Multi-isotopic regional-scale screening on drinking groundwater in Lombardy Region (Italy)

Screening multi-isotopico a scala regionale sulle acque sotterranee ad uso potabile in Lombardia (Italia)

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Abstract: Groundwater is the main and safest source of water used for drinking purposes in many urban and rural communities worldwide. A deep knowledge of aquifer systems in terms of quality, vulnerability and renewability is fundamental to preserving groundwater resources. Thanks to contributions by different members of Water Alliance in synergy with Sapienza University, during November 2019 a multi-isotopic regional scale analysis was carried out on groundwater tapped for drinking purposes in a wide area of the Lombardy Region. The study aimed to improve knowledge of recharge mechanisms, the groundwater’s relative age, and the impact of human activities on groundwater quality. Each Water Alliance supplier selected some wells and springs drawing water from different aquifer groups and distributed from north to south, for a total of 121 samples. Groundwater stable isotope analyses were performed on all the monitoring points; the trizio, the nitrogen isotopes (15N and 18O), the sulphate isotopes (34S and 18O) and the 13C in Dissolved Inorganic Carbon (DIC), were analysed in selected monitoring wells based on previous data and major ion concentration results. The results confirm the key role of a multi-isotopic approach in defining aquifer recharge processes, relative groundwater age and the origin of pollutants, offering a useful tool to highlight local issues which could be investigated in depth by each water supplier.

Keywords: multi-isotopic approach, water utilities, Water Alliance, groundwater resources, Lombardy Region.

Parole chiave: approccio multi-isotopico, gestori servizi idrici, Water Alliance, risorse idriche sotterranee, Regione Lombardia.
Introduction

Groundwater is a valuable strategic reserve, and in the last decades a growing interest was placed on this resource, in terms of both quantity and quality, considering the uncertainty posed by climate change regarding its availability. In developed countries, urban environments and densely populated areas represent complex systems (Grönwall and Oduro-Kwarteng 2018), where the water demand is ever increasing for both drinking purposes and human activities. A sustainable (i.e. adjustment of withdrawals to recharge) exploitation of aquifers (Veléz-Nicolés et al. 2020) involves a deep knowledge of groundwater bodies and a clear vision of recharge mechanisms.

Isotope approach was demonstrated very useful in recent literature for solving different problems; in this framework a multi-isotopic study was carried out in a portion of Lombardy, to better understand, aquifer recharge mechanisms, relative groundwater age, origin of contamination and contribution from deep fluids or from surface water.

Oxygen and hydrogen isotopes are ideal tracers of water origin and movement because they are integral constituents of water molecules (Kendall et al., 1998). They can be used to determine the contributions of precipitation or evaporation processes because the rain or snowmelt and vapour are often isotopically different from the water already present in the catchment (Kendall et al. 1998; Longinelli and Selmo 2003, Guffanti et al. 2010; Lucianetti et al. 2020); in addition they can represent a necessary tool for the interpretation of groundwater-surface water interaction (Petitta et al. 2010; Tallini et al. 2014; Marchina et al. 2015) and of salinization processes (Sbarbati et al. 2015).

In addition to the $^{18}$O and $^2$H isotopic analyses, tritium measurements in hydrological studies, give information on the transit or turnover time of water within a system (Clark and Fritz 1997; Mook and de Vries 2001; Stonestrom et al. 2013). After the thermonuclear bomb testing (1963), tritium concentration in atmosphere and in rainwater increased significantly; the tritium concentration mainly originates from the atmosphere, the pedosphere, the lithosphere, and anthropogenic sources of pollution which can enter the aquifer through infiltration and recharge processes, and as a result of the water-rock interaction (Otero and Soler 2002). Each source and each process, such as sulphur oxidation or sulphate reduction, has its own sulphur and oxygen isotope fingerprint.

Investigations were developed under a research collaboration between "Water Alliance" and Sapienza University of Rome. Water Alliance represents a group of water utilities belonging to eight Lombardy’s provinces: Gruppo CAP (Milan Province), BrianzaAcque (Monza/Brianza Province), Lario Reti Holding (Lecco Province), SECAM (Sondrio Province), Uniacque (Bergamo Province), Padania Acque (Cremona Province), Società Acqua Lodigiana (Lodi Province) and Pavia Acque (Pavia Province).

