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Effects of the 2017 drought on isotopic and geochemical gradients in the Adige catchment, Italy

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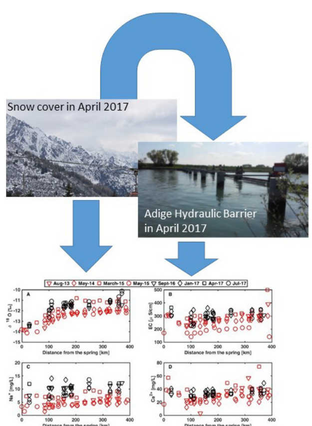
HIGHLIGHTS

- Isotopic and geochemical dataset for the Adige catchment during drought conditions
- Analysis of spatial and temporal variability in isotopic and geochemical composition.
- Source of the 2017 drought was lack in winter precipitation.
- Isotopic water composition highly sensitive to the drought
- Water geochemical composition generally not affected by the drought

GRAPHICAL ABSTRACT



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ABSTRACT

Drought events can significantly influence the isotopic and geochemical composition of surface water even in large (>1000 km^2) catchments. Monitoring this variability is challenging, due to the practical difficulty in carrying on adequately resolved (both in time and space) sampling campaigns. This study presents a dataset collected during the drought occurred in 2017 in the Adige catchment. The low flow conditions were caused by a remarkable lack of fall and winter precipitations throughout the entire catchment. This led to higher $\delta^{18}O$ and δD values during spring and summer than in samples collected for the period 2013–2016. The low discharge was generally not associated with an isotope fractionation effect due to evaporation and the river water signature was still in agreement with the local meteoric water line. The drought had an important impact on the geochemical composition of the water close to the river mouth, evidencing the occurrence of saltwater intrusion up to the hydraulic barrier (4.2 km far from the river mouth) constructed with the purpose of limiting this negative effect. The Alpone subbasin was the most impacted one by the drought showing anomalously high values in ionic content, EC (up to 647 μS/cm) and isotopic composition (up to −7.58‰ and −51.4‰ for $\delta^{18}O$ and δD, respectively). The Adige catchment overall showed a good resilience towards this extreme event thanks to the contribution of baseflow, highlighting the importance of groundwater resources management in the catchment.

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1. Introduction

The analysis of isotopic and geochemical parameters provides important information about the hydrological functioning of a catchment (Chiogna et al., 2014; Leibundgut et al., 2009; Penna et al., 2017a; Tetzlaff et al., 2017). Studies using tracer time series with a high temporal resolution are getting more and more common (e.g., Birkel et al., 2010; Penna et al., 2017b; Engel et al., 2018; Volkmann and Weiler, 2014) and facilitate the understanding of local scale hydrological processes in medium to small size catchments (i.e., smaller than 10–100 km^2). The investigation of hydrological processes in large catchments (i.e., >1000 km^2) are still challenging due to the large number of sampling locations needed to get a comprehensive overview of the ongoing processes and the inherent costs and technical as well as organizational difficulties related to a highly resolved sampling campaign over a large area (Marchina et al., 2016; Nasrabadi et al., 2016; Halder et al., 2015; Reckerth et al., 2017). Moreover, large-scale event-based sampling campaigns have often the limitation of representing only a snapshot of the existing conditions in the catchment and the representativeness of the outcomes could be questionable.

Water stable isotopes and water geochemical composition have been used in large catchments to identify the hydrological behaviour under stress conditions (e.g., Lambs et al., 2005; Petelet-Giraud et al., 2017), such as drought events. Among others, Wu et al. (2018) observed that the isotopic composition along the Yangtze River in drought years changes depending on the regulation of the Three Gorge Dams and they were able to identify the major role played by lakes and artificial reservoirs in the catchment. Vanplantinga et al. (2017) identified that, in the highly regulated Brazos River catchment, drought events enhance reservoir discharge dominance while under undammed conditions a run-off and baseflow dominance would be expected. Martínez et al. (2017) applied hydrochemical and stable isotope data to differentiate between baseflow and direct runoff in the Quequén Grande River and were able to identify the characteristic water signature occurring during La Niña phase of the ENSO (El Niño Southern Oscillation). Marchina et al. (2017) showed the impact of the 2015 drought event on the water composition of the Po river delta and observed a high sensitivity of the isotopic signature to drought events.

This work aims at identifying the effects of the 2017 drought on the isotopic and geochemical composition of the Adige river water. The comparison of our results with those presented in Natali et al. (2016) for the same catchment allows us describing the temporal dynamics of the isotopic and geochemical signature of the Adige catchment over 4 years. Therefore, in our study, we do not limit our investigation to the spatial and seasonal variability of water composition, but we can provide a more comprehensive temporal analysis comparing data collected in different hydrological years (2013–2017). Moreover, we present novel results about the isotopic and geochemical composition of important tributaries of the Adige river, i.e., Passirio, Talvera, Isarco, Noce, Avisio, Fersina, Leno and Alpone, to investigate the effect of the drought on different parts of the catchment.

The collection of isotopic and geochemical information at the river basin scale is beneficial to manage the effects of multiple stressors on aquatic ecosystems with water scarcity. This is the final goal of the FP7 European project Globaqua (Navarro-Ortega et al., 2015) and the Adige catchment is one of the Globaqua river basins under investigation. A review about the hydrological and chemical studies available for this river basin was provided by Chiogna et al. (2016). The authors highlighted the lack of an integrated and comprehensive characterization of the Adige river at the basin scale. In the framework of the Globaqua project, new studies focusing on water quality (Diamantini et al., 2018; Lutz et al., 2016; Mandaric et al., 2017), eco-hydrology (Vigiak et al., 2018), climate change (Gampe et al., 2016; Marcolini et al., 2017) and hydrology (Chiogna et al., 2018; Laiti et al., 2018; Tuo et al., 2018a; Tuo et al., 2018b; Tuo et al., 2016) have partially filled this gap of knowledge. Complementary to these existing studies we additionally focus on the consequences of hydrological variably in the lower part of the river basin (i.e., the part of the river located in the Veneto Region, about 210 km downstream the spring of the river) and we investigate the behaviour of the entire catchment under the drought occurred in 2017. The Adige catchment allows us to investigate the behaviour during a drought of a river basin entailing both Alpine as well as Mediterranean hydrological conditions, in the upper and lower part, respectively, and highly affected by anthropic activities (e.g., damming).

The goals of this work are therefore i) to complement the available dataset presented by Natali et al. (2016), including an analysis of the main tributaries of the Adige catchment, ii) to explore the seasonal dynamics in the isotopic and geochemical composition of the water in the Adige catchment and iii) to investigate how the drought occurred in 2017 differently affected the geochemical and isotopic water composition of different parts of the Adige river basin.

2. Material and methods

2.1. Catchment description

The Adige river basin (Fig. 1) has a catchment area of about 12,100 km^2 and the discharge shows the typical behaviour of Alpine catchments, with peaks usually registered during the melting period from June to September. More details about hydrological and chemical stressors of the catchment as well as its ecological status are given in Chiogna et al. (2016). Precipitation is not evenly distributed in the catchment and varies between 500 mm/y in Val Venosta (north-west part of the catchment) and 1600 mm/y in the southern part of the basin (Duan et al., 2016; Laiti et al., 2018). Temperature is also highly variable in the catchment due the high elevation gradient. Mean monthly temperatures range between 14 °C in July and −4 °C in January and December (Laiti et al., 2018). The mean water discharge is about 202 m^3/s at the Boara Pisani gauging station. The catchment in its northern part is characterized by the presence of large artificial reservoirs mainly used for hydropower production, which significantly alter the flow regime and influence water availability (Zolezzi et al., 2009; Chiogna et al., 2018). The Adige river is affected by salt water intrusion, particularly during low flow conditions, potentially up to a distance of 20 km from the river mouth (Bogoni, 2013). In order to prevent a deterioration of the river fresh water quality a hydraulic barrier is present to prevent the intrusion of saline water in the river channel. Fig. 1 shows the catchment area, the sampling locations and the boundaries of the sub-catchments covering the main tributaries, i.e., Isarco, Talvera, Passirio, Noce, Avisio, Leno, Fersina and Alpone.

2.2. Sampling campaigns and analytical methods

Four sampling campaigns were performed between September 2016 and July 2017: sampling campaign 1 in September 2016 (23–24.9.2016), sampling campaign 2 in January 2017 (13–15.01.2017), sampling campaign 3 in April 2017 (03.–06.04.2017) and sampling campaign 4 in July 2017 (17.–18.07.2017). The sampling campaigns were performed after a period of at least 4 days where no significant precipitation events interested large parts of the catchment (though in the sampling campaign of July local storm events occurred) and in days free of precipitation events to avoid isotopic signatures influenced by rainfall and direct runoff or diluted ionic composition. However, in sampling campaign 4, the point 03 (Campo di Trens) was sampled during a heavy precipitation event. During sampling campaign 4, the point 16 (Alpone), was almost dried out. Flow was discontinuous and the water sampling was conducted in a remaining pond in a shadowed place.

The samples were taken using a rope and bucket if taken from bridges or a telescope bar in order to sample the water from the main part of the stream. The sampling locations were chosen considering the locations for which discharge and water level data were publically available

Table 1
Sampling point coordinates, distance from the source and elevation.

