Ca-HCO₃ hydrochemical facies persisted
6 in the river water at least for the last 40 years (Fossato, 1971; Fuganti et al., 2005) and that the unique
7 parameter that significantly increased is the nitrate, plausibly related to anthropogenic pollution, similarly to
8 what observed in the Po river water where a drastic increase of nitrate has been related to agricultural and
9 zootechnical activities (Marchina et al., 2016). Additional anthropogenic trace element input could be
10 represented by the occasional observation (August 2013) of anomalous Li and B contents, often referred as
11 proxies of pollution related to human activities (Kszos and Steward, 2003). Further, anthropogenic anomalies
12 affecting the Adige river water composition have been recorded by Möller et al. (2003) that emphasized high
13 gadolinium concentration with respect to other Rare Earth Elements (REE).
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22 The spatio-temporal distribution of the chemical species is regulated by the hydrological regime, with
23 general increase in concentration during the low discharge periods. This phenomenon, also observed in the
24 past (Fossato, 1971), cannot only be related to dilution/concentration processes, but necessarily requires the
25 involvement of groundwater contributions (Fig. 7), which variously mix within the river in specific sites
26 mainly located in the hinge zone between UP and LP. UP waters (identified by fields in Fig. 7a) are
27 generally characterized by TDS decreasing from the Rio Ram (draining sedimentary rocks) confluence
28 downstream to the LP, resulting from a subsequent income of water draining “unweatherable” metamorphic
29 rocks, which induces a dilution effect. TDS progressively increase in LP waters due to the presence of more
30 weatherable lithologies and to the contribution of groundwater, which become significant at 200-300 km
31 from the source during the drought period of March 2015 (Fig 7b). In particular, hyporheic exchange seems
32 to be very effective in a meandering sector of the river, in accordance with numerical flow models
33 suggesting that surface- groundwater interaction is strongly tied to river morphology, and that any
34 irregularity in an otherwise straight river induces localized hyporheic exchange (Buss et al., 2009). In fact,
35 in this sector of the river we observed a sudden increase of Ca²⁺ (and more in general TDS) which is coupled
36 with marked trace element variations (low Rb/Sr) and an isotopic shift toward less negative compositions.
37 This trend is induced by rainwater infiltrated in the foothill alluvial fans constituted of coarse to medium
38 grained (mainly carbonatic) high-permeability sediments, which represent the phreatic reservoirs of the area
39 (Castagna et al., 2015).
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56 **Conclusions**

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58 The Adige river waters investigated along the whole stream path in distinct seasonal periods give insights on
59 the current hydrological regime and on natural and anthropogenic components from local to basin scale. The
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1 spatio-temporal distribution of some geochemical tracers help identify the relative contribution of distinct
2 water end-members: a glacio-nival component characterized by the most negative isotopic composition (δD
3 down to -120 ‰, Penna et al., 2014) and extremely low TDS, a rainfall component characterized by
4 intermediate isotopic and elemental composition and groundwater from phreatic aquifers which is
5 characterized by the less negative isotopic composition (δD up to -59 ‰, Fuganti et al., 2005) and
6 comparatively higher TDS mainly represented by elements released by carbonate-bearing lithologies
7 (relatively high Ca and Sr). An additional component is represented by sea-water, which is recorded at the
8 lowest reach of the river during drought periods. These contributions variously mix along the stream path in
9 the distinct hydrological periods, and the presented data reflect, as a snapshot, the current hydroclimatic
10 conditions. Systematic future investigations will help evaluate hydrological variations, in turn related to
11 meteo-climatic changes. This is of fundamental importance for the future water management policy, which
12 will tackle and try to overcome the vanishing of a significant water end-member of the basin. Particular
13 attention has to be devoted to the glacio-nival reservoir, nowadays regulating the hydrological regime and
14 providing the water especially in the warmer and drought period (Huss, 2011). Note that, in case of
15 significantly high glacier melting as a consequence of climatic warming, a response is expected on the future
16 parameters of the δD - $\delta^{18}O$ RWL (Zhou et al., 2014). Moreover, the presented results provide insights into
17 the seasonal hydrological budget that can improve the understanding of relationships between the river and
18 the connected aquifers, thus improving the groundwater management at a local scale (*e.g.* Castagna et al.,
19 2015).

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33 Most of the dissolved components reflect a natural (geogenic) signature, which is related to the weathering
34 processes of the rocks existing in the basin and sharp geochemical variations reflect confluences of
35 tributaries having peculiar lithologies in the sub-basins (*e.g.* Rio Ram), and/or remarkable discharge (*e.g.*
36 Isarco); additional geochemical variations are locally induced by significant contribution from groundwater,
37 a process that is particularly highlighted in the hinge zone between UP and LP. The recorded hydrochemical
38 facies remained constant over the last decades, and only nitrogen compounds showed temporal variations.
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44 On the whole, considering an average annual water volume of ca. 8 km^3 of the Adige river (period 2013-
45 2015), the observed TDS implies a solute flux in the order of $1,371 \cdot 10^3 \text{ t/y}$ transferred from the river toward
46 the Adriatic Sea, a value that is intimately related to the weathering processes occurring in the basin. These
47 weathering processes are in turn intrinsically related to annual temperature, meteoric precipitations, and CO_2
48 activity (Viers et al. 2014; Donnini et al., 2016).
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53 Although the measured concentrations of dissolved components are below the thresholds indicated by the
54 environmental legislations for drinking purposes, the historical trend of nitrate increase clearly reflects the
55 growing of anthropogenic inputs occurred in the last decades at a basin scale. Accordingly, the nitrate
56 distribution doesn't correlate with the hydrological regime, but is deeply influenced by the agricultural cycles
57 and during the drought seasons reflects local effects. The average dissolved nitrate delineates a river load of
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1 ca 32.9 10³ t/y, which represents a significant portion of the nitrogen budget transferred to the Adriatic Sea,
2 together with the nitrogen fraction associated to the suspended particulate matter (Corazzari et al. 2016). The
3 data can therefore be useful to refine estimates of the geochemical fluxes conveyed toward the sea, which are
4 mainly based on data relative to the Po river (Pettine et al., 1998; Naldi et al., 2010; Cozzi and Giani, 2011;
5 Marchina et al., 2015; 2016; Corazzari et al., 2016) and have to be taken into account by scientists that
6 evaluate the processes occurring in the sensitive costal ecosystems (Viaroli et al., 2015).
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10 **Acknowledgments**

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13 the manuscript. The study was funded in part by the European Fund of Regional Development (POR FESR
14 2007-2013), Terra&AcquaTech Labs., Technopole of Ferrara.
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21 **Conflict of interest**

22 The authors declare that they have no conflict of interest.
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20 **Table captions**

21 **Table 1** - Sampling locations (expressed with geographic coordinates, name of the locality and abbreviation of the
22 province - capital letters in brackets) and physico-chemical parameters measured in the Adige river waters sampled in
23 distinct hydrological periods from August 2013 to May 2015.

24 **Table 2** - Hydrogen (δD) and oxygen ($\delta^{18}O$) isotope ratios recorded in the Adige river waters sampled in distinct
25 hydrological periods from August 2013 to May 2015.

26 **Table 3** - Chemical composition of Adige river waters sampled in distinct hydrological periods from August 2013 to
27 May 2015. bdl = below detection limit.

28 **Figure captions**

1 **Figure 1** – (a) Simplified geological setting of northern Italy and stream path location of the Adige river (frame). (b)
2 Hillshade of the Adige river catchment with sampling locations. (c) Elevation profile of the Adige river from the source
3 to the mouth with sampling locations. For interpretation, refer to the colored web version of the paper.
4

5 **Figure 2** – (a) Hydrogen (δD) and oxygen ($\delta^{18}O$) isotope ratios of the Adige river waters in distinct seasons of the
6 biennia 2013-2015. Isotopic composition of rainfalls (light gray field) and snow/glacier melts (dark gray field) from the
7 Saldur creek catchment (UP of the Adige river) are reported for comparison (data from Figs 3 and 4 in Penna et al.,
8 2014, excluding extreme compositions). Global Meteoric Water Line - GMWL from Craig (1971). Local Meteoric
9 Water Line - LMWL (Northern Italy, dashed line) from Longinelli and Selmo (2003); (b) $\delta^{18}O$ value of the Adige river
10 waters vs sampling elevation. The isotopic composition of the Isarco river sampled in May 2015 (sample IS) and of the
11 Saldur creek sampled in August 2013 (Penna et al., 2014) and March 2015 (sample S) are also reported.
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16 **Figure 3** – (a) Oxygen ($\delta^{18}O$) and (b) hydrogen (δD) isotopic variation along the stream path of Adige river waters
17 sampled in distinct hydrological periods from August 2013 to May 2015. The isotopic composition of the Isarco river
18 sampled in May 2015 (sample IS) and of the Saldur creek sampled in August 2013 (Penna et al., 2014) and March 2015
19 (sample S) are also reported. (c) Adige river average daily discharge recorded at the hydrometric stations of Spondigna,
20 Tel, Ponte Adige, Bronzolo, Trento S. Lorenzo, Villa Lagarina, Boara Pisani during the distinct sampling periods (data
21 from Provincia autonoma di Bolzano, Meteotrentino, Autorità di Bacino del fiume Adige, ARPA Veneto). The location
22 of the confluence of some tributaries along the main streamflow is also indicated .
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28 **Figure 4** – (a) Gibbs - TDS vs $[Na+/(Na^{+}+Ca^{2+})]$ - and (b) Piper classification diagrams of Adige river waters sampled
29 in distinct hydrological periods from August 2013 to May 2015. Waters from the Isarco river (sample IS) sampled in
30 May 2015 and of the Saldur creek (sample S) sampled in and March 2015 are also reported. The Po river water
31 compositional variation (Marchina et al., 2015) is also reported for comparison (gray fields).
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35 **Figure 5** – Na^{+} (a) and Ca^{2+} (b) variation along the stream path of the Adige river waters sampled in distinct
36 hydrological periods from August 2013 to May 2015. The main lithologies outcropping along the river profile are also
37 reported.
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40 **Figure 6** – Rb vs Sr binary diagram of the Adige river waters sampled in distinct hydrological periods from August
41 2013 to May 2015. Composition of Po river water (gray field) is also reported for comparison (data from Marchina et
42 al., 2015)
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46 **Figure 7** – (a) TDS vs $\delta^{18}O$ binary diagram of the Adige river waters sampled in distinct hydrological periods from
47 August 2013 to May 2015. Fields represent the UP samples. (b) TDS variation along the stream path of Adige river
48 waters. The isotopic composition of the Isarco river sampled in May 2015 (sample IS) and of the Saldur creek sampled
49 March 2015 (sample S) are also reported. Groundw. Int. stands for samples recording groundwater interaction. See text
50 for further details.
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Dear Editor,