The main novelty of this research is related to the extensive application of multi-isotopic approach to such a wide hydrogeological basin, both in terms of drinking withdrawals and of served people, becoming significantly representative also at national and European levels.

Data and methods

Site description

The investigated area is located in Northern Italy, specifically in a portion of Lombardy including, from North to South, eight provinces: Sondrio, Lecco, Bergamo, Monza/Brianza, Milano, Pavia, Lodi and Cremona (Fig.1).

The simplified hydrogeological setting, according to the classification defined by the Regione Lombardia administration and ARPA (Regional Agency for Environmental Protection), is summarized below.

In the Po Plain area including Milan, Monza Brianza, Pavia, Lodi and Cremona Provinces, four main depositional sequences corresponding to different aquifer groups have been recognized (Pilla et al. 2005; Regione Lombardia and ENI 2002). The shallow aquifer named Aquifer Group A has a thickness ranging between 20 m and 100 m and consists mainly of gravel with a sandy matrix. The sequence was developed during the Middle–Late Pleistocene and consists of proximal braid-plain deposits composed by coarse and poorly sorted gravels (Garzanti et al. 2011; Scardia et al. 2012). The Aquifer Group A is also identifiable in the northern sector of the Plain near the river valley areas.

Under the shallow aquifer A, the Aquifer Group B was identified. It is represented by sands and sandy gravels with a thickness between 50 m and 150 m (Regione Lombardia and ENI 2002). The lower portion of the aquifer consists of clay and silt layers, and locally of conglomeratic units (locally known as Ceppo). This second sequence developed during Middle and Lower Pleistocene and directly outcrops in moraine hills area.

In order to assess the impact of human activities and the possible contribution of deep fluids, analyses on $^{15}$N, $^{18}$O in dissolved nitrate and $^{34}$S, $^{18}$O in dissolved sulphate were carried out.

In fact, the isotope composition of the NO$_3^-$ is controlled by the isotopic composition of the sources (fertilizers, manure, soils) and by transformation processes such as nitrification, denitrification (Aravena and Robertson 1998; Di Lorenzo et al. 2012; Sacchi et al. 2013, Caschetto et al. 2018; Sbarbati et al. 2018). On the other hand, sulphate in groundwater mainly originates from the atmosphere, the pedosphere, the lithosphere, and anthropogenic sources of pollution which can enter the aquifer through infiltration and recharge processes, as well as a result of the water-rock interaction (Otero and Soler 2002). Each source and each process, such as sulphur oxidation or sulphate reduction, has its own sulphur and oxygen isotope fingerprint.
The Aquifer Group C consists of sandy lenses within clay and silt units representing the lower Pliocene continental-marine facies. This sequence mainly consists in meandering river plain deposits fed from the Western and Central Alps (Muttoni et al. 2003; Garzanti et al. 2011).

The deeper Aquifer Group D is represented by a Coarsening Upward sequence characterized by silty-clay and silt deposits interbedded with sand and gravels tiny layers in the upper part of the sequence. The multi-layer aquifer sequence ends with Pliocene continental-marine deposits (Regione Lombardia and ENI, 2002).

This simplified aquifer partitioning within the study area is well defined in the Po Plain sector, where most of the investigated provinces are located; as regards the Sondrio and Lecco Provinces, located in the northern sector of the area, the locally different hydrogeological setting is summarized below.

The main aquifer of Sondrio Province is known as Fondovalle Valtellina Aquifer (ARPA Lombardia 2014). This aquifer has a variable thickness (up to 100 m) due to the irregular shape of the underlying silty-sand and loam deposits; it is formed mainly by coarse alluvial sediments and represents one of the most relevant aquifers of the Province.

In Lecco Province, the most relevant water resources are located in the southern area and are hosted in sand and gravel alluvial deposits. These aquifers are mainly fed by meteoric recharge and are in direct connection with aquifer hosted in Ceppo formation (ARPA Lombardia 2013).

Most of the collected groundwater pertains to the above described aquifers, other than spring water samples located in Sondrio, Lecco and northern area of Bergamo Districts: their origins are more related to carbonate and metamorphic domains (ARPA Lombardia 2013, 2014).