#	Sampling point	Latitude	Longitude	Distance from source [km]	Elevation (sampling location) [m a.s.l.]
1	Adige_a_Spondigna	46°37′57.66″N	10°36′48.38″E	28	885
2	Passirio_al_Saltusio (Merano)	46°39′58.39″N	11° 8′48.68″E	75.5	305
3	Campo_di_Trens	46°52′11.23″N	11°28′53.78″E	–	938
4	Talvera Bolzano (inflow to Isarco)	46°29′41.64″N	11°20′53.11″E	103	270
5	Ponte_d'Adige	46°29′4.62″N	11°17′57.02″E	101	242
6	Isarco_a_Bolzano_Sud	46°28′12.72″N	11°18′30.78″E	103	241
7	Adige_Bronzolo	46°24′50.41″N	11°18′55.08″E	110	231
8	Noce_Mezzolombardo	46°13′45.7″N	11°04′31.4″E	141	252
9	Avisio_Lavis	46°08′17.78″N	11°07′7.65″E	148	246
10	Adige_Ponte_SanLorenzo	46°04′13.11″N	11°06′52.97″E	155	191
11	Torrente_Fersina	46°03′18.46″N	11°07′24.71″E	157	195
12	Adige_Mattarello	46°00′34.05″N	11°07′22.10″E	162	185
12.5	Adige_Isera (before Leno)	45°53′ 4.056″N	11°01′1.992″E	181	168
13	Leno_Rovereto	45°53′0.78″N	11°02′1.86″E	180	186
14	Adige_Rovereto	45°51′46.34″N	10°59′57.49″E	184	161
15	Adige_Verona	45°25′38.81″N	11°01′17.01″E	249	46
16	Alpone	45°25′17.61″N	11°17′13.65″E	270	35
17	Boara_Pisani	45°06′20.02″N	11°47′3.65″E	327	5
18	Pre_Portesine (pre_barrier)	45°06′38.4″N	12°11′27.0″E	386	3,3
19	after_barrier	45°08′35.21″N	12°18′32.73″E	398	0

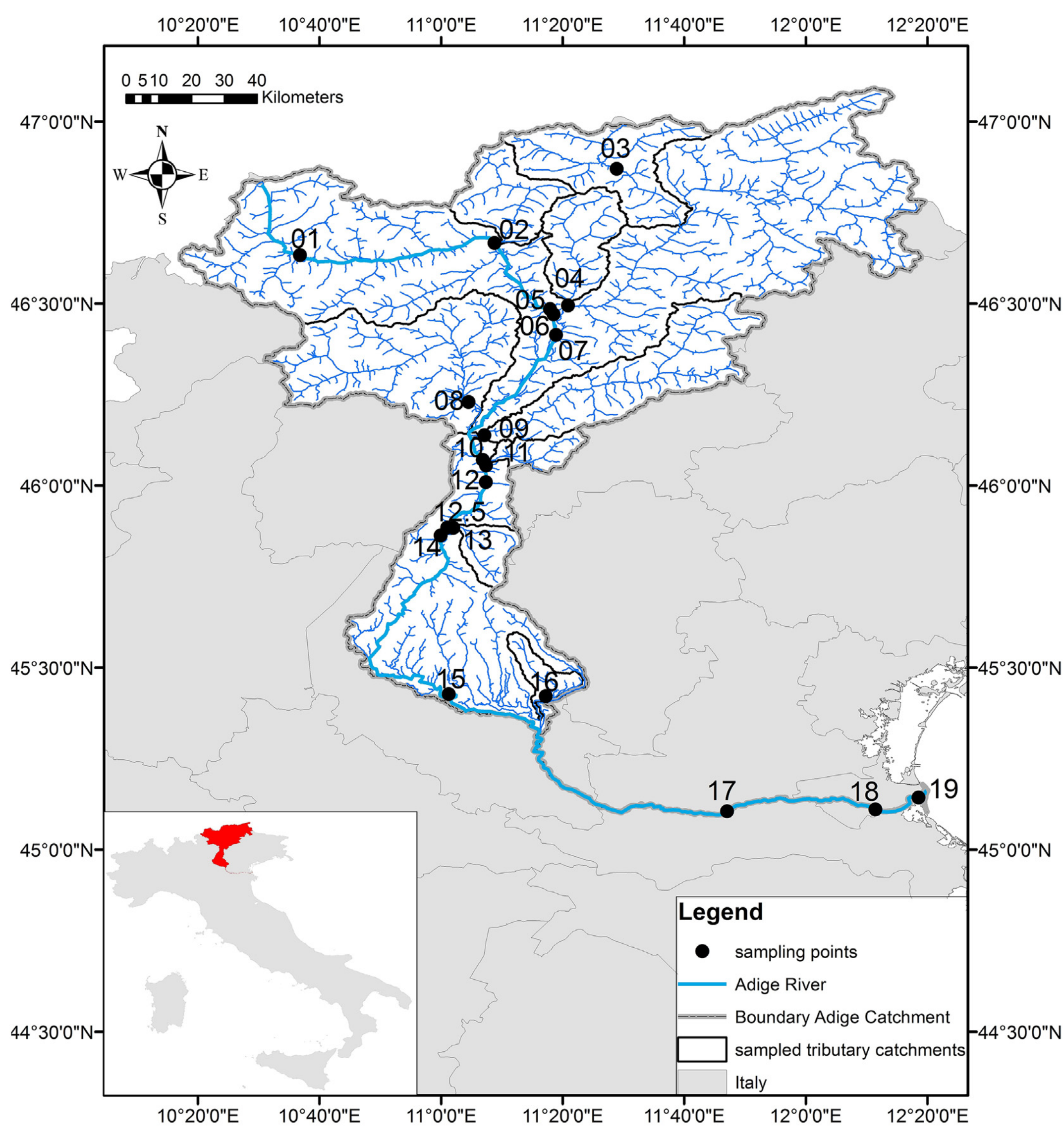

Fig. 1. The Adige catchment and the sampling locations (the name of the sampling points are reported in Table 1). The boundary of the sampled tributary catchments is indicated with a black contour line.

on the web page of the water authority of the Adige river. The information about discharge and water level is important for the interpretation of the results, since tributaries located in the upper and middle part of the catchment as well as the Adige river are affected by hydropeaking, i.e., sudden fluctuations in river stage caused by the release or storage of water in artificial reservoirs (Hauer et al., 2017).

LDPE (low density polyethylene) samplings bottles were used in double amount (50 ml and 100 ml each sample) to allow for replicates. Samples were taken without any headspace in the bottle which increases accuracy of pH measurements in the laboratory. The samples were stored at about 10 °C during the duration of the sampling campaigns to prevent isotopic fractionation due to evaporation and freezing. After each campaign, the samples were stored between 8 °C and 16 °C in the dark. Electrical conductivity (EC, considered the specific value at 25 °C) and pH were measured before the samples were prepared for the analysis of water stable isotopes and ions by filtering through 0.45 μm nylon filters. The pH was measured using a pH sensor (Inlab Micro, Mettler Toledo) connected to a pH-meter (pH 3110, WTW). The electrical conductivity was measured using a portable conductivity meter (Cond 3110, WTW). Samples for both ion and stable water isotope (δ^2H, δ^{18}O) measurements were transferred to 2 ml glass vials and stored at 4 °C before analysis. The stable isotopes of water (δ^2H, δ^{18}O) were determined using a water isotope analyzer (L-2130i, Picarro Inc. Santa Clara, USA), with precision of the instrument (1σ) better than 0.03‰ and 0.2‰ for δ^{18}O and δ^2H, respectively. Standard deviations of repeated measurements (five to six times) were on average 0.07‰ and 0.3‰ for δ^{18}O and δ^2H, respectively. A two-point calibration with laboratory reference material calibrated against VSMOW-SLAP (Vienna Standard Mean Ocean Water-Standard Light Antarctic Precipitation) scale was used. Results of stable isotopes of water are presented as δ-values (‰). The d-excess values were computed assessing potential evaporation effects (d-excess $=\delta$D-8 δ^{18}O). Ion analyses (NO_3^-, Cl^-, HPO_4^{3-}, SO_4^{2-}, K^+, Mg^{2+}, Ca^{2+}, Na^+) were conducted by means of ion chromatography using a coupled Dionex ICS 1100 system equipped with a AS4A 4 × 250 mm and a CS12 A 4 × 250 mm column for anions and cations respectively. The analytical precision of the instrument is <3% and the standard deviation of repeated (2×) measurements is on average 1.9% of sample concentration. The HCO_3^- concentration was computed considering the ionic balance.

3. Results

3.1. Hydrological and meteorological conditions

The Adige Water Authority, the meteorological survey of the Province of Trento and the one of the Province of Bolzano, highlighted in several technical reports the fact that the hydrological year 2017 was very dry (see Fig. 2 for a monthly comparison with a long term average for the meteorological station of Trento-Laste). In particular, low amount of precipitation fell during fall and winter (e.g., Egiatti, 2017; Munari et al., 2018; Barbiero et al., 2017), while starting from June we had precipitations above the average, yet occurred in spatially limited storm events (Munari et al., 2018). As an example, in Fig. 2 we provide the data for the meteorological station of Trento-Laste (close to the gauging station of Trento Ponte San Lorenzo), which is one with the longest record of precipitations in the catchment. Although it is difficult to describe the precipitation of a catchment with such a complex morphology with a single station, in the specific case of 2017, due to the extensive lack of precipitation, we can consider the station of Trento-Laste as a good example for the entire catchment, in particular for the winter period. There was no measurable precipitation in December and also January was scarce in terms of precipitation. The total winter precipitation, computed considering December, January and February, reached 76.5 mm in 2017 which is about 50% less than the average value computed for the entire time series over the period 1920–2017.