we are sending you a further revision of our paper No. ESPR-D-15-04563R1, titled “**Geochemistry of the Adige river water from the Eastern Alps to the Adriatic Sea (Italy): evidences for distinct hydrological components and water-rock interactions**” in which we addressed all the comments expressed by the reviewers.

Please find below detailed responses to their specific comments. Changes are visible in the “track-changes” version of the manuscript.

Kindest Regards,

Gianluca Bianchini and Co-Authors

Reviewers' comments:

Reviewer #1: I think the Authors properly replied to my comments and that the submitted manuscript can be accepted in the present form.

Reviewer #2: The revised manuscript is significantly improved following changes based on comments from all of the reviewers. In particular, the overall flow and the groundwork laid in the introduction make the objectives and methodology of the study much clearer, and it was a pleasure to read. My only hesitation in immediately recommending approval for publication is that it appears that the last page of comments in my review (#2) was not included in the revision. There are a few issues from these comments that I think still need to be addressed. First, please state whether water samples were filtered, and if so, how it was done. **THIS DETAIL HAS BEEN INCLUDED**

This is especially important for trace elements. Second, how was HCO_3^- determined? There is no description of a dedicated sample collected for dissolved inorganic carbon or an alkalinity analysis. If DIC was calculated from alkalinity and pH, and HCO_3^- was assumed to be equal to either of these quantities, this needs to be stated. **THIS DETAIL HAS BEEN INCLUDED**

Finally, the shaded areas of Fig. 7a are not explained anywhere. If these issues are addressed, I recommend publishing this manuscript and I don't need to review a revised version. **A NEW SENTENCE HAS BEEN INCLUDED IN THE TEXT PROVIDING AN EXHAUSTIVE EXPLANATION OF FIG. 7.**

Reviewer #3: I thank the authors for considering the comments provided by the reviewers. The manuscript has improved significantly compared to the first version, especially in the introduction and the discussion part. Minor comments are reported in the attached pdf file. Furthermore, the manuscript would benefit from a careful proofreading and English should be checked by a native speaker.

ALL THE LINGUISTIC IMPROVEMENTS SUGGESTED BY REVIEWER#3 HAVE BEEN INCLUDED IN THE NEW VERSION OF THE MANUSCRIPT. THE ADDITIONAL REFERENCE CARTURAN ET AL. (2015) REQUIRED BY THE REVIEWER HAS BEEN PROPERLY CITED.

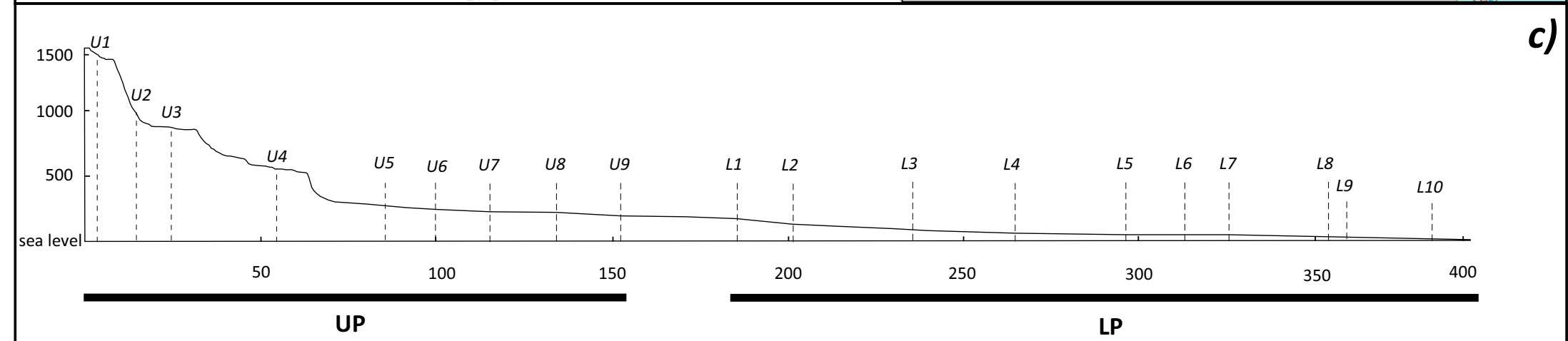
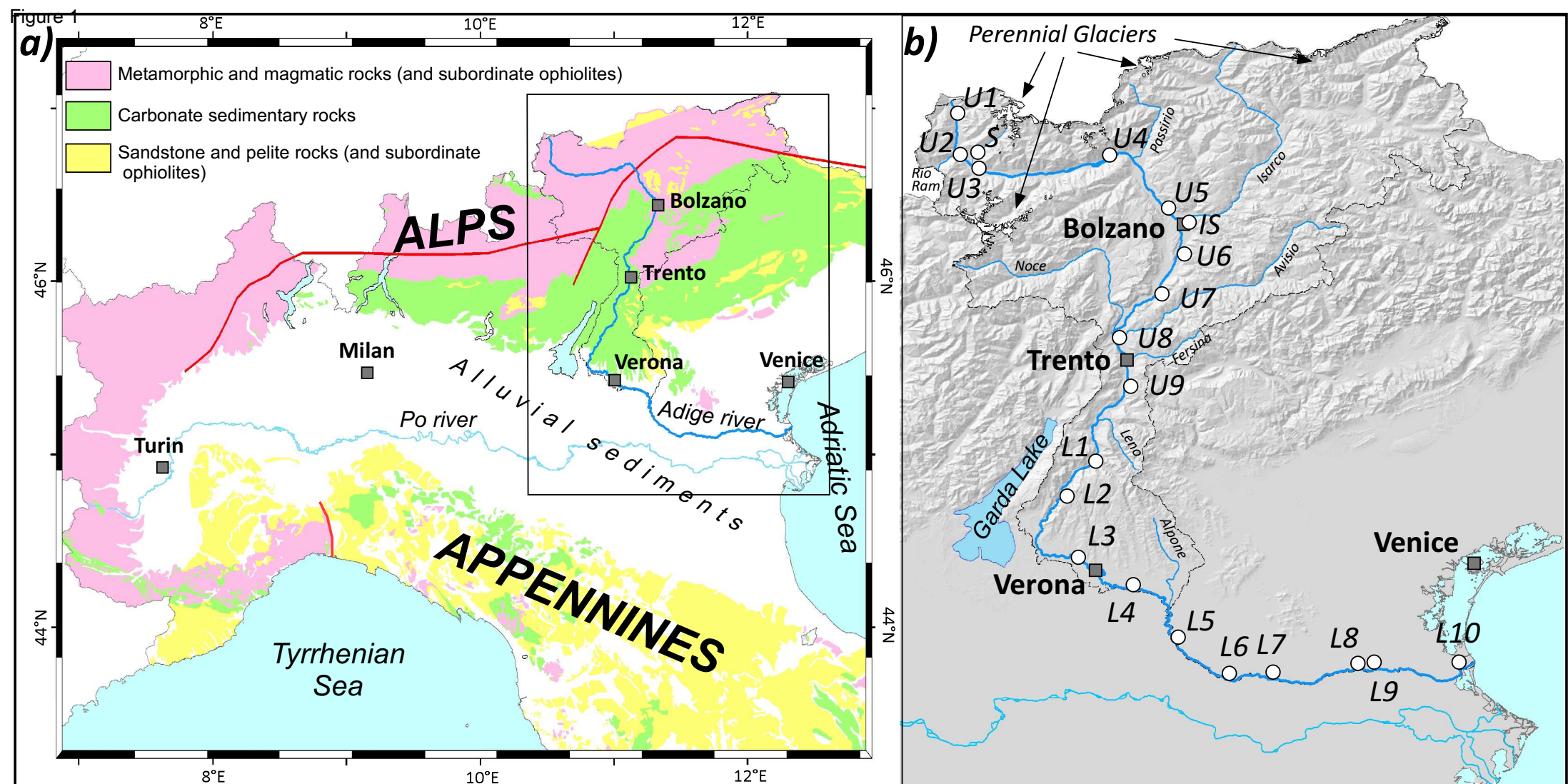