**Sampling survey and laboratory analyses**

A groundwater sampling survey was performed in November 2019 by water utilities of the Water Alliance in cooperation with hydrogeology laboratory of Sapienza University. Each of Water Alliance partner collected, for quality and isotopes investigation, an average of 15 water samples from wells and springs tapped for drinking purposes, for a total amount of 121 samples (see Fig.1 for sampling location). Each water supplier, where possible, collected groundwater samples from wells catching different aquifer groups. Due to the complexity and variety of layers screened in water wells, only a grouped classification was possible for identifying the tapped aquifers. According to Regione Lombardia and ARPA aquifer classification, groundwater samples were grouped in: shallow (sampled in A+B aquifer group), deep (sampled in C+D aquifer group), mixed (sampled in B+C or C+D) and spring.

Samples were stored in boxes at 4°C, and immediately transported in the 8 water utilities laboratories to determine ions concentrations, necessary to assess groundwater geochemistry and to select water samples for different isotopes analyses.

Groundwater stable isotopes analyses were performed on the entire dataset (121 samples) and carried out in the Isotopes Laboratory of the University of Parma. Oxygen isotopic composition was measured by means of the water–CO₂ equilibration technique suggested by Epstein and Mayeda (1953), either by manual preparation of the samples or by the Finnigan GLF 1086 automatic equilibration device (Longinelli and Selmo 2003). The hydrogen measurements were carried out reducing the water sample to hydrogen by passage over hot zinc at about 520°C according to the
were performed on 60 water samples. Analyses of $d^{13}$C in DIC isotopes analyses were carried out in the Environmental Isotopes Laboratory of University of Waterloo (ON, Canada).

Tritium unit determination in groundwater samples were performed on 115 samples by electrolytic enrichment through a LKB Wallac 1220 Quantulus liquid scintillation counter. Three different backgrounds were used for each batch of samples and $^3$H results were reported in the tritium units (T.U.), with standard deviation ($\pm$ 1$\sigma$) of $\pm$ 0.8 T.U.

Nitrates isotopes were analysed using the silver nitrate ($\text{AgNO}_3$) method (Silva et al. 2000). Nitrogen gas for $d^{15}$N analysis was produced by combustion in the presence of CuO, Cu, and CaO; for $d^{18}$O analysis, nitrate oxygen was converted to CO$_2$ by combusting AgNO$_3$ with excess graphite. $d^{13}$N and $d^{18}$O were analysed using a VG-Micromass spectrometer and a VG Prism Micromass spectrometer respectively, with an accuracy of $\pm$ 0.5‰ for both the isotopes. Based on the minimum concentration of 2 mg N - NO$_3$ necessary to perform the analyses, a total of 45 groundwater samples have been selected for $d^{15}$N and $d^{18}$O determination in nitrate.

The $d^{18}$O analyses were carried out by a RoboPrep-CN Europa TraceMass IRMS (Europa Scientific Limited, UK) and the $d^{15}$N analyses were carried out on an EA-Isotope IRMS (Micromass Inc., UK). The accuracies for the $d^{13}$S and $d^{18}$O analyses in sulphate are $\pm$0.3‰ and $\pm$0.5‰, respectively. As for nitrate, based on sulphate concentration detected in groundwater a total of 52 samples were selected for isotopes analyses.

Finally, the $d^{13}$C analyses on DIC were determined using a GC-C-IRMS system with a CARBONPLT column (0.32 mm internal diameter, 30 m length, 3 lm stationary phase) with an analytical precision of $\pm$0.2‰. Analyses of $d^{18}$O in DIC were performed on 60 water samples.

Results and discussion

Water chemistry

The selected monitoring points (wells and springs) are characterized by variable major ions concentrations with electrical conductivity values increasing from north to south and ranging between 56 $\mu$S/cm, recorded in a spring located in Sondrio Province, and 1290 $\mu$S/cm, detected in a well in Pavia Province (see Fig. 1 for provinces locations). The variability in major ions contents is not reflected in hydro-geochemical feature, which is dominated by calcium-bicarbonate equilibrium as highlighted in Chebotarev diagram (Fig. 2). In fact, this facies characterizes groundwater hydrochemistry in the studied area with a slight trend toward alkaline elements. Specifically, these outliers are represented by two springs and 4 pumping wells; the alkaline component is evident in a water well located in Lecco Province (light blue triangle in Fig. 2).