Considering temperature, the year 2017 was not excessively warm, as shown for the station of Trento-Laste in comparison to the mean temperature computed over the period 2003–2017 (Fig. 2). The scarcity in snowfall events during the winter had important consequences for the discharge in the following spring and summer months. For example, the minimum flow registered in April 2017 at the gauging station of Boara Pisani (24.9 m^3/s) had a return period of 59 years (Egiatti, 2017), while the river gauging stations located in South-Tyrol registered

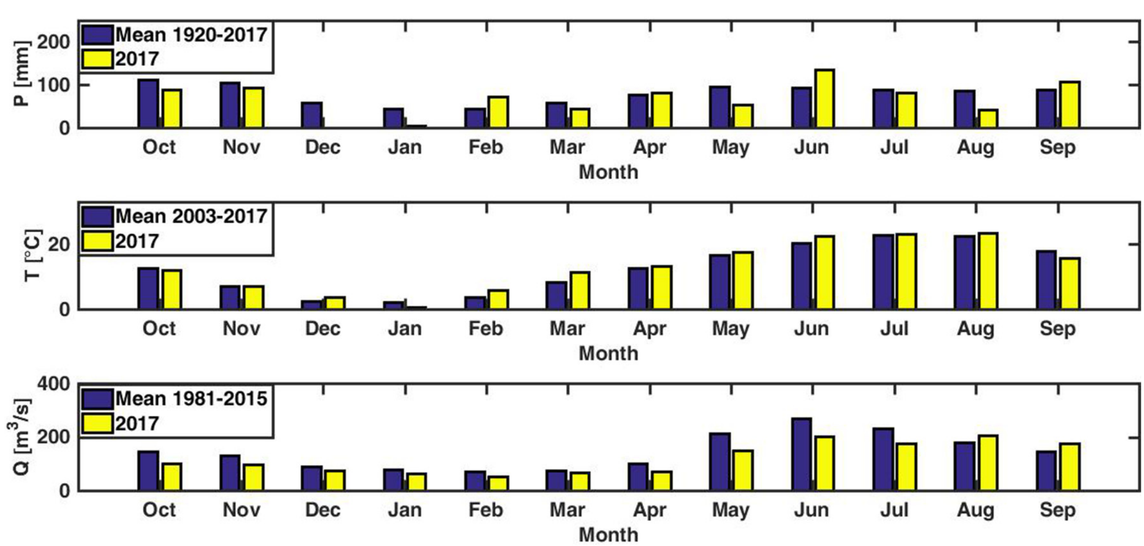

Fig. 2. Comparison between cumulative monthly precipitation of the hydrological year 2017 and the mean from 1920 to 2017 for the station Trento Laste (upper panel); Comparison between mean monthly temperature of the hydrological year 2017 and the mean from 2003 to 2017 for the station Trento Laste (central panel); comparison between mean monthly discharge of the hydrological year 2017 and the mean monthly discharge computed over the period 1981–2015 for the gauging station Bronzolo (lower panel).

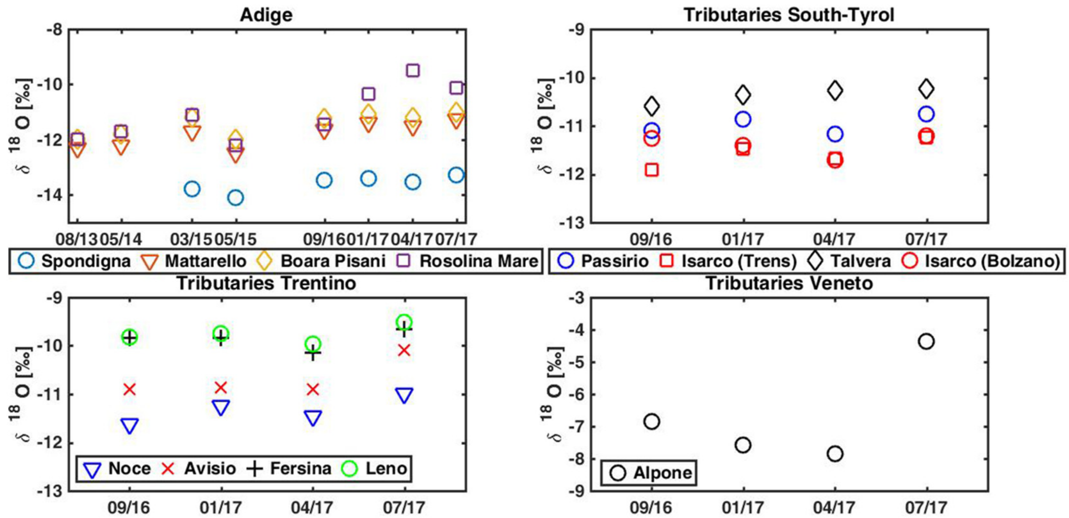

Fig. 3. Temporal variability of $\delta^{18}O$ in four gauging stations along the Adige river and some of its tributaries. Data for the Adige in 2013, 2014 and 2015 are from Natali et al. (2016).

mean monthly discharge values between 10% and 30% lower than the mean values computed over the period 1981–2016 from October 2016 until July 2017 (see for example in Fig. 2 the mean monthly discharge in Bronzolo).

3.2. Spatial and temporal isotopic variability

Fig. 3 shows the temporal variability of the oxygen isotopic composition of the Adige and of its main tributaries in the upper part of the river (South-Tyrol), in the middle part of the river (Trentino) and in the Southern part of the river (Veneto). Considering the Adige river, we provide the results for the stations where samples were taken also by Natali et al. (2016), i.e., Spondigna, Mattarello and Rosolina mare (in our study called "after barrier") or in location which are close enough to be compared accurately (Boara Pisani). We can observe an increase in the $\delta^{18}O$ values over time. Such increase is not monotonic as it depends on the relative contribution of snow and glacier melt which leads in general to more negative values during the melting season than during winter time (e.g., Chiogna et al., 2014). The isotopic signature of the tributaries shown in Fig. 3, varies from the highest observed negative values in the upper part of the catchment towards less negative values in the lower part of the catchment.

The increase in the isotopic values depends mainly on the mean catchment elevation of the subcatchments contributing to the streamflow of the Adige river (Fig. 4). Precipitation is characterized by a more negative signature at higher elevations than at lower elevations, although isotopic signature of snow melt can be highly variable (Dietermann and Weiler, 2013; Chiogna et al., 2014; Engel et al., 2018), and the contribution to discharge of snow and glacier melt is also elevation-dependent (Engel et al., 2016; Leibundgut et al., 2009). As shown in Fig. 4, subbasins with a mean elevation larger than 1500 m a.s.l. (Isarco, Passirio, Talvera, Noce and Avisio) have a more negative oxygen signature than lower elevation catchments (Fersina, Leno and Alpone). Similarly, the water samples of the Adige river are characterized by different $\delta^{18}O$ values depending on the mean elevation of the basin drained up to the sampling location. Both for the tributaries as well as for the Adige catchment, we computed an increase of about 0.3‰/100 m for $\delta^{18}O$.

For most of the samples, we cannot observe fractionation effects in surface water (Fig. 5), although the Adige River and most of its tributaries are severely affected by water retention in artificial reservoirs which control streamflow variability (Chiogna et al., 2018; Zolezzi et al., 2009). In fact, almost all samples lay on the local meteoric water line for North Italy proposed by Giustini et al. (2016) which slightly

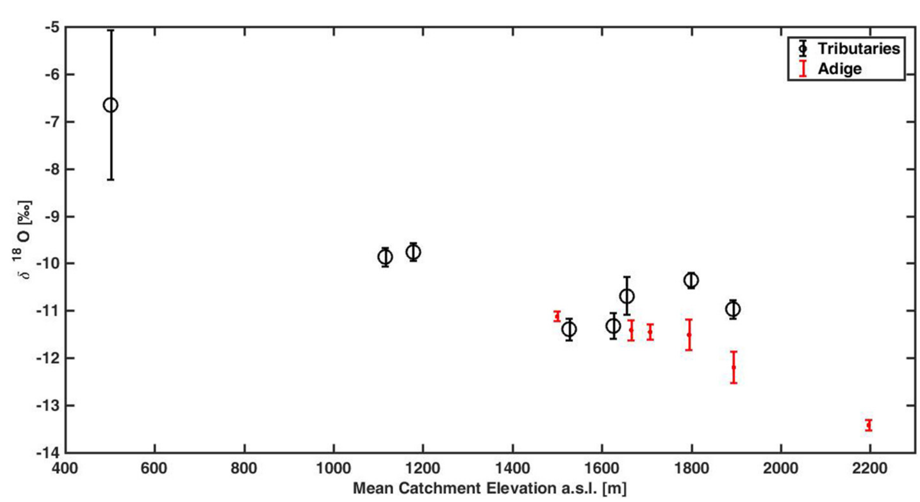

Fig. 4. Variability of $\delta^{18}O$ as a function of the mean catchment elevation of the subbasins (Passirio, Talvera, Isarco, Avision, Noce, Leno, Fersina and Alpone, in decreasing order of mean catchment elevation) and the Adige catchment closed at six different gauging stations (Spondigna, Ponte d'Adige, Bronzolo, Mattarello and Boara Pisani, in decreasing order of mean catchment elevation), with circles and dots respectively.