Figure 2

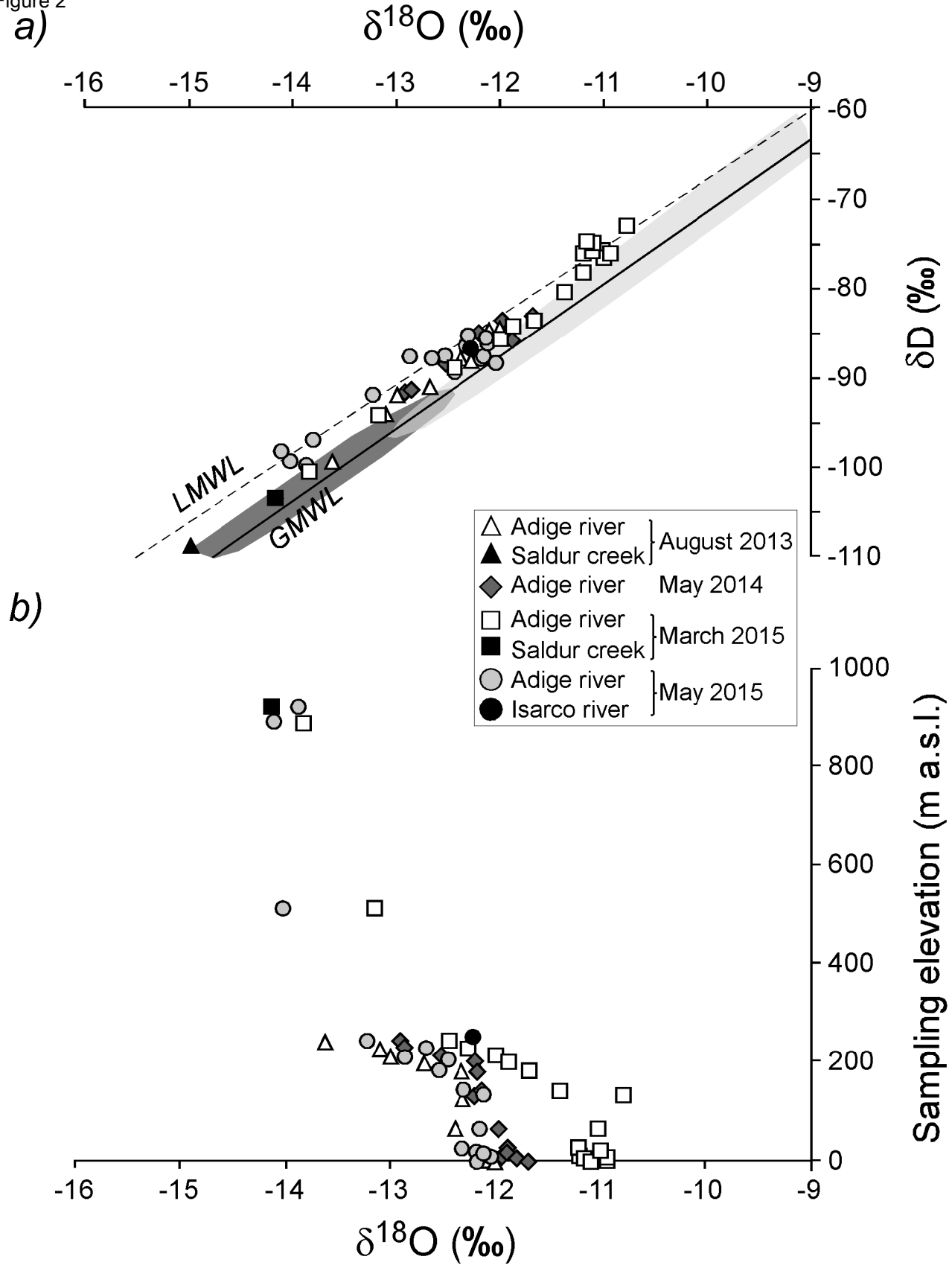


Figure 3

Distance from the source (km)

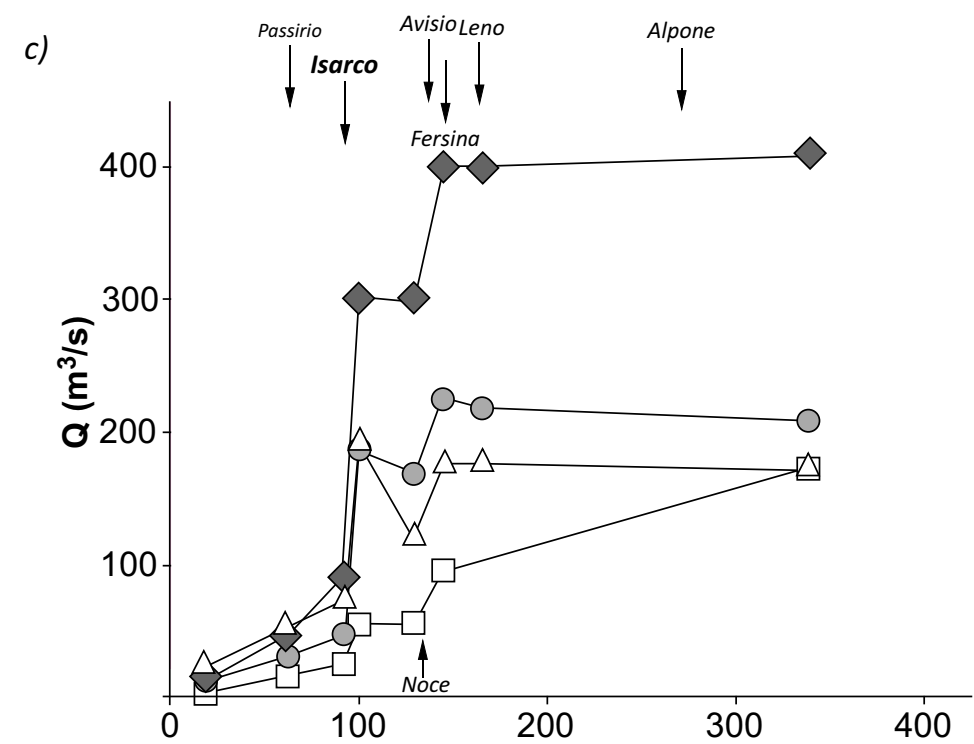
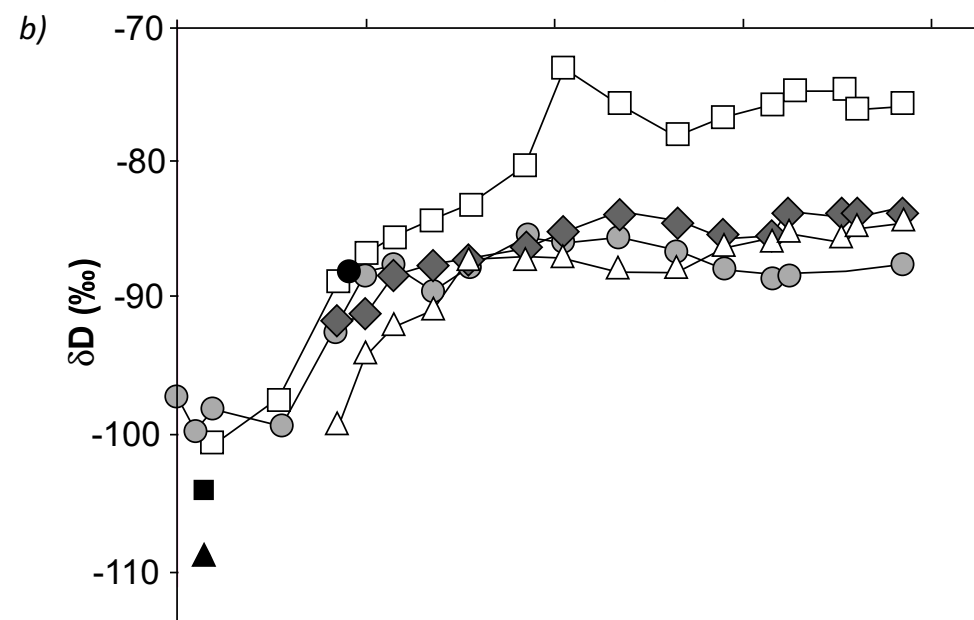
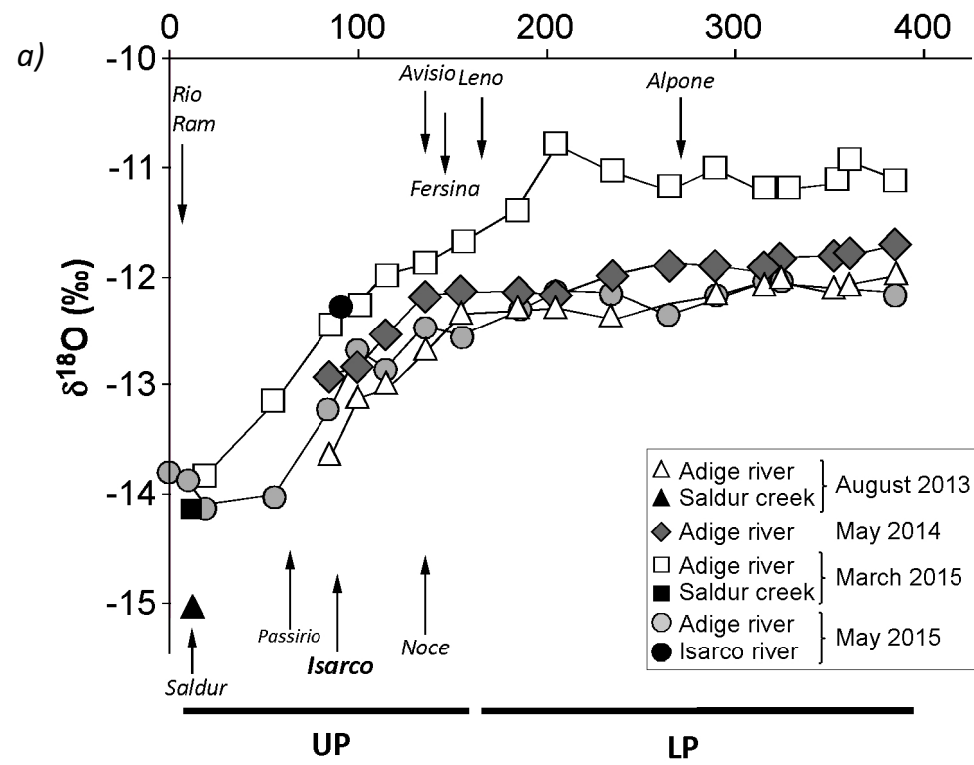