The hydro-geochemical features of the system confirm the results obtained in previous studies carried out in the same areas (Gorla 2018, Petitta 2018).

Isotope results and aquifer recharge mechanisms

A multi-isotope approach was adopted for this study to obtain a better understanding of aquifer recharge mechanisms, groundwater relative age and flowpath ($d^{18}$O, $d^2$H and $d^3$H in tapped water, $d^{13}$C of DIC).

Stable isotopes data collected in 121 monitoring points show a wide variability with $d^{18}$O values ranging between -13.2‰ and -7.8‰ and $d^2$H from -94.7‰ to -50.2‰. These values, as shown in Figure 3, are comparable with those calculated for Northern Italy by Longinelli and Selmo (2003), with data collected during a regional-scale preliminary sampling survey performed in 2017 (Gorla et al. 2018; Petitta 2018) and with isotope composition of groundwater and rainwater measured at local level (Guffanti et al. 2010; Giustini et al. 2016; Rotiroti et al. 2019). In the same graph are also plotted rain isotope values (Longinelli and Selmo 2003) from three meteorological stations located in Milan (122 m a.s.l.), Sarnico (197 m a.s.l.) and Passo Presolana (1290 m a.s.l.). Comparing isotope results in collected groundwater and in reference rainwater, a clear contribution on aquifer recharge from high-altitude areas is evident. In fact, all the analysed samples have depleted isotopic values, if compared with rain waters collected in the Plain area (Milan and Sarnico stations), showing instead isotopic signal comparable with Passo Presolana station located in the Prealpi Bergamasche Ridge. The calculated elevation gradient value for this area is -0.10‰/100 m (Longinelli and Selmo 2003).
Three groups having different isotope signals were found in the groundwater samples. The first group of waters, which includes all the sample collected in Sondrio Province, shows the more depleted δ¹⁸O (less than -10.0‰) and δ²H values (less than -70.0‰), indicating the clear influence of recharge from high-altitude areas. The second group of samples is characterized by the most enriched values with isotopic signal falling between the rain collected at Sarnico and Passo Presolana stations. This group is representative of the tapped water collected in Monza Brianza and Pavia Provinces, and the values suggest the influence of both local meteoric recharge and surface water infiltration occurrence on isotopic signal. The third group shows δ¹⁸O values ranging between -8.9‰ and -10.0‰ and includes most of the samples collected in the Lombardy Plain area, specifically in the Provinces of Lodi, Cremona, Milan and Lecco.

Additional information about aquifer recharge mechanisms on a regional scale can be inferred analysing δ¹⁸O distribution in the investigated area (Fig. 4). As mentioned before, the northern sector shows the most depleted isotopic signal, which testifies that recharge water comes from high altitude areas both in liquid and solid phases. Moving southwards, the aquifer underlying Monza Brianza and the southern areas of Lecco and Bergamo Provinces is characterized, on the contrary, by the most enriched values, with δ¹⁸O values generally higher than -8.5‰. This evidence points out the key role of local rainfall on aquifer recharge in this portion of the Lombardy Region. Groundwater sampled in wells located in Milan, Pavia, Lodi and Cremona appear again generally more depleted, establishing that the aquifer recharge areas are located at higher elevations.

Furthermore, the good match with the results obtained in the preliminary regional sampling survey carried out during November 2018 (Gorla et al. 2018; Petitta 2018), allowed to assess that the aquifers are recharged regularly (i.e. without variations over time), since there are no isotopic drifts that could suggest variations in feeding mechanism.
Tritium Unit (T.U.) distribution across Lombardy is shown in Figure 5: concentrations vary from minimum values lower than 0.8 T.U., corresponding to the detection limits, to maximum values of 6 T.U.

Fig. 5 - Distribution of tritium (T.U.) in the investigated area; values are ranked in 6 representative classes; symbols represent different aquifer groups (triangle: shallow aquifer (A+B); square: deeper aquifer (C+D); circle: mixed aquifers; diamond: spring).