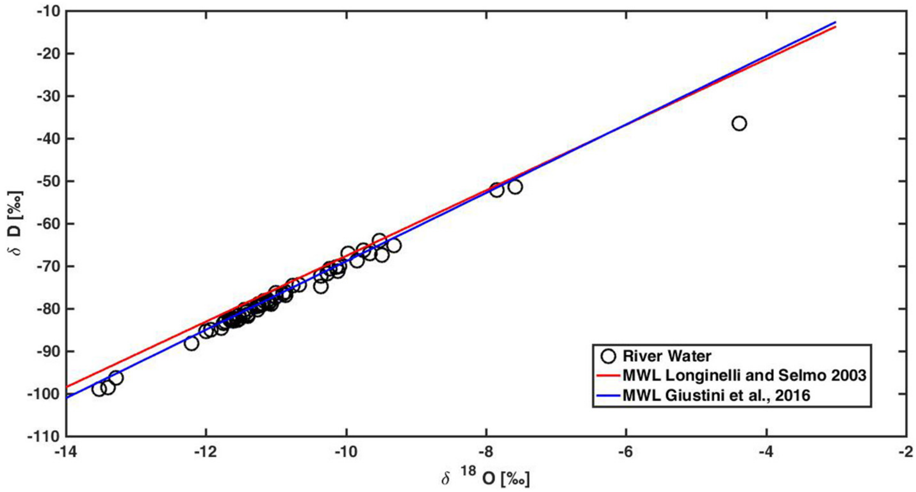

Fig. 5. Comparison between the of δD-$\delta^{18}O$ isotopic signature of the river water samples collected in this study and the local meteoric water line proposed by Giustini et al. (2016), i.e., $\delta D = 8.04\cdot\delta^{18}O + 11.47$ and Longinelli and Selmo (2003), i.e., $\delta D = 7.7094\cdot\delta^{18}O + 9.4034$.

differs from the one of Longinelli and Selmo (2003). The difference between the two local meteoric water lines, is due to the larger number of sampling stations at high elevations considered by Giustini et al. (2016) than by Longinelli and Selmo (2003), and this is the reason why it captures better the most negative isotope values observed in the Adige catchment. The only samples clearly showing a deviation from the local meteoric water line are those collected at the Alpone sampling point. The river was almost dry during the entire hydrological year 2017 and with a low water level, such that it was not possible to estimate its discharge value (see Tables 2 to 5).

Fig. 6 shows how the isotopic signature of $\delta^{18}O$, EC and two important ionic species (Na^+ and Ca^{2+}) vary in the longitudinal direction, from the spring to the river mouth and compare our sampling campaigns with the ones of Natali et al. (2016). Considering the oxygen isotopic signature, we can observe that the general trend observed in Natali et al. (2016) is preserved, i.e. $\delta^{18}O$ increases from its source

Table 2
Measured parameters during sampling campaign 1.

#	Name	Date	Time	Discharge [m^3/s]	pH	EC [μS/cm]	$\delta^{18}O$ [‰]	δ^2H [‰]	d-excess [‰]	Na^+ [mg/l]	K^+ [mg/l]	Mg^{2+} [mg/l]	Ca^{2+} [mg/l]	Cl^- [mg/l]	NO_3^- [mg/l]	SO_4^{2-} [mg/l]	HCO_3^- [mg/l]
1	Adige Spondigna	23.09.2016	10:10	20	7.73	301	−13.46	−98.4	9.28	7.5	1.48	9.0	31.1	1.1	1.0	88.8	46.62
2	Passirio	23.09.2016	11:20	4.3	7.43	175	−11.10	−78.2	10.60	8.1	2.90	3.3	18.4	1.6	2.3	25.3	62.83
3	Campo di Trens	24.09.2016	17:20	9.32	7.22	247	−11.91	−84.8	10.48	10.5	3.16	6.3	28.7	5.8	1.8	25.4	108.4
4	Talvera Bolzano	23.09.2016	12:25	1.2	7.14	247	−10.59	−75.1	9.62	9.6	0.99	2.1	10.7	1.6	2.2	10.8	52.12
5	Adige Ponte Adige	23.09.2016	12:50	70	6.82	289	−12.67	−90.9	10.46	10.3	2.84	7.3	29.8	3.2	2.0	61.1	75.53
6	Isarco Bolzano	23.09.2016	13:10	79	6.94	258	−11.27	−82.2	7.96	9.4	1.53	6.4	25.4	3.5	1.9	20.8	103.9
7	Adige Bronzolo	23.09.2016	13:50	133	6.93	237	−11.43	−82.7	8.74	10.1	1.42	6.2	24.4	2.9	1.8	28.8	91.49
8	Noce Mezzolomb	23.09.2016	14:45	18.44	6.91	211	−11.62	−83.4	9.56	8.3	1.28	6.7	22.6	1.6	2.4	25.5	89.09
9	Avisio Lavis	23.09.2016	15:00	46.7	7.10	303	−10.90	−77.3	9.90	10.8	0.80	7.2	35.8	3.3	1.3	36.4	122
10	Adige SanLorenzo	23.09.2016	15:30	198.11	6.97	296	−11.81	−84.9	9.58	10.4	1.98	8.0	34.6	3.8	2.1	44.6	112.3
11	Fersina	23.09.2016	16:05	0.78	6.99	305	−9.84	−68.8	9.92	13.1	2.15	8.2	34.2	7.3	4.7	19.4	141.9
12	Adige Mattarello	23.09.2016	16:40	n.a.	6.92	288	−11.64	−84.4	8.72	10.5	1.94	7.8	32.2	4.0	2.4	42.8	105
12.5	Adige Isera	23.09.2016	17:35	134	6.82	281	−11.44	−85.1	6.42	10.3	2.34	8.0	31.3	4.3	2.6	39.7	107.6
13	Leno Rovereto	23.09.2016	17:00	0.65	7.29	295	−9.81	−68.5	9.98	7.3	0.62	11.1	34.0	2.4	1.7	11.1	160.1
14	Adige Rovereto	23.09.2016	17:20	128.99	7.14	276	−11.49	−84.5	7.42	11.1	1.82	7.8	30.8	3.8	2.5	36.2	111
15	Adige Verona	24.09.2016	13:30	97	7.05	303	−11.76	−84.6	9.48	11.9	2.44	8.2	33.1	5.1	2.7	39.0	116.6
16	Alpone	24.09.2016	10:30	n.a.	7.21	497	−6.86	−50.0	4.88	23.7	2.93	20.3	38.4	15.3	4.7	36.0	211.4
17	Adige Boara_Pisani	24.09.2016	11:25	97	7.23	319	−11.23	−82.6	7.24	11.3	3.10	8.1	35.0	6.1	3.2	37.8	124.2
18	Adige PrePortesine	24.09.2016	10:30	97	7.19	305	−11.55	−82.2	10.20	11.4	2.90	8.0	33.5	5.5	3.1	39.0	117
19	Adige after barrier	24.09.2016	09:45	97	7.23	306	−11.46	−83.3	8.38	12.3	1.86	8.1	33.5	7.0	2.9	38.7	114.6

Table 3
Measured parameters during sampling campaign 2.