Figure 4

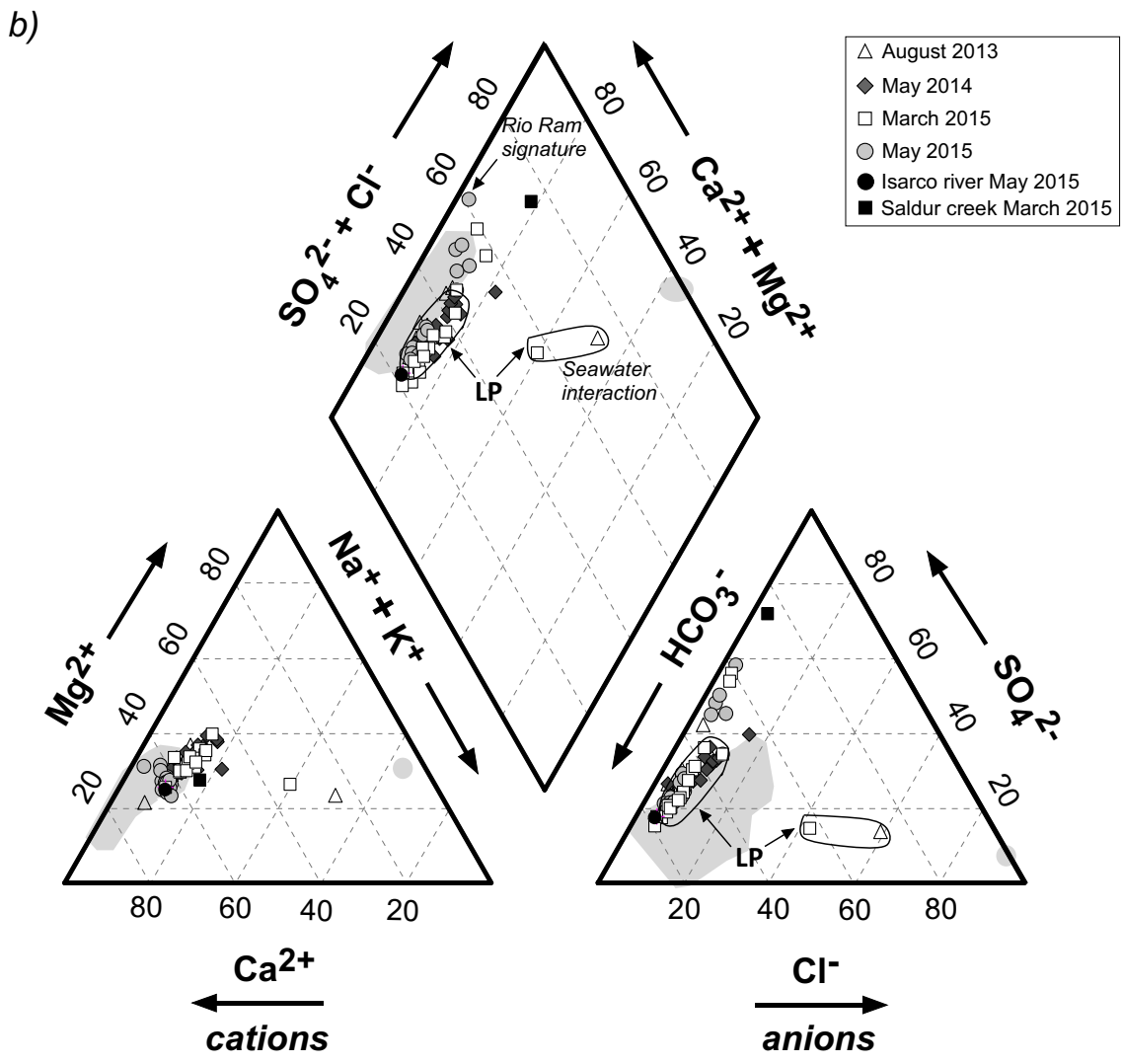
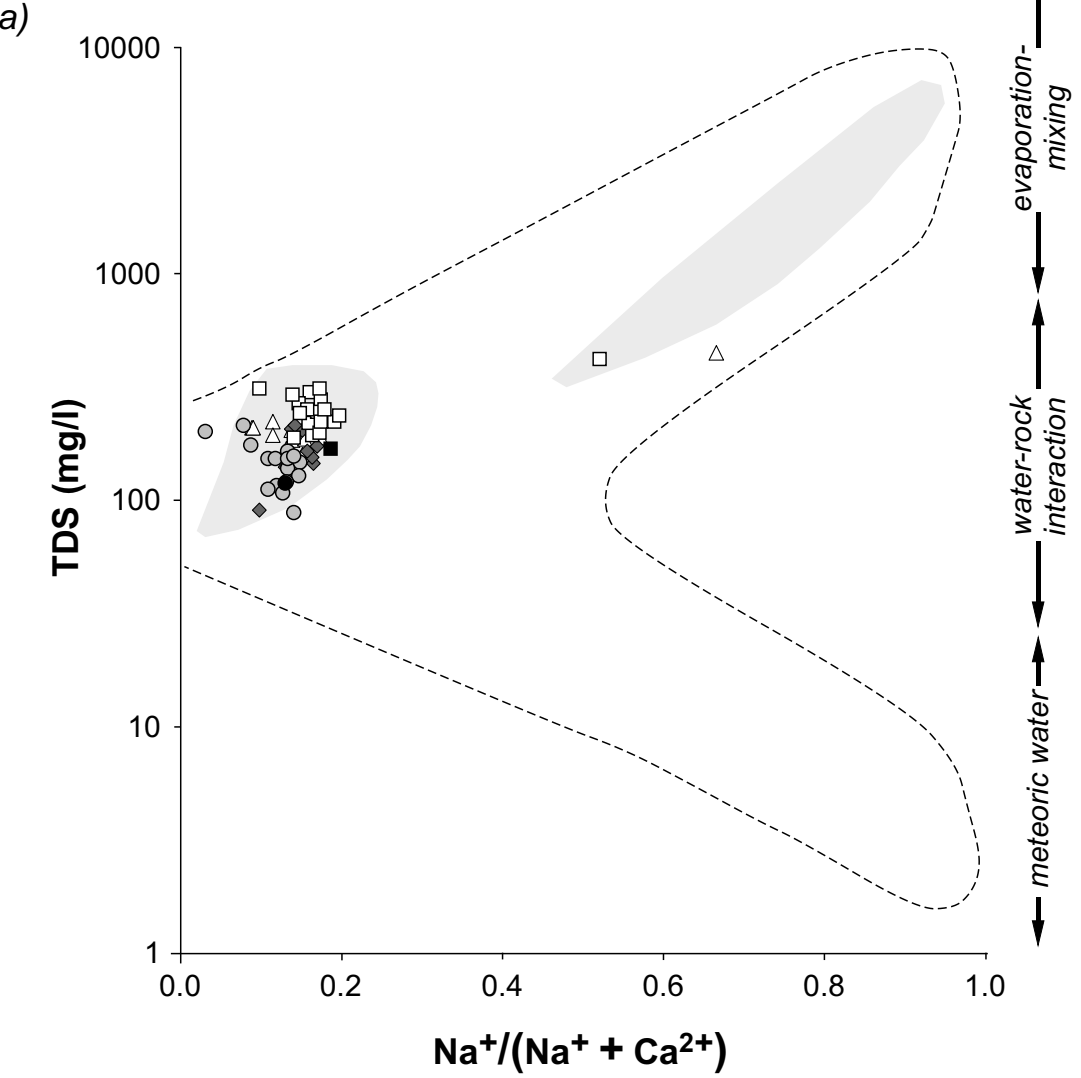