Tritium content results were classified in 6 significant classes of distribution (Fig. 5). Specifically, 26 samples, all located in the southern sector of the region, have T.U. content lower than 0.8, which implies a relatively old groundwater with long time of residence in the aquifer. Other samples show tritium concentrations always higher than 1 T.U., with more than 70 samples (about 64% of the total) characterized by values higher than 3 T.U. This evidence suggests that the feed of tapped regional aquifer is strongly dependent upon meteoric recharge rate, since actual rainfall tritium values recorded in Italy range between 3 and 6 T.U. in winter months (IAEA 2013, Tazioli 2011).

To shed further light on the recharge conceptual model of the aquifer, a comparison between δ18O (‰) and tritium content is proposed below (Fig.6).

Fig. 6 - δ18O versus tritium concentration (T.U.) for 115 samples; different colors represent provinces, different symbols represent different aquifer groups (triangle: shallow aquifer (A+B); square: deeper aquifer (C+D); circle: mixed aquifers; diamond: spring).

From this comparison it is possible to identify three different groups of groundwater. The first group includes most of the samples, and is characterized by a tritium content always higher than 2 T.U., with enriched values of δ18O (>-8.5‰); this is typical of aquifer directly fed by recent infiltration and relatively short residence-time of tapped groundwater in the aquifer. As already highlighted by groundwater stable isotopes, the clear heterogeneity in δ18O values is due to the wide altitude range of recharge areas.

The second group has T.U. concentrations higher than 2 with enriched values of δ18O (> -8.5‰); this testifies a strong contribution of local recharge on aquifer feeding. This group includes all groundwater collected in Monza/Brianza Province and additional samples belonging to Lecco, Bergamo and Pavia Provinces. The relatively high content in tritium concentration, coupled with the enriched values of δ18O, enables us to infer that, within this limited area of Lombardy, the aquifer is particularly influenced by the groundwater/surface water interaction linked to the high infiltration rate characterizing this area of Po Plain (Martinelli et al. 2018). The last group is represented by samples having tritium concentration lower than 0.8 T.U. with limited variation in δ18O. This groundwater was collected in Cremona, Pavia, Lodigiani and in a deep aquifer layer (brown squares or circles in Fig. 6) of Milan areas. These isotopic features prove that in this sector the aquifer is recharged by water from mountain areas, far from the Plain, and consequently characterized by relatively long residence times.

From this evidence, it is possible to establish that the shallow aquifers (triangles in Fig.6) in the northern area of the region, have groundwater always characterized by short residence time and directly dependent upon meteoric and local recharge. On the contrary, shallow aquifer groups in the Plain area show different residence times. Deeper aquifer groups (squares or circles in Fig.6), where sampled, naturally show a sharp trend toward “older” groundwater.

To deeply investigate the recharge mechanisms and the interaction between shallow and deep aquifer levels, analyses to determine 13C in Dissolved Inorganic Carbon (DIC) on 60 selected samples were carried out.

In addition to groundwater isotopes, analyses on 813C in DIC were performed. Due to the observed dominant calcium-bicarbonate conditions in the aquifer, DIC is assumed to be equal to HCO3\(^-\) concentrations. The isotope data for 813C...
in DIC vary between -13.0‰ and -7.4‰; the correlation presented in Figure 7 shows a high variability in bicarbonate concentrations versus a relatively low variation in $\delta^{13}$C.

Most of the samples show HCO$_3^-$ concentration values ranging between the minimum of 83 mg/l recorded in Sondrio Province to the maximum value of 381 mg/l measured in a sample collected in Lecco area, within a range of variation of $\delta^{13}$C of about -3‰.

The isotopic results for DIC originated from soil CO$_2$ and dissolution of carbonates (Clark and Fritz 1997); in addition, the trend toward more enriched values (over -10‰ of $\delta^{13}$C) is an indication of further carbonate dissolution due to chemical reactions (i.e. cation exchange Ca by Na), which triggered further dissolution of carbonates.

**Isotope results and aquifer pollution**

Groundwater analyses show that, on a regional scale, nitrate concentrations do not exceed the legislation limit for drinking water of 50 mg/l of dissolved nitrate (D. Lgs. 31/2001). The demographic density and the associated high number of human activities are consistent with the highest nitrate concentrations recorded within the territories of Milan and, Monza/Brianza territories, in the southern sectors of Bergamo and Lecco Provinces and in the northern areas of Lodi and Cremona Provinces. In groundwater devoid of tritium, such as that collected in Pavia or Cremona Provinces, nitrate concentrations are very low, confirming that local recharge, surface water or pollutants deriving from human activities do not affect the groundwater flow in these areas.