#	Name	Date	Time	Discharge [m^3/s]	pH	EC [μS/cm]	$\delta^{18}O$	δ^2H [‰]	d-excess [‰]	Na^+ [mg/l]	K^+ [mg/l]	Mg^{2+} [mg/l]	Ca^{2+} [mg/l]	Cl^- [mg/l]	NO_3^- [mg/l]	SO_4^{2-} [mg/l]	HCO_3^- [mg/l]
1	Adige Spondigna	13.01.2017	19:30	3.8	7.6	334	−13.40	−98.5	8.70	5.9	2.55	11.4	40.5	3.4	1.1	96.7	72.11
2	Passirio	13.01.2017	20:55	2.3	7.6	175	−10.87	−76.1	10.86	5.4	3.29	3.2	18.5	3.7	2.8	22.8	54.79
3	Campo di Trens	15.01.2017	23:00	4.9	7.9	325	−11.47	−81.8	9.96	8.0	2.74	7.5	31.4	7.5	2.1	24.9	112
4	Talvera Bolzano	14.01.2017	09:45	1.2	7.5	157	−10.36	−72.4	10.48	7.4	1.63	3.1	16.8	4.2	4.4	12.8	61.89
5	Adige Ponte Adige	14.01.2017	12:10	22	7.4	322	−12.20	−88.2	9.40	7.5	2.85	9.1	35.9	3.7	2.6	63.3	90.53
6	Isarco Bolzano	14.01.2017	12:35	26.3	7.4	314	−11.40	−81.7	9.50	9.0	2.39	9.0	36.7	7.6	3.2	30.9	130.1
7	Adige Bronzolo	14.01.2017	13:20	45.3	7.4	346	−11.78	−84.6	9.64	14.0	4.17	10.0	38.8	10.8	2.7	41.6	140.6
8	Noce Mezzolomb	14.01.2017	15:10	5.21	7.5	283	−11.24	−79.4	10.52	5.2	1.39	9.9	35.6	2.5	3.0	18.0	144.1
9	Avisio Lavis	14.01.2017	16:00	3.32	7.6	406	−10.86	−76.9	9.98	8.1	1.51	10.7	54.4	5.8	4.3	59.1	155.2
10	Adige SanLorenzo	14.01.2017	17:30	61.7	7.5	318	−11.55	−82.7	9.70	8.3	2.60	9.7	36.8	5.9	2.9	40.5	123.4
11	Fersina	14.01.2017	18:00	0.5	7.5	332	−9.84	−68.9	9.82	12.2	1.94	9.2	36.3	14.2	5.2	21.1	136.6
12	Adige Mattarello	14.01.2017	18:30	n.a.	7.3	359	−11.40	−81.5	9.70	13.5	3.30	10.0	38.2	12.8	3.3	41.6	132.5
12.5	Adige Isera	14.01.2017	19:10	58.31	7.3	334	−11.61	−83.0	9.88	11.1	2.80	10.2	39.4	3.4	1.3	15.7	178.8
13	Leno Rovereto	14.01.2017	19:35	0.6	7.4	311	−9.75	−66.4	11.60	3.8	0.65	11.9	40.9	3.0	2.5	10.3	174.6
14	Adige Rovereto	14.01.2017	20:30	58.91	7.6	316	−11.40	−81.5	9.70	10.0	2.46	9.3	35.6	8.3	3.5	38.2	120
15	Adige Verona	15.01.2017	10:10	64	7.5	326	−11.52	−82.3	9.86	10.3	2.64	10.1	37.9	7.9	4.0	42.2	126.4
16	Alpone	15.01.2017	11:11	n.a.	7.7	647	−7.58	−51.4	9.24	20.7	2.32	22.9	79.4	17.6	12.4	35.0	329.3
17	Adige Boara_Pisani	15.01.2017	14:00	90	7.7	346	−11.07	−79.0	9.56	9.3	2.72	10.4	39.5	8.1	4.4	39.1	135.2
18	Adige PrePortesine	15.01.2017	16:15	88	7.7	346	−11.26	−80.3	9.78	9.8	2.50	10.0	39.7	8.1	4.2	39.9	133.7
19	Adige after barrier	15.01.2017	15:30	88	7.6	9170	−10.36	−74.8	8.08	534.8	20.4	66.6	48.7	987.05	3.68	144.99	47.74

along the flow paths to its mouth. We can also clearly observe a shift towards less negative values of the entire catchment during the drought in 2017 as compared to the situation in 2013, 2014 and 2015. This shift is generally larger than the analytical uncertainty of the measurements. In fact, the data collected in 2017 overlap to some extent with the data collected in March 2015 by Natali et al. (2016), when snow and glacier melt are generally negligible for the Adige river. The measurements of EC show remarkable differences between 2017 and the other years: The 2017 values are larger than the previous years, in particular if we compare April 2017 with May 2014 and May 2015.

Table 4
Measured parameters during sampling campaign 3.

#	Name	Date	Time	Discharge [m^3/s]	pH	EC [μS/cm]	$\delta^{18}O$ [‰]	δ^2H [‰]	d-Excess [‰]	Na^+ [mg/l]	K^+ [mg/l]	Mg^{2+} [mg/l]	Ca^{2+} [mg/l]	Cl^- [mg/l]	NO_3^- [mg/l]	SO_4^{2-} [mg/l]	HCO_3^- [mg/l]
1	Adige Spondigna	03.04.17	14:15	10.5	7.7	363	−13.53	−98.9	9.34	11.8	4.93	11.0	37.9	7.2	13.1	95.9	62.76
2	Passirio	03.04.17	15:30	4.55	7.5	146	−11.17	−78.2	11.16	8.4	3.76	2.7	15.4	4.1	5.9	17.2	53.57
3	Campo di Trens	07.04.17	23:00	7.39	7.4	325	−11.67	−82.3	11.06	16.2	8.36	6.9	31.3	15.8	2.1	23.1	137.8
4	Talvera Bolzano	03.04.17	16:15	1.68	7.3	185	−10.27	−71.8	10.36	12.7	3.43	3.1	17.0	8.6	3.1	10.2	79.96
5	Adige Ponte Adige	03.04.17	16:45	33.62	7.4	268	−12.00	−85.4	10.60	10.5	3.51	7.5	29.2	5.5	5.7	51.7	79.31
6	Isarco Bolzano	03.04.17	17:30	68.54	7.3	296	−11.72	−83.2	10.56	10.1	2.55	6.7	29.1	7.3	4.9	24.1	104.8
7	Adige Bronzolo	03.04.17	18:00	99.21	7.3	241	−11.75	−83.4	10.60	10.2	2.57	7.0	29.2	5.9	3.8	33.1	99.39
8	Noce Mezzolomb	03.04.17	19:45	35.61	7.3	326	−11.45	−80.3	11.30	9.8	3.20	9.3	34.4	6.0	9.8	21.6	134.9
9	Avisio Lavis	04.04.17	09:30	4.03	7.3	387	−10.89	−76.6	10.52	10.4	1.44	10.0	50.2	6.4	3.9	62.7	138.1
10	Adige SanLorenzo	04.04.17	09:00	105.84	7.3	297	−11.60	−82.4	10.40	10.0	2.60	7.7	31.6	6.1	4.6	32.6	108.8
11	Fersina	05.04.17	18:30	0.34	7.3	311	−10.14	−70.3	10.82	10.7	2.50	7.3	30.2	8.4	9.2	17.7	114.9
12	Adige Mattarello	05.04.17	20:00	n.a.	7.2	322	−11.52	−81.6	10.56	8.5	2.65	7.7	29.8	5.7	11.1	32.7	93.89
12.5	Adige Isera	06.04.17	08:45	90.49	7.4	326	−11.64	−82.4	10.72	10.4	3.14	9.1	35.6	7.6	8.3	38.5	116.5
13	Leno Rovereto	06.04.17	09:10	5.33	7.5	319	−9.97	−67.1	12.66	6.0	0.88	10.7	40.7	3.7	7.1	10.1	168.2
14	Adige Rovereto	06.04.17	09:30	121.83	7.4	319	−11.65	−82.6	10.60	10.5	4.69	9.6	36.6	8.3	7.8	40.0	121.9
15	Adige Verona	06.04.17	11:00	73.77	7.2	342	−11.42	−80.8	10.56	10.4	3.15	8.2	32.3	8.0	7.6	31.9	110.3
16	Alpone	06.04.17	11:45	0.35	7.3	627	−7.85	−52.1	10.70	22.7	3.18	20.7	63.6	20.1	18.2	30.7	271.2
17	Adige Boara_Pisani	07.04.17	09:15	81.56	7.4	344	−11.19	−79.0	10.52	12.1	3.30	9.7	39.6	9.4	6.5	36.5	137.4
18	Adige PrePortesine	06.04.17	16:00	95.67	7.3	348	−11.10	−78.4	10.40	12.1	2.85	10.4	41.8	10.2	7.9	37.9	142.7
19	Adige after barrier	06.04.17	15:00	95.67	6.9	9170	−9.49	−67.5	8.42	1873.8	60.51	198.9	97.7	493.3	14.6	542.2	10,346

Table 5
Measured parameters during sampling campaign 4.