Figure 5

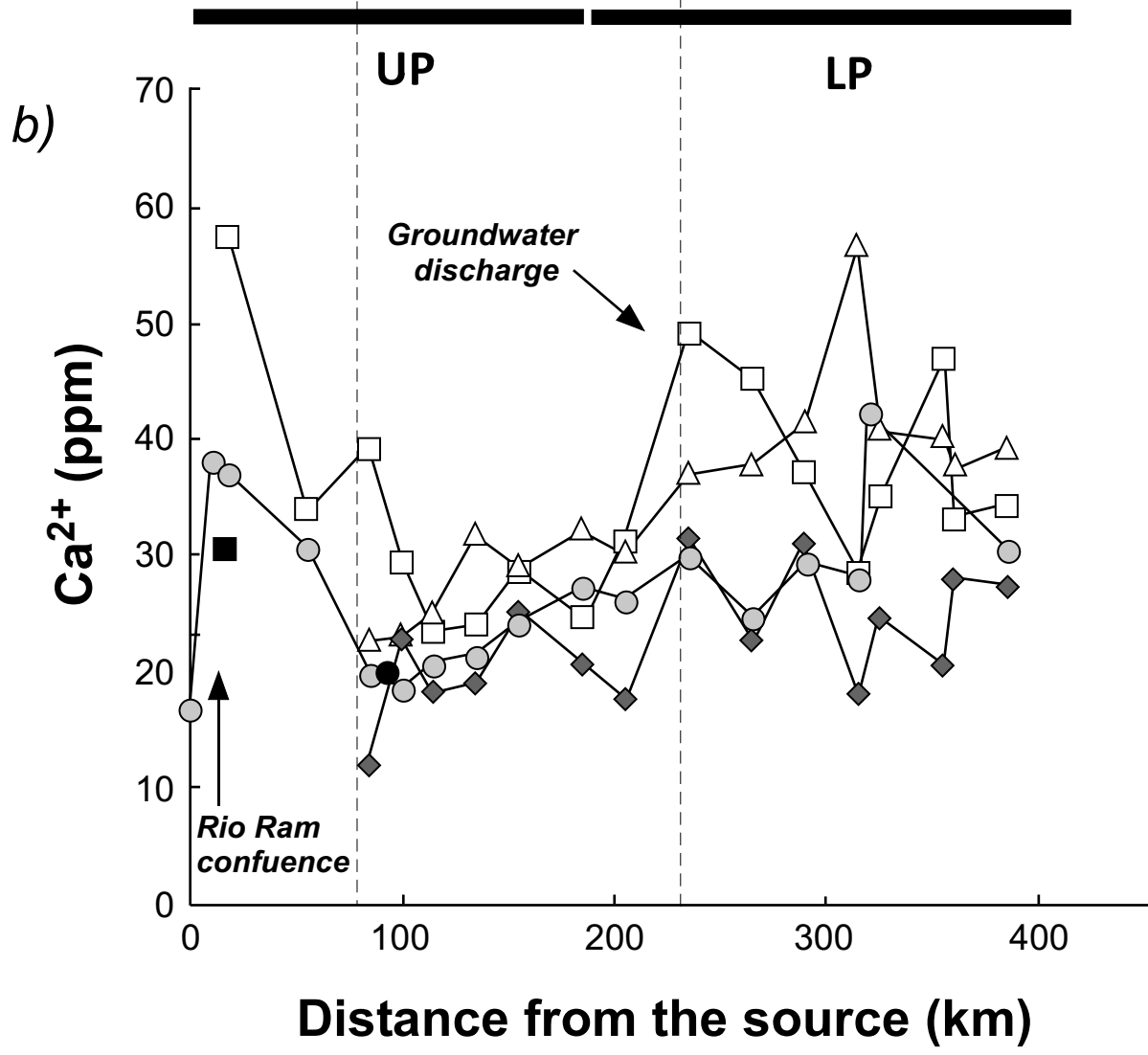
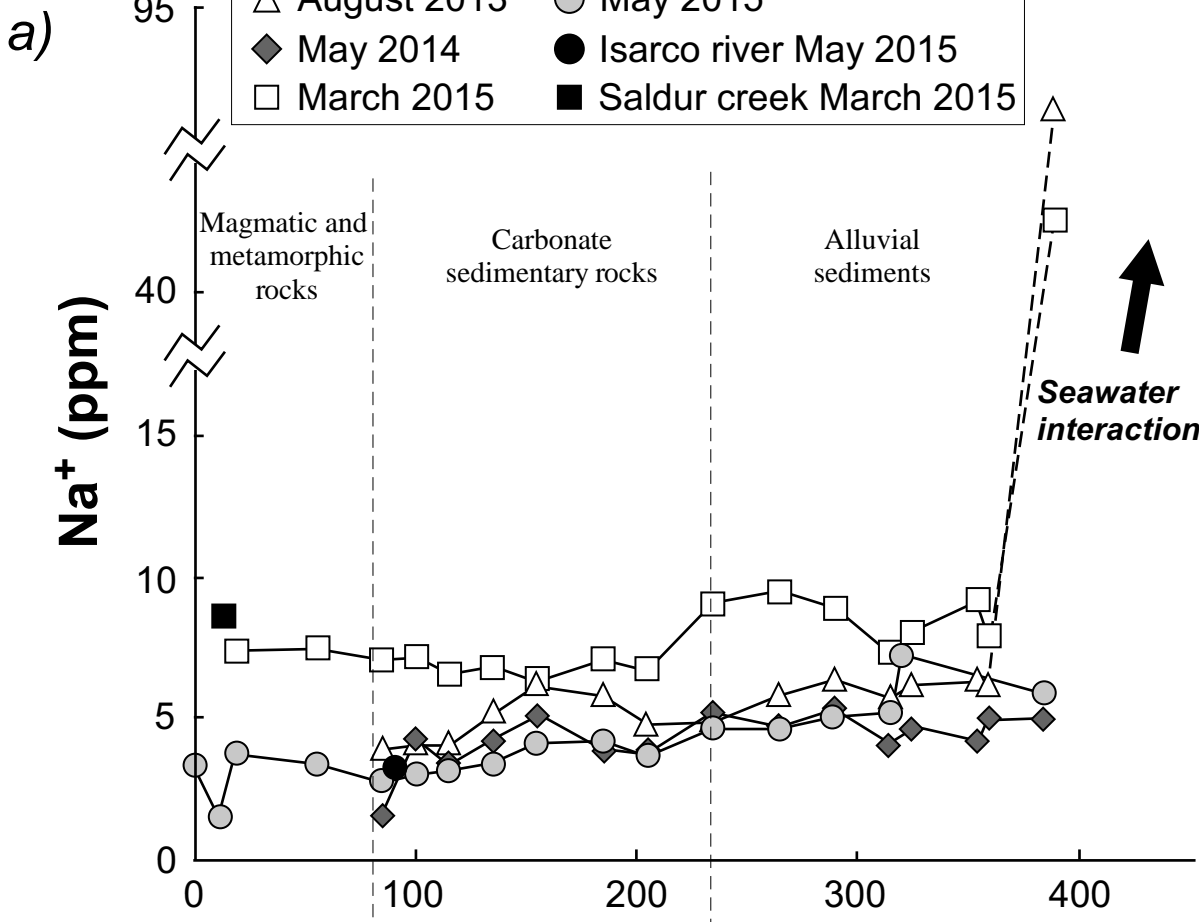
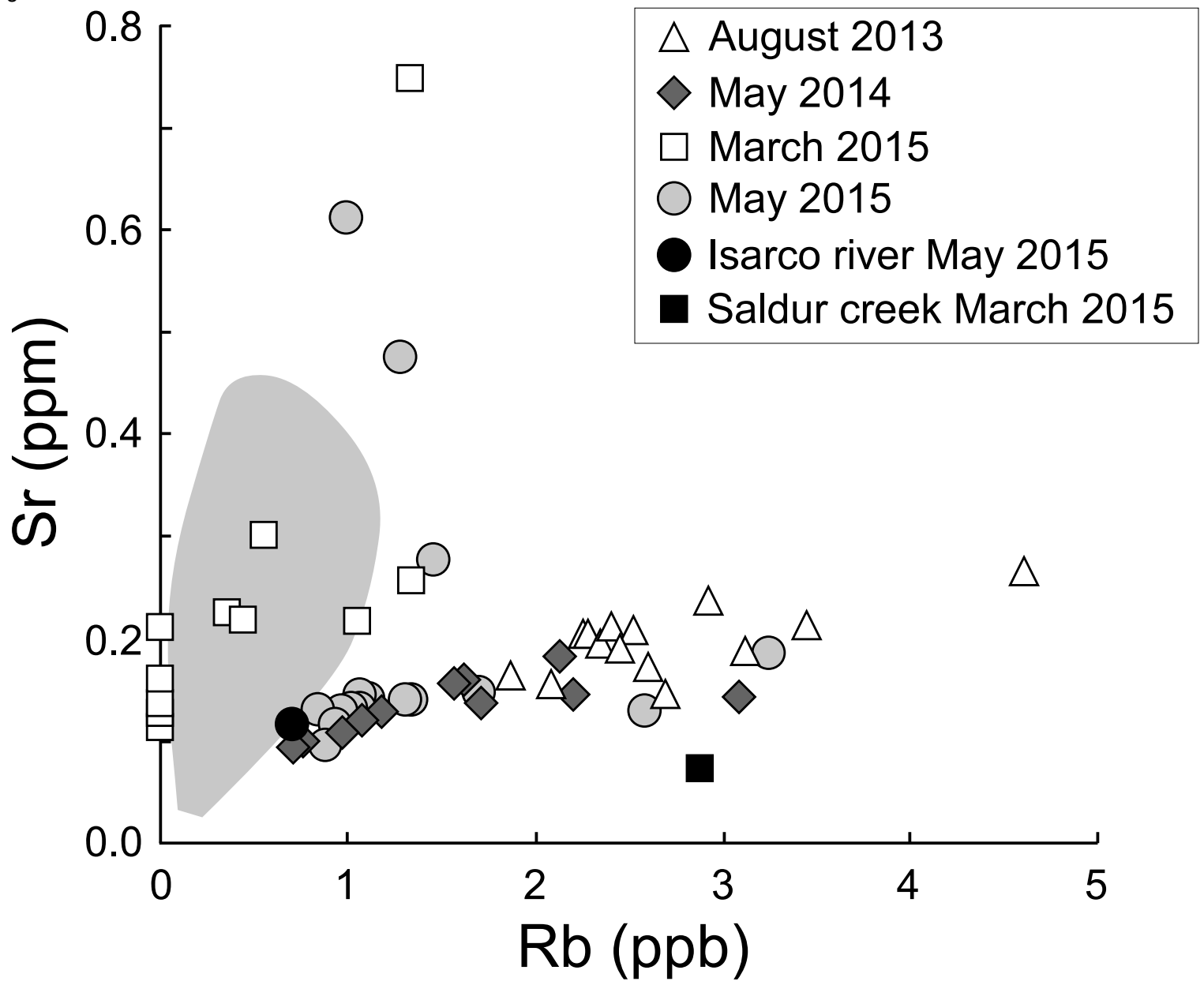