Isotopes results for $\delta^{15}$N and $\delta^{18}$O in nitrate vary respectively between +1.1‰ and +19.7‰, and between +0.2 and +10.3‰. The most depleted values were detected in a sample collected in Sondrio Province, whereas the most enriched values are associated to a sample from Lodi area.

To understand the origin and the processes involving dissolved nitrate in Lombardy aquifers, $\delta^{15}$N and $\delta^{18}$O data were compared with literature data, modified and updated, defined by Kendall (1998), only for the nitrates associated to manure and sewage, and with data defined in Aravena and Robertson (1998) and Caschetto et al. (2018). The obtained results are plotted in Figure 8.

The use of combined $\delta^{15}$N and $\delta^{18}$O generally reveals source separation and mixing relationship, as well as occurring degradation processes (Petitta et al. 2009; Sacchi et al. 2013).

In the study area the origin of nitrates is associated to two main sources: nitrates related to manure, animal waste and leakage from sewage pipelines (green box in Fig.8), and nitrates linked to the use of ammonium fertilizers (blue box in Fig.8).

The $\delta^{18}$O values show a range between 0.2‰ and 10.3‰, with most of the values around 1.8‰ and 5.0‰. Since nitrification is one of the main processes responsible for production of nitrates, and it has been documented that during nitrification 1/3 of the oxygen comes from the atmosphere O$_2$ and 2/3 from the oxygen in the water (Anderson and Hooper 1983; Hollocher 1984), it is possible, based on the $\delta^{18}$O in H$_2$O, to estimate the $\delta^{18}$O of the nitrate associated to nitrification of ammonium. Based on the same dataset of 45 samples, $\delta^{18}$O of groundwater ranges between -7.8 and -10.8‰, and tacking into account that the $\delta^{18}$O of the atmospheric O$_2$ is +22‰, the nitrates associated to nitrification of ammonium in the study area should range between 0.1‰ and 2.1‰. This range tends to be lower than the measured data. This estimation approach assumed that the water involved in nitrification is represented by the groundwater in each area; however, it is possible that the water used in the irrigation areas can be affected by some evaporation in the fields: this could partially explain the enrichment observed in the measured data compared to the estimated values.

The estimated $\delta^{18}$O values for nitrates suggested also that nitrate is mainly produced by nitrification of ammonium. The sources of ammonium in the study area could be urea, ammonium fertilizers and ammonium from manure and sewage. It is well documented that volatilization of ammonia enriches the remaining ammonium in $^{15}$N, which could “move” the isotope composition of the nitrate from nitrification of urea and ammonium fertilizers toward the field of sewage and manure.

In addition, few samples show typical isotopes signature associated to denitrification processes (most enriched values), which are two wells located in Lodi Province and one in Cremona. Sacchi et al. (2013) demonstrate that in the south-east sector of the lower plain denitrification processes mainly occur when water table is shallower than 5 m from ground surface. Groundwater sampled at such a shallow depth in our survey confirms the occurrence of denitrification processes, but the limited number of samples with these characteristics does not allow a direct comparison with the results from previous studies.

Sulphate in groundwater is evenly distributed along the investigated area due both to natural and to anthropogenic
Origin. Maximum concentrations were detected in Sondrio Province, whereas minimum concentrations, even below detection limit, were measured in the aquifer in the Cremona, Lodi and Pavia Provinces. The latter are the same pumping wells with both tritium and nitrates below the detection limits. This evidence confirms that this sector of the aquifer is not directly fed by local recharge.

Isotopes values for $\delta^{34}S$ vary between -3.8‰ and +12.3‰, while $\delta^{18}O$ values range between 0.4‰ and +14‰, not showing a depletion or enrichment trend along regional flow directions. $\delta^{34}S$ most depleted value was detected in Lecco Province (-3.8‰), on the contrary the most enriched one was measured in Bergamo Province (+12.3‰).