#	Name	Date	Time	Discharge [m^3/s]	pH	EC [μS/cm]	$\delta^{18}O$ [‰]	δ^2H [‰]	d-excess [‰]	Na^+ [mg/l]	K^+ [mg/l]	Mg^{2+} [mg/l]	Ca^{2+} [mg/l]	Cl^- [mg/l]	NO_3^- [mg/l]	SO_4^{2-} [mg/l]	HCO_3^- [mg/l]
1	Adige Spondigna	17.07.2017	10:30	18.54	9.1	302	−13.28	−96.4	9.84	4.9	1.57	9.5	32.9	1.2	1.5	96.2	153.2
2	Passirio	17.07.2017	12:00	7.92	8.2	136	−10.76	−74.7	11.38	4.6	2.47	2.7	14.5	1.7	1.7	20.8	102.9
3	Campo di Trens	18.07.2017	22:45	31.65	7.9	167	−11.25	−78.9	11.10	10.1	6.13	2.9	13.6	10.2	1.3	12.5	118.4
4	Talvera Bolzano	17.07.2017	12:45	11.88	7.9	101	−10.23	−70.6	11.24	6.4	1.46	1.8	9.6	2.3	2.2	9.3	76.08
5	Adige Ponte Adige	17.07.2017	13:30	53.42	7.8	224	−11.93	−85.1	10.34	6.3	2.37	7.2	28.6	2.7	2.2	52.1	178.5
6	Isarco Bolzano	17.07.2017	14:00	102.72	7.7	257	−11.21	−79.1	10.58	6.6	1.91	5.6	25.4	4.2	2.1	21.4	190.5
7	Adige Bronzolo	17.07.2017	14:30	140.48	7.8	223	−11.09	−78.6	10.12	7.0	2.05	5.7	25.7	4.2	2.3	23.3	191.3
8	Noce Mezzolomb	17.07.2017	15:45	20.79	7.8	261	−11.00	−76.3	11.70	6.2	1.71	7.7	31.2	2.8	2.8	11.2	245.2
9	Avisio Lavis	17.07.2017	16:45	3.64	7.8	319	−10.10	−70.0	10.80	7.6	1.74	7.7	37.9	5.0	1.7	38.5	271
10	Adige SanLorenzo	17.07.2017	17:45	148.19	7.8	280	−11.27	−79.5	10.66	7.3	2.06	6.6	28.7	4.3	2.1	32.7	204.1
11	Fersina	17.07.2017	18:15	0.25	6.8	310	−9.66	−67.1	10.18	8.5	1.72	7.0	29.2	6.5	3.8	16.7	225.5
12	Adige Mattarello	17.07.2017	18:45	n.a.	7.7	286	−11.25	−79.1	10.90	7.5	1.91	7.3	31.8	4.3	2.6	37.1	220.3
12.5	Adige Isera	17.07.2017	19:15	134.60	7.8	276	−11.26	−79.4	10.68	7.7	2.28	7.0	30.0	4.8	2.5	33.3	209.8
13	Leno Rovereto	17.07.2017	19:45	0.83	7.9	304	−9.52	−64.0	12.16	5.6	0.74	8.7	40.2	4.0	2.8	6.8	322.2
14	Adige Rovereto	17.07.2017	20:00	127.46	7.6	268	−11.13	−78.3	10.74	7.8	1.89	7.0	29.3	4.3	2.7	31.0	209.7
15	Adige Verona	18.07.2017	19:30	78.86	7.6	344	−11.12	−78.1	10.86	13.6	8.11	7.4	32.2	12.4	2.9	31.7	219
16	Alpone	18.07.2017	17:45	0	7.3	511	−4.38.	−36.6	−1.56	24.6	13.63	19.3	30.5	28.9	18.5	0.63	235.0
17	Adige Boara_Pisani	18.07.2017	15:15	73.2	7.6	282	−11.00	−77.2	10.80	8.8	2.61	7.4	32.6	5.4	3.1	32.4	233.2
18	Adige PrePortesine	18.07.2017	14:10	76.24	7.8	272	−10.67	−74.5	10.86	8.8	2.44	6.9	30.8	6.2	5.6	29.9	221.3
19	Adige after barrier	18.07.2017	13:45	75.23	7.7	2807	−10.12	−71.2	9.76	346.3	14.23	45.6	37.9	813.3	2.6	128.0	317.4

Moreover, a clear increasing trend can be observed for May 2014 and May 2015, when melting is generally a relevant component for water discharge in the Adige river. In contrast, such behaviour cannot be clearly identified in April 2017 or in July 2017. Notice that the anomalously high values of EC and increased values of SO_4^{2-} concentration were registered in Spondigna are due to the different water chemistry of the Rio Ram, as it drains Triassic dolomitic rocks, a tributary of the Adige which joins the river shortly upstream the sampling point. This effect was already observed and discussed by Natali et al. (2016). The behaviour of Na^+ along the river also shows a remarkable difference between the years 2013–2015 and 2017. The measured Na^+ concentration in 2017 are always larger than those observed in previous years

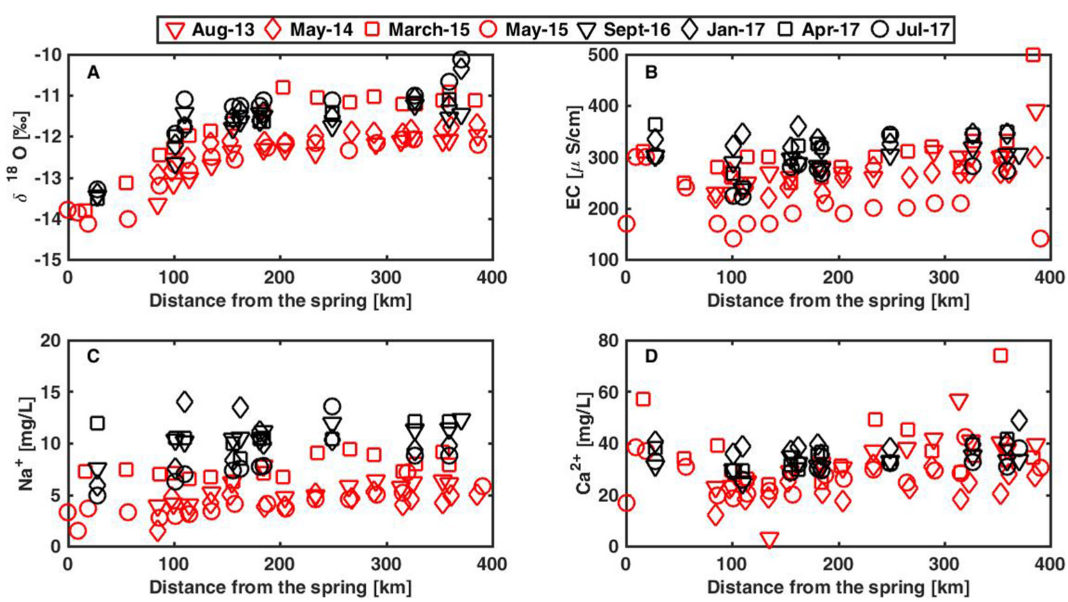

Fig. 6. Variability of $\delta^{18}O$ (panel A), EC (panel B), Na^+ (panel C) and Ca^{2+} (panel D) along the Adige River. Notice that the values of EC, Na^+ and Ca^{2+} for the last sampling point (after barrier) collected in 2017 are not shown since they are out of range (see Tables 2 to 5). Data for the Adige in 2013, 2014 and 2015 are from Natali et al. (2016).

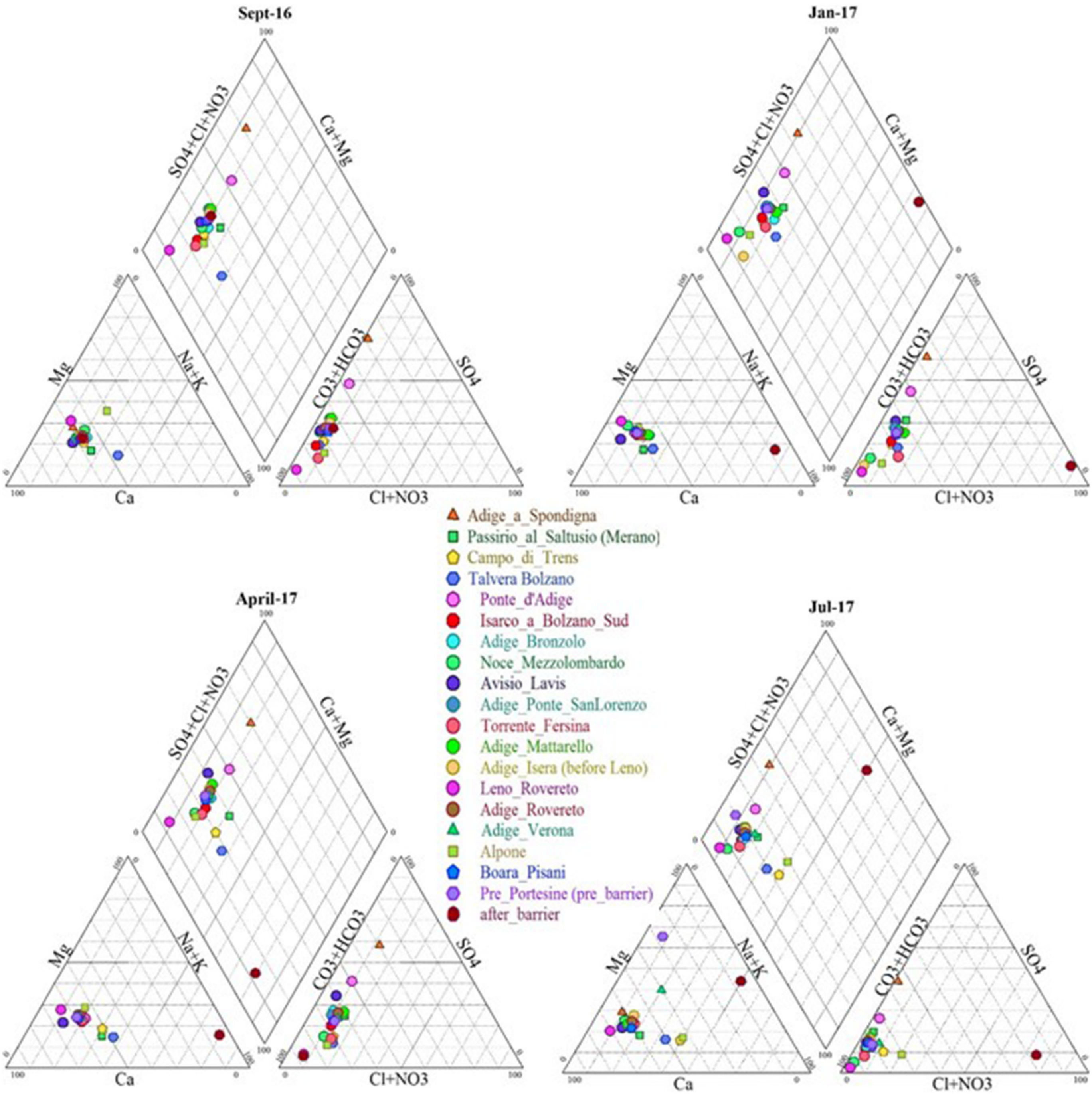

Fig. 7. Piper diagram diagrams for the Adige catchment and its tributaries.

in the same season (i.e., August 2013 is compared with July 2017, May 2014, March 2015 and May 2015 are compared with April 2017). This difference is not visible or at least not to the same extent for Ca^{2+} concentrations (Fig. 6).