Figure 6



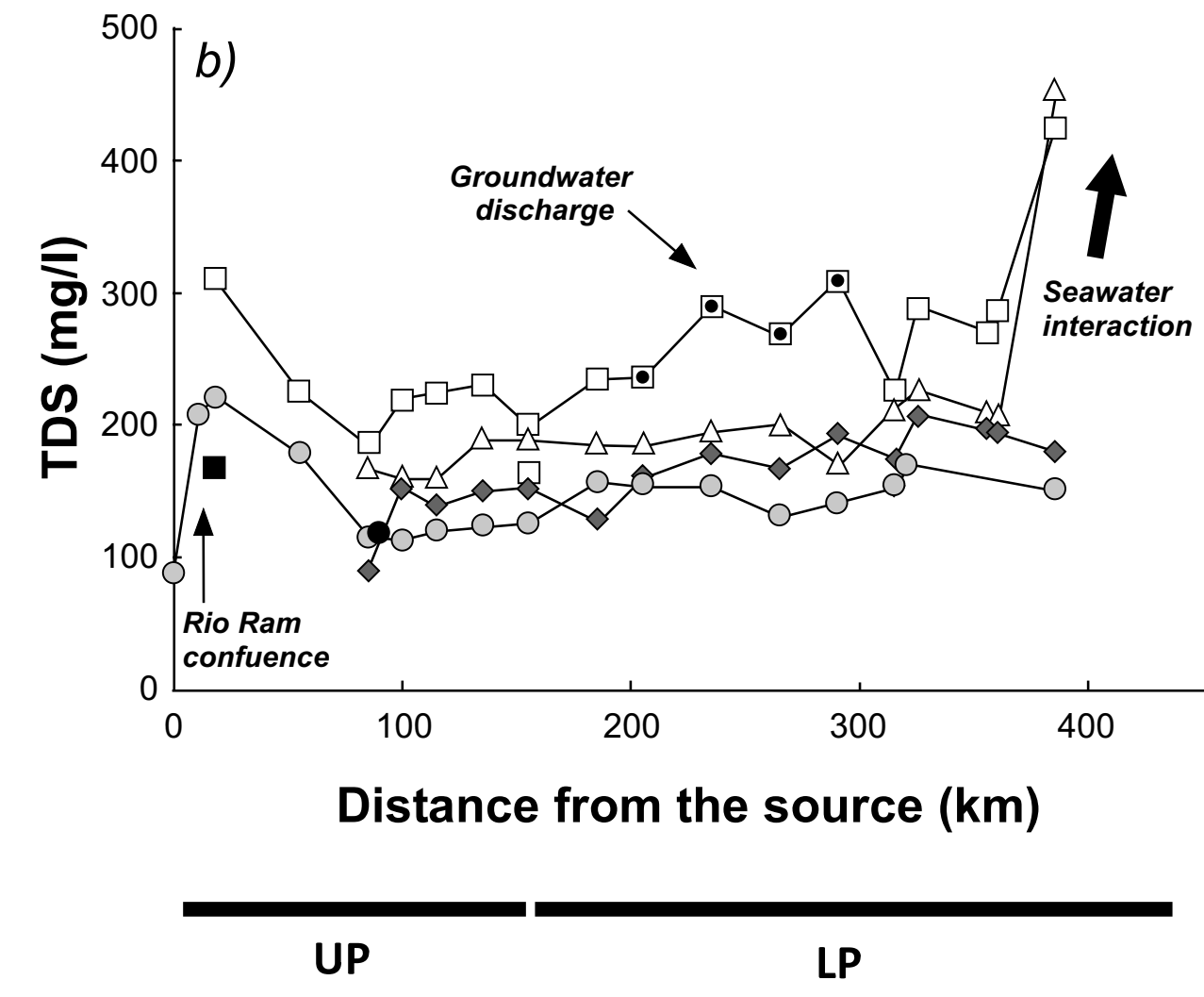
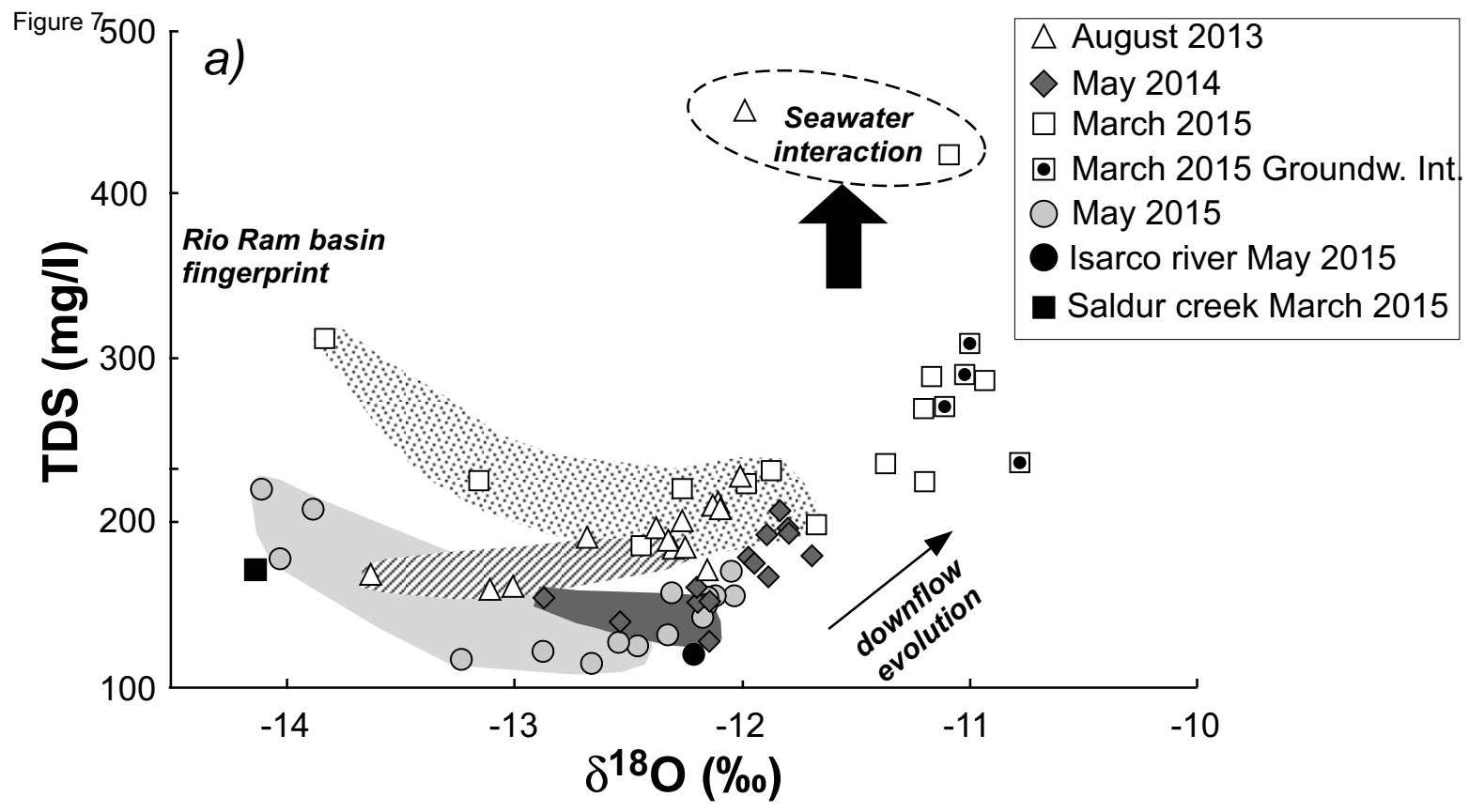