To correctly assess source and processes involving dissolved sulphate in the regional aquifer, $\delta^{34}S$ and $\delta^{18}O$ were compared with literature data (Carucci et al. 2012), as shown in Figure 9. The data confirm that marine sulphate (evaporites, orange field in Fig.9) is one of the main sources of sulphate in the aquifer and the other one is linked to oxidation of sulphide minerals (green field in Fig. 9). Consequently, can be postulated that most of the sulphate is a mixture of these end members, but sulphate from fertilizers could be also considered as a source of this compound in groundwater. The relatively high sulphate concentrations in groundwater certainly allows to exclude an origin related to atmospheric deposition (blue field in Fig. 9).
Fig. 9 - $\delta^{34}S$ versus $\delta^{18}O$ in dissolved sulfate for 52 samples, compared with literature data (Carucci et al. 2012); different colours represent provinces, symbols represent different aquifer groups (triangle: shallow aquifer (A+B); square: deeper aquifer (C+D); circle: mixed aquifers; diamond: spring).

Conclusions

Lombardy is one of the most inhabited regions of Italy, characterized by an increasing population density, and consequently of human activities, from north to south, as far as permitted by the physiography of the region. A detailed knowledge of aquifer systems in terms of recharge of the aquifers, groundwater flow and quality is a crucial point to safeguard water resources used for drinking purpose.

This study deals with the application on a regional scale of a multi-isotopic approach applied to an investigation, involving different Lombardy’s provinces and water suppliers belonging to the Water Alliance. The results of the study provide an uncommon regional isotope characterization, confirming the usefulness of a multi-isotopic approach in defining origin and relative ages of groundwater resources, and in assessing the impact of human activities.

In detail, the most relevant findings and results obtained from the chemical and isotopic investigations carried out can be summarized as follows.

Groundwater chemistry is clearly calcium-bicarbonate in the whole region, with slight changes toward alkaline elements in few samples collected in the northern sector of the region, showing an increase in electrical conductivity from north to south.

Stable water isotopes demonstrated that aquifers are generally recharged by meteoric water coming from areas with different altitudes, as testified by the wide range of variability of both $\delta^{18}O$ and $\delta^2H$ values, decreasing with altitude increase. Nevertheless, in Monza/Brianza Province enriched values of stable isotopes highlighted a clear influence of local recharge linked to the high infiltration rate characterizing the aquifer in this portion of the region, possibly due to irrigation and direct surface-water infiltration.

Tritium results, which define groundwater relative age and turnover time of water within the aquifer, generally confirm the recharge conceptual model defined by groundwater stable isotopes. Most of the samples showed tritium concentration comparable or slightly lower than tritium detected in rainwater, testifying a regular and continuous renewal rate of groundwater resources and relatively short circulation times. On the other hand, in the southern area of the region, tritium values below detection limit measured in a significant number of wells, highlighted longer times of residence of groundwater in the aquifer, not directly influenced by rainwater.

Additional information was obtained through the use of $\delta^{13}C$ isotope in DIC (Dissolved Inorganic Carbon), which revealed that the origin of DIC is mainly linked to carbonate dissolution, as confirmed also by carbon isotope fractionation values.

Through the help of $\delta^{15}N$ and $\delta^{18}O$ in dissolved nitrate, the origin of nitrate and the occurrence of degradation processes into the aquifer were preliminarily inferred. Nitrate in groundwater is associated both to ammonium fertilizers and to manure and leakage from sewage pipelines. Nitrate isotope signal suggests that, in the investigated area, significant degradation processes in the aquifer occur only to a limited extent and locally.

The plain area of Lombardy is the most affected by nitrate pollution, except for the area characterized by the lowest tritium content, where also nitrate is under detection limit. This portion of the aquifer can be considered sufficiently isolated and not directly influenced by local infiltration processes. Nitrate occurrence is mainly associated to shallow aquifers, but also deeper aquifer groups sometimes show relevant nitrate concentration.

The analyses of $\delta^{34}S$ and $\delta^{18}O$ in dissolved sulphates show...
that the main sources of sulphate are associated with evaporites (marine sulphates) and oxidation of sulphide minerals. In agricultural areas, sulphate origin could be also correlated to the use of fertilizers. Even for sulphate no evidence of natural attenuation was highlighted by the isotope analyses.

We are confident the results obtained through this regional isotope screening will be useful for water suppliers, especially if coupled with further and deeper hydrogeological and hydro-geochemical research, for the optimization of future management options, applied to a more local scale or even down to the single water well.

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