3.3. Geochemical characteristics

Fig. 7 presents the chemical content of all analysed water samples with a Piper trilinear diagram (Piper, 1944). The water samples collected in the Adige river and its tributaries show medium mineralization. Calcium, magnesium, and bicarbonate are the major components and no significant variations are found between most water facies in the different sampling stations during September 2016, January 2017, April 2017 and July 2017. Calcium-bicarbonate ($CaHCO_3$) is the dominant hydrochemical facies in most of the sampling stations in all four sampling campaigns. The abundant content of calcium and magnesium is due to the extended presence of calcite and dolomite materials within the catchment.

Evident differences are observed in the samples collected in the "after barrier" sampling point (i.e., downstream the hydraulic barrier constructed to prevent salt water intrusion in the river channel), in January 2017, April 2017 and July 2017. In the "after barrier" station, the water samples showed sodium-chloride (Na-Cl) hydrochemical facies in January 2017 and July 2017, which can be related to the effect of seawater intrusion due to the low discharge of the Adige river during droughts. The amount of seawater intrusion is estimated to be between 3% in January 2017 and April 2017 and 1% in July 2017. The "after barrier" station showed different hydrochemical facies in September 2016

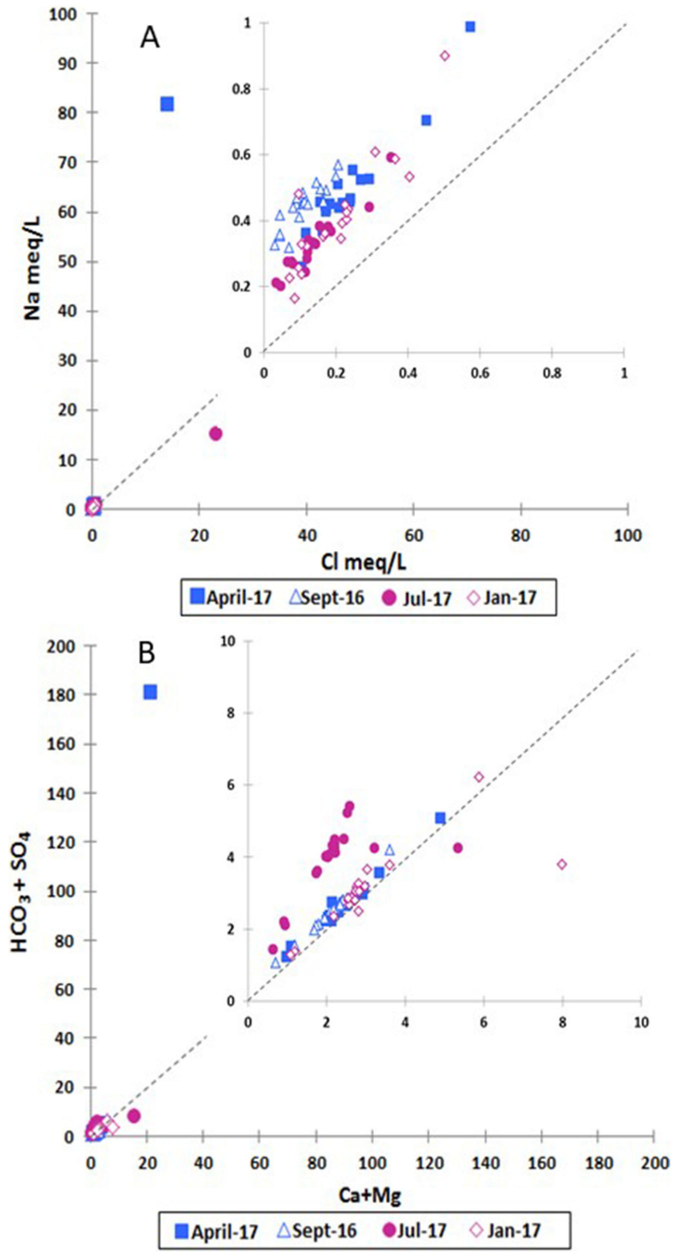

Fig. 8. Ionic ratios: (A) Na versus Cl; (B) Ca + Mg versus HCO_3 + SO_4.

and April 2017 seasons. Although, $CaHCO_3$ is a dominant hydrochemical facies in fall, collected water sample show a significant sodium and bicarbonate content in April 2017. The $NaHCO_3$ water type can be observed when water invades an area that previously contained seawater by exchanging Ca of standard $CaHCO_3$-type water with the Na in seawater (Choi et al., 2014).

Dissolution, ion exchange, mineral's alternation are the main processes controlling the natural hydrochemistry of surface and groundwater flow. Negative charges which are carried in the surface of minerals can absorb the cation dissolved in the water changing its chemical composition. The relationship between Na and Cl was used to identify the process that control the salinity and saline intrusion in different sampling seasons. Considering Fig. 8(A), we can observe that Na vs Cl ratios are above the 1:1 line in all four different sampling campaigns. If halite dissolution is responsible for the occurrence of sodium, the Na vs Cl molar ratio is approximately one, whereas a ratio greater than one is typically interpreted as Na released from a silicate weathering reaction (Meybeck, 1987). All the collected samples have ratio greater or equal to 1 indicating that ion exchange is the major process which is replaced by silicate weathering. According to the results from the piper diagram. Considering Fig. 8(A), three samples showing high Na vs Cl values (81.4 and 14 meq/l in April 2017, 23.2 and 28.2 meq/l in January 2017, and 15 and 23.2 meq/L in July 2017, respectively) belong to water collected from the "after barrier" sampling point. The samples collected in January and July 2017 show Na-Cl water type according to the results from piper diagram. Since the Cl/HCO3 ratio values of these two samples were above 0.5 (31.6 and 3.9 in January 2017 and July 2017, respectively), we can conclude that the "after barrier" sampling point is affected by mixing with seawater. Moreover, the plot of Ca + Mg versus HCO_3 + SO_4 was prepared to identify the importance of carbonate, sulphate, and silicate minerals in the dissolution processes, in different sampling seasons. Based on Fig. 8(B), the 1:1 stoichiometry ratio for Ca + Mg vs HCO_3 + SO_4 suggests that these ions have resulted from weathering of carbonate rocks in winter, fall, and spring. However, water samples from summer are shifted slightly above the 1:1 line due to excess of sulphate and bicarbonate, as a result of ion exchange. Only one water sample (after barrier station) showed very high concentration of HCO_3 + SO_4 in spring, as a consequence of a strong ion-exchange potential between Ca in freshwater (Ca-HCO_3) and Na in seawater (Na-Cl), which showed great affinity with bicarbonate.

The behaviour of nitrate in the catchment is also reported in Tables 2 to 5. We can observe anomalously high concentrations, in particular during April 2017, in comparison the ones reported in Lutz et al. (2016).

4. Discussion

4.1. Spatial variability of isotopic and geochemical parameters

The $\delta^{18}O$ isotopic signature of the water samples collected along the Adige river indicates that the alpine part of the catchment up to Trento displays more negative values than the lower part of the catchment (Fig. 6). Although this outcome was shown already by Natali et al. (2016), in this work it is possible to observe that this behaviour persists even during a drought year, like 2017, where snowfall was exceptionally low. It has therefore to be expected that also the baseflow in the upper part of the Adige river and of its Alpine tributaries is characterized by more negative isotopic composition than the lower part of the catchment. This is consistent with the elevation effect characterizing the isotopic composition of precipitation events and with the conservative nature of stable isotopes in aquifers. As stated for example by Longinelli and Selmo (2010) "the original isotopic composition of a groundwater is normally preserved over extremely long periods and, consequently, the isotopic composition of meteoric groundwater is often found to match reasonably the mean isotopic composition of precipitation over the recharge area". The low variability in groundwater isotopic composition and the similarity with the local meteoric water line of headwater catchments of the Adige was observed for example by Chiogna et al. (2014). On the short term, it also appears that the baseflow in terms of its isotopic composition is not affected by the drought thanks to groundwater contribution. Moreover, we have shown that both the $\delta^{18}O$ signature of the tributaries and of the Adige river follow the expected elevation dependent pattern (the higher the mean elevation of the catchment, the lower the value of $\delta^{18}O$), despite the presence of large artificial reservoirs. This indicates that we cannot observe any large isotopic enrichment due to evaporation in these reservoirs. The altitude effect observed in the river water of the Adige and its tributaries is comparable to gradients of Middle European river basins (Reckerth et al., 2017) and larger than the altitude effect affecting precipitations −0.23‰/100 m (Giustini et al., 2016), indicating more recharge from higher elevations compared to lower parts of the catchment. Notice, however, that these results should be carefully interpreted. Practically all tributaries of the Adige catchment, and the Adige River itself are affected by hydropeaking (Zolezzi et al., 2011; Carolli et al., 2017; Chiogna et al., 2016; Chiogna et al., 2018;

Premstaller et al., 2017). Considering the discharges observed during the sampling and reported in Tables 2 to 5, the observed isotopic signature is the mixture between river water and water released from reservoirs located at higher elevations.