Table 1

n.	sample	Location	Date	Latitude	Longitude	Elevation (m)	Source d. (km)	pH	T(°C)	EC (µs/cm)
<i>Upper part (UP)</i>										
1	U1	S. Valentino alla Muta (BZ)	05/2015	46°46'31"	10°32'2"	1465	0	8.1	11.8	170
2	U2	Glorenza (BZ)	05/2015	46°40'13"	10°31'56"	921	11	8.1	13.0	300
	S	Saldur - Sluderno (BZ)	03/2015	46°39'53"	10°35'10"	900		8.4	10.0	190
3	U3	Spondigna (BZ)	03/2015	46°38'08"	10°36'23"	888	18.2	8.2	12.0	310
4			05/2015					7.9	13.0	300
5	U4	Tel (BZ)	03/2015	46°40'37"	11°05'06"	509	55	8.4	13.0	250
6			05/2015					8.1	14.0	240
7	U5	Andriano (BZ)	08/2013	46°52'21"	11°24'60"	242	85	7.9	13.9	230
8			05/2014					7.7	14.2	220
9			03/2015					8.0	13.0	280
10			05/2015					7.9	15.0	170
	IS	Isarco-Bolzano	05/2015	46°29'13"	11°19'56"	248		8.0	12.0	140
11	U6	Vadena Nuova (BZ)	08/2013	46°41'35"	11°31'52"	228	100	8.1	16.4	230
12			05/2014					8.0	17.9	270
13			03/2015					8.1	12.0	260
14			05/2015					8.0	12.0	140
15	U7	S. Floriano (BZ)	08/2013	46°28'68"	11°23'85"	213	115	8.1	17.2	250
16			05/2014					8.1	14.9	240
17			03/2015					8.1	12.0	300
18			05/2015					8.0	13.0	170
19	U8	Zambana (TN)	08/2013	46°15'36"	11°08'36"	201	135	8.0	18.4	270
20			05/2014					8.0	18.2	220
21			03/2015					8.1	11.0	300
22			05/2015					7.8	13.0	170
23	U9	Mattarello (TN)	08/2013	46°00'06"	11°12'33"	185	155	8.4	18.0	260
24			05/2014					8.1	16.9	240
25			03/2015					8.2	13.0	250
26			05/2015					7.9	13.0	190
<i>Lower part (LP)</i>										
27	L1	Pilcante (TN)	08/2013	45°76'62"	11°00'14"	142	185	8.4	19.1	280
28			05/2014					8.1	16.2	230
29			03/2015					8.5	13.0	260
30			05/2015					8.0	14.0	210
31	L2	Brentino Belluno (VR)	08/2013	45°65'69"	10°89'43"	133	205	8.5	18.4	270
32			05/2014					7.9	15.9	260
33			03/2015					8.4	12.0	280
34			05/2015					7.9	14.0	190
35	L3	Parona (VR)	08/2013	45°46'41"	10°94'10"	66	235	8.5	18.3	260
36			05/2014					8.1	15.8	280
37			03/2015					8.5	13.0	300
38			05/2015					8.1	15.0	200
39	L4	Zevio (VR)	08/2013	45°38'13"	11°13'51"	25	265	8.6	21.0	280
40			05/2014					8.1	16.8	260
41			03/2015					8.2	12.0	310
42			05/2015					8.5	18.0	200
43	L5	Bonavigo (VR)	08/2013	45°21'41"	11°29'79"	14	290	8.4	20.7	310
44			05/2014					8.3	18.6	270
45			03/2015					8.1	13.0	320
46			05/2015					7.8	18.0	210
47	L6	Badia Polesine (RO)	08/2013	45°10'49"	11°48'06"	13	315	8.4	21.5	300
48			05/2014					8.2	19.3	270
49			03/2015					8.0	11.0	280
50			05/2015					8.0	18.0	210
51	L7	Boara Polesine (RO)	05/2015	45°06'34"	11°47'31"	12	320	8.0	17.0	210
52		Trona (RO)	08/2013	45°10'80"	11°63'56"	11	325	8.3	23.6	300
53			05/2014					8.3	18.1	270
54			03/2015					8.1	13.0	330
55	L8	Beverare (RO)	08/2013	45°13'75"	11°94'39"	5	355	8.2	21.7	300
56			05/2014					8.3	16.7	270
57			03/2015					8.1	15.0	300
58	L9	Pettorazza (RO)	08/2013	45°13'95"	12°00'17"	4	360	8.3	20.7	290
59			05/2014					8.3	16.9	270
60			03/2015					8.2	13.0	330
61	L10	Rosolina Mare (RO)	08/2013	45°14'29"	12°30'71"	0	385	8.4	21.5	690
62			05/2014					8.3	17.1	300
63			03/2015					8.0	16.0	500
64			05/2015					8.0	12.0	140

Table 2

n.	sample	Location	Date	δD (‰)	$\delta^{18}O$ (‰)	d-exc (‰)
<i>Upper part (UP)</i>						
1	U1	S. Valentino alla Muta (BZ)	05/2015	-96.9	-13.8	13.4
2	U2	Glorenza (BZ)	05/2015	-99.7	-13.9	11.3
	S	Saldur - Sluderno (BZ)	03/2015	-103.3	-14.1	9.8
3	U3	Spondigna (BZ)	03/2015	-100.3	-13.8	10.4
4			05/2015	-98.2	-14.1	14.6
5	U4	Tel (BZ)	03/2015	-97.5	-13.1	7.7
6			05/2015	-99.2	-14.0	12.9
7	U5	Andriano (BZ)	08/2013	-99.3	-13.6	9.7
8			05/2014	-91.6	-12.9	11.7
9			03/2015	-88.9	-12.4	10.6
10			05/2015	-92.0	-13.2	13.8
	IS	Isarco-Bolzano	05/2015	-88.1	-12.2	9.6
11	U6	Vadena Nuova (BZ)	08/2013	-94.2	-13.1	10.6
12			05/2014	-91.4	-12.9	11.5
13			03/2015	-86.9	-12.3	11.2
14			05/2015	-87.9	-12.7	13.4
15	U7	S. Floriano (BZ)	08/2013	-91.8	-13.0	12.2
16			05/2014	-88.5	-12.5	11.7
17			03/2015	-85.7	-12.0	10.1
18			05/2015	-87.6	-12.9	15.3
19	U8	Zambana (TN)	08/2013	-91.0	-12.7	10.5
20			05/2014	-87.3	-12.2	10.3
21			03/2015	-84.3	-11.9	10.7
22			05/2015	-89.3	-12.5	10.3
23	U9	Mattarello (TN)	08/2013	-87.0	-12.3	11.6
24			05/2014	-86.8	-12.2	10.5
25			03/2015	-83.5	-11.7	9.9
26			05/2015	-87.7	-12.5	12.6
<i>Lower part (LP)</i>						
27	L1	Pilcante (TN)	08/2013	-86.9	-12.3	11.1
28			05/2014	-86.3	-12.1	10.8
29			03/2015	-80.3	-11.4	10.7
30			05/2015	-85.3	-12.3	13.1
31	L2	Brentino Belluno (VR)	08/2013	-86.8	-12.3	11.6
32			05/2014	-85.1	-12.2	12.5
33			03/2015	-73.0	-10.8	13.2
34			05/2015	-86.0	-12.1	10.9
35	L3	Parona (VR)	08/2013	-88.0	-12.4	11.0
36			05/2014	-83.8	-12.0	12.0
37			03/2015	-75.9	-11.0	12.3
38			05/2015	-85.5	-12.1	11.7
39	L4	Zevio (VR)	08/2013	-87.8	-12.3	10.2
40			05/2014	-84.3	-11.9	10.7
41			03/2015	-78.2	-11.2	11.4
42			05/2015	-86.5	-12.3	12.1
43	L5	Bonavigo (VR)	08/2013	-86.3	-12.2	10.9
44			05/2014	-85.8	-11.9	9.3
45			03/2015	-76.7	-11.0	11.3
46			05/2015	-87.8	-12.2	9.6
47	L6	Badia Polesine (RO)	08/2013	-86.0	-12.1	10.8
48			05/2014	-85.2	-11.9	10.3
49			03/2015	-76.1	-11.2	13.5
50			05/2015	-88.0	-12.0	8.2
51	L7	Boara Polesine (RO)	05/2015	-88.3	-12.0	8.1
52		Trona (RO)	08/2013	-85.1	-12.0	10.9
53			05/2014	-83.9	-11.8	10.8
54			03/2015	-74.7	-11.2	14.6
55	L8	Beverare (RO)	08/2013	-85.9	-12.1	11.1
56			05/2014	-83.7	-11.8	10.7
57			03/2015	-75.0	-11.1	13.9
58	L9	Pettorazza (RO)	08/2013	-84.8	-12.1	11.9
59			05/2014	-83.9	-11.8	10.4
60			03/2015	-76.3	-10.9	11.2
61	L10	Rosolina Mare (RO)	08/2013	-84.3	-12.0	11.6
62			05/2014	-83.2	-11.7	10.3
63			03/2015	-75.9	-11.1	12.8
64			05/2015	-87.6	-12.2	9.6