Considering the 2017 drought, in the Adige we could think of two different kind of droughts: (i) those caused by scarcity in winter precipitation and that have further effects in the following spring and summer season as observed in 2017; and (ii) those that may occur due to both scarce precipitation and elevated temperatures. For the latter, a deviation of the river water samples from the meteoric water line would be expected even though isotopic signature and fractionation in alpine lakes can vary also according to elevation and lake mixing processes (Perini et al., 2009; Flaim et al., 2013). The absence of a clear pattern that departs from the local meteoric water line indicates that the drought was mainly caused by the scarcity in the winter precipitation rather than by excessive evaporation due to temperatures above the average. Lower d-excess values, i.e. values plotting below the LMWL, in river water are indicative of evaporation processes and are mainly encountered in the Adige water samples as well as in the water samples of the tributaries in the lower part of the catchment (after Mattarello) for September 2016. This shows that isotopic enrichment due to evaporation is possible in the catchment, but it was only observed for September 2016 and not for the following drought. In July 2017, evaporation effects do not play a major role in the river water isotopic composition.

The EC data do not display a clear increase along the course of the Adige river during the 2017 drought. This indicates that the contribution of snow and glacier melt, typically characterized by low EC values, is limited. Moreover, low sodium concentration, due to the absence of evaporitic sediments in the region, increase at the river mouth due to seawater intrusion into freshwater. Calcium concentrations, show only a slightly increase towards the lower part of the basin as a result of contribution from water that interacted with sedimentary lithology.

The analysis of the piper diagrams shows that the geochemical composition of the water in the Adige river are dominated by $CaHCO_3$ and the geochemical composition of the water along the river is not affected in general by the drought.

4.2. Temporal variability of isotopic and geochemical parameters

Considering the temporal variability in the collected dataset, we can identify two relevant time scales. First, we can observe that, during the drought occurred in 2017 we have a shift towards less negative $\delta^{18}O$ values than in the previous years along the Adige catchment. This shift is particularly evident during spring and summer where the contribution of snowmelt is missing. Second, the variability of the isotopic signature during the year is limited, since we do not have a large change in the main water source leading to streamflow. The tributaries, as well as most stations located along the Adige, show the typical cyclical pattern observed in Alpine catchments: the $\delta^{18}O$ value increases from fall to winter and then decreases due to the onset of snow and glacier melt (Chiogna et al., 2014; Penna et al., 2017a; Penna et al., 2014). The limited increase in $\delta^{18}O$ values occurring in July shows that by that date snowmelt was not large and that also glacier melt was not the main water source in the river. The area covered by glaciers in the Adige catchment is relatively small (less than 1%) and the signature of glacier melt can be observed in headwater catchments but gets rapidly diluted in the downstream part of the river basin. The tributary with the largest temporal variability in $\delta^{18}O$ is the Alpone river. The water samples of the Alpone river deviate from the local meteoric water line indicating impact of evaporation and are characterized by low values of deuterium excess in particular in September 2016 and July 2017, when the river had no flow and sampling was only possible in disconnected ponds.

The larger EC values in 2017 than in previous years are indicative of a larger contribution of groundwater to the total discharge. This highlights the relevance of good groundwater management practices in the Adige aquifer, in order to limit the negative effects of droughts in the river basin (Castagna et al., 2015). Larger EC values in 2017 can be explained also by the higher sodium concentrations in 2017. Decreases in water levels due to the drought in 2017 can affect catchment functioning such as storage and release of water, which finally can cause an increase in solutes concentrations in rivers (Nosrati, 2011). Moreover, according to Nosrati (2011), sodium and also calcium concentrations could be associated with evaporation from rivers and the ground surface, as well as with the increase of residence time in the catchment and contact of waters with soils during recharge and discharge of groundwater into rivers. The latter cause is the most probable, considering that the isotopic analysis did not evidence much evaporation effects.

The Piper diagrams show that the temporal variability in the processes affecting the geochemical water composition is limited and if we compare them with the one presented by Natali et al. (2016) we do not observe a large difference among them, despite the change in the hydrological conditions. This indicates that a drought like the one occurred in 2017 is not sufficient to cause a change in the dissolution processes occurring along the Adige river. As also outlined by Natali et al. (2016), the $CaHCO_3$ hydrochemical facies have been the dominant ones for the last 40 years. Still concentrations of some individual elements are higher compared to previous years most likely due to the lack of dilution with snow melt water.

Nitrate displays a peak value during April 2017. Elevated concentrations can be observed in most of the stations sampled, in tributaries as well as along the main river. However, to drive robust conclusions, we should have a dataset with a higher temporal resolution, to appreciate the nitrate dynamic during the year.

4.3. Identification of sensitive regions in the catchment

The results of this study allow us to identify some interesting points along the catchment for further research to investigate the interplay between hydrological variability and ecosystem functioning. The first is the Adige at Spondigna, where, as outlined also by Natali et al. (2016), we observe a sudden change in the geochemical composition of the water. Such change is generally considered of geological nature and is not a concern for the environmental protection agency although the status of the water body is deteriorated, according to the water framework directive. The cause of the deterioration is assumed to be mainly due to changes in river morphology and the presence of hydropower plants and not of chemical origin (APPA Bolzano, 2009). Though, the ionic composition of the water is untypical for the Adige catchment and this condition can be observed also in the work of Natali et al. (2016). The present study shows that measured EC values during 2017 as well as Na^{+} values are even higher than in previous years, showing the impact of the lack of snowmelt on the geochemical composition of the water.

The second critical point is the Alpone river, which was under clear stress during the drought. The water scarcity was caused by high evaporation as indicated by the deviation of the isotopic composition of the samples from the local meteoric water line and by the increase in electrical conductivity and ionic content. This situation highlights that the drought in this subcatchment had a much larger impact than in any other investigated part of the basin. In this subcatchment, snow plays a minor role due to the low mean elevation (502 m a.s.l.) and the lack of fall and winter precipitations has an important impact also on the baseflow of the river and in recharging the aquifer. Agricultural activities and drinking water supply are also important water uses in the area (Boscolo and Mion, 2008) and this contributes in reducing the water availability in the river due to groundwater abstraction and exacerbating the effect of the drought.

Finally, the hydraulic barrier is of main importance to protect the Adige river from salt water intrusion; particularly during droughts. The sampling point 19 “after barrier” is highly affected by saline intrusion and the water of the Adige river during the drought was largely mixing with sea water, more than observed in Natali et al. (2016).

This is the only point in which we can observe a clear deterioration of water resources due to saltwater intrusion, which is a problem for the entire area, including the Po river delta and the outflow of the Brenta river (Gattacceca et al., 2009).

5. Conclusion

This study presented the effect of the drought occurred in 2017 in the Adige catchment on its isotopic and geochemical water composition. It was possible to show that the drought was mainly driven by the scarce precipitation occurred during winter rather than an increase in evaporation. In fact, no significant kinetic isotopic fractionation was observed in the collected samples of the Adige river and most of its tributaries indicating negligible evaporation within surface water, despite an expected effect due the presence of large reservoirs in the upper Adige catchment. The isotopic signature of the river water was still more negative in the upper part of the river basin and in the alpine tributaries than in the lower part of the catchment. We concluded that this is due to the more negative signature of precipitations in high elevation catchments which influences also the baseflow water composition. The importance of the groundwater contribution during the drought is also evidenced by the EC values, and this highlights the relevance of sustainable groundwater resources management in the catchment. The processes influencing the geochemical composition of the water do not seem to be significantly affected by the drought, although an increase sodium concentrations along with a reduction of dilution effect due to a lack in snowmelt contribution can be observed. The peak in nitrate concentration occurred in April 2017 could be indicative for the interplay between hydrological stressors, anthropogenic activities and water quality, but this aspect requires further investigations.

The Adige catchment as a whole has displayed a good resilience towards the drought of 2017, mainly due to the fact that baseflow sustained the river discharge. The study still allowed us identifying three critical locations within the catchment, which deserve further monitoring to understand the effect of hydrological stressors on the ecosystem. These points are distributed both in the upper (Spondigna) and lower (Alpone and from the hydraulic barrier to the river mouth) part of the catchment, showing that it is important to maintain a comprehensive monitoring of the entire river basin.

Despite large scale experimental studies are challenging to be carried on, this study highlights their importance also for catchments which do not show a critical status in terms of biological and chemical water quality. In fact, the collected information about isotopic and geochemical water composition during extreme hydrological conditions, such as droughts, can improve the understanding of the system dynamics and can provide useful information to water managers to preserve the ecosystem integrity and prevent stakeholder conflicts.

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