Table 3

n.	Sample	Location	Date	Major dissolved ions (mg/L)										Trace elements (µg/L)		
				Na ²⁺	Mg ²⁺	K ⁺	Ca ²⁺	Fe _(tot)	Cl ⁻	NO ₃ ²⁻	SO ₄ ²⁻	HCO ₃ ⁻	TDS	Li	Rb	Sr
<i>Upper part (UP)</i>																
1	U1	S. Valentino alla Muta (BZ)	05/2015	3.25	5.50	1.38	16.8	0.02	2.15	0.65	n.a.	33	88	2.11	0.88	95.0
2	U2	Glorenza (BZ)	05/2015	1.49	11.1	0.91	38.2	0.01	2.11	0.96	82.8	69	207	1.90	0.99	610
	<i>S</i>	<i>Saldur - Sluderno (BZ)</i>	<i>03/2015</i>	<i>8.22</i>	<i>9.51</i>	<i>5.87</i>	<i>30.9</i>	<i>bdl</i>	<i>2.26</i>	<i>0.86</i>	<i>78.0</i>	<i>33</i>	<i>171</i>	<i>13.4</i>	<i>2.84</i>	<i>76.8</i>
3	U3	Spondigna (BZ)	03/2015	7.29	20.3	4.95	57.2	bdl	3.92	1.15	112	102	311	7.08	1.33	748
4			05/2015	3.69	11.5	1.58	37.1	0.01	3.09	1.03	71.0	90	219	2.85	1.28	475
5	U4	Tel (BZ)	03/2015	7.42	12.7	5.71	34.1	bdl	3.62	1.31	79.3	78	224	9.21	1.34	257
6			05/2015	3.33	9.01	1.52	30.7	0.02	2.35	1.54	59.3	69	177	4.78	1.46	276
7	U5	Andriano (BZ)	08/2013	3.91	9.83	2.80	22.8	0.01	2.49	4.48	46.3	75	160	45.2	2.70	146
8			05/2014	1.50	3.70	1.27	12.0	0.01	1.05	0.76	16.1	54	91	1.05	0.71	94
9			03/2015	7.02	12.2	4.36	39.1	bdl	9.11	3.69	36.6	72	185	10.0	0.55	300
10			05/2015	2.75	5.46	1.47	19.8	0.01	1.91	1.64	33.6	48	115	3.11	1.70	147
	<i>IS</i>	<i>Isarco-Bolzano</i>	<i>05/2015</i>	<i>3.18</i>	<i>4.93</i>	<i>1.34</i>	<i>20.1</i>	<i>0.05</i>	<i>2.57</i>	<i>1.52</i>	<i>13.0</i>	<i>72</i>	<i>119</i>	<i>1.29</i>	<i>0.71</i>	<i>116</i>
11	U6	Vadena Nuova (BZ)	08/2013	4.08	8.52	1.92	23.2	0.01	3.80	2.71	21.6	93	110	44.4	1.74	150
12			05/2014	4.17	8.76	12.96	22.6	0.02	10.6	0.27	37.9	54	152	3.70	2.13	181
13			03/2015	7.11	10.3	3.98	29.4	bdl	6.97	1.94	52.7	105	219	7.05	0.37	225
14			05/2015	2.97	4.73	1.21	18.6	0.01	2.93	1.70	14.6	66	113	1.55	0.94	114
15	U7	S. Floriano (BZ)	08/2013	4.01	8.77	1.88	24.9	0.01	3.17	2.02	30.9	84	120	46.7	2.09	156
16			05/2014	3.37	8.05	4.96	18.2	bdl	5.47	1.64	24.2	72	138	1.52	0.96	131
17			03/2015	6.52	9.75	3.33	23.3	bdl	7.66	2.61	47.0	123	224	5.31	bdl	188
18			05/2015	3.07	5.32	1.22	20.5	0.03	2.62	1.63	22.2	63	120	2.00	1.05	138
19	U8	Zambana (TN)	08/2013	5.18	10.7	2.37	31.8	0.01	4.75	3.60	32.1	99	135	45.6	3.13	187
20			05/2014	4.15	9.6	6.78	18.9	0.01	6.99	1.83	26.2	75	150	1.89	1.18	129
21			03/2015	6.75	10.6	3.27	24.0	bdl	7.99	3.76	49.2	123	229	2.92	bdl	156
22			05/2015	3.39	5.6	1.28	21.4	0.02	3.12	1.84	20.8	66	124	2.07	0.97	129
23	U9	Mattarello (TN)	08/2013	6.17	10.8	3.00	29.1	0.01	5.63	5.85	31.9	96	130	44.8	2.60	171
24			05/2014	5.01	8.6	6.07	25.1	0.04	5.04	1.59	22.2	78	45	3.59	3.09	145
25			03/2015	6.27	10.2	2.53	28.7	bdl	6.77	3.58	34.9	105	198	4.27	bdl	158
26			05/2015	4.08	6.6	1.40	24.2	0.04	3.33	1.41	21.1	63	125	2.09	1.01	131
<i>Lower part (LP)</i>																
27	L1	Pilcante (TN)	08/2013	5.78	11.0	2.50	32.3	0.01	4.62	4.01	31.7	93	125	47.0	2.45	191
28			05/2014	3.79	8.10	1.70	20.6	bdl	3.48	2.11	20.9	66	127	1.49	1.07	119
29			03/2015	7.07	13.1	3.57	24.6	bdl	6.81	2.55	32.1	144	235	4.21	bdl	149
30			05/2015	4.10	7.7	1.53	27.4	0.03	3.80	2.57	22.0	87	156	2.12	1.05	146
31	L2	Brentino Belluno (VR)	08/2013	4.73	10.9	1.88	30.4	0.01	3.77	3.48	27.9	102	120	44.3	1.87	163
32			05/2014	3.83	9.12	6.07	17.6	bdl	3.48	2.11	20.9	66	127	1.10	0.87	99.2
33			03/2015	6.68	12.0	2.79	31.3	bdl	6.12	3.12	22.9	150	236	3.24	bdl	114
34			05/2015	3.62	6.83	1.25	26.2	0.02	3.25	1.98	20.4	90	154	1.66	0.84	130
35	L3	Parona (VR)	08/2013	4.90	11.0	2.71	37.0	0.02	3.95	3.08	29.9	102	130	43.6	2.29	206
36			05/2014	5.10	9.74	4.84	31.4	0.00	8.65	4.69	34.8	75	160	1.83	1.57	155
37			03/2015	9.03	15.4	4.53	49.2	bdl	8.76	3.70	35.0	162	289	5.75	0.58	225
38			05/2015	4.59	7.01	1.55	29.8	0.04	3.93	2.46	19.7	84	153	2.21	1.29	139
39	L4	Zevio (VR)	08/2013	5.83	11.1	3.00	38.0	0.01	4.93	4.09	30.3	102	130	43.0	2.42	210
40			05/2014	4.64	10.2	3.41	22.7	0.01	8.30	4.50	35.5	78	178	1.60	1.06	130
41			03/2015	9.42	14.6	5.15	45.2	bdl	9.00	4.05	35.8	144	269	6.06	1.04	217
42			05/2015	4.58	6.45	1.50	24.8	0.03	4.53	bdl	19.8	69	131	2.13	1.05	131
43	L5	Bonavigo (VR)	08/2013	6.31	12.7	3.33	41.6	0.62	5.59	5.79	30.6	63	145	42.8	3.46	213
44			05/2014	5.27	11.1	5.77	30.9	0.01	8.94	4.95	36.1	75	166	2.24	1.62	159
45			03/2015	8.84	13.8	4.28	37.1	bdl	8.99	3.67	35.2	195	308	5.57	0.45	217
46			05/2015	4.97	7.31	1.60	29.5	0.05	4.28	3.52	20.5	69	141	1.96	1.11	141
47	L6	Badia Polesine (RO)	08/2013	5.76	10.5	2.88	56.7	0.01	5.21	4.55	29.7	93	140	41.7	4.61	265
48			05/2014	4.03	9.26	3.50	18.1	bdl	9.04	5.07	37.4	87	192	1.15	0.76	100
49			03/2015	7.26	12.3	2.77	28.5	bdl	8.38	3.14	35.6	126	224	2.59	bdl	138
50			05/2015	5.15	6.96	1.87	28.3	0.05	4.60	3.70	20.1	84	155	1.92	1.33	140
51	L7	Boara Polesine (RO)	05/2015	7.19	9.71	3.19	42.2	0.18	4.70	3.08	20.7	78	169	3.84	3.24	185
52		Trona (RO)	08/2013	6.13	12.2	3.14	40.8	0.02	4.86	4.09	29.0	126	150	42.8	2.26	204
53			05/2014	4.59	10.5	4.62	24.6	0.01	8.83	3.75	36.4	90	174	1.80	1.18	129
54			03/2015	7.93	12.8	3.30	35.1	bdl	9.14	3.60	36.3	180	289	3.98	bdl	162
55	L8	Beverare (RO)	08/2013	6.35	12.5	2.86	40.2	0.02	4.99	3.77	29.6	108	140	42.2	2.53	206
56			05/2014	4.15	9.25	4.40	20.5	bdl	8.07	5.13	46.8	102	207	1.07	0.96	110
57			03/2015	9.10	14.7	3.67	47.0	bdl	9.31	3.91	37.4	144	270	5.20	bdl	212
58	L9	Pettorazza (RO)	08/2013	6.12	12.1	2.74	37.7	0.02	4.52	3.48	28.9	111	130	41.8	2.35	194
59			05/2014	4.94	9.9	5.57	27.9	0.02	7.83	4.52	49.5	96	196	2.71	2.21	144
60			03/2015	7.83	12.8	3.72	33.2	bdl	9.16	4.56	36.9	168	287	3.84	bdl	150
61	L10	Rosolina Mare (RO)	08/2013	91.2	22.7	5.59	39.3	0.01	139	3.32	43.5	108	300	43.9	2.93	236
62			05/2014	5.03	10.4	3.52	27.2	0.02	6.65	3.73	32.1	90	179	2.13	1.71	138
63			03/2015	43.5	16.2	4.33	34.3	bdl	99.6	4.51	46.5	174	424	4.18	bdl	160
64			05/2015	5.79	6.85	2.79	30.6	0.16	2.57	1.52	13.0	72	119	2.97	2.59	129