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Assessing nitrate origin in a volcanic aquifer using a dual isotope approach

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Abstract Identifying the origin of nitrate is important for the control and management of groundwater quality in aquifer systems. In the southern Apennines (Italy), the Mount Vulture volcanic aquifer is a large and valuable resource of potable and mineral water supply. Unfortunately, signs of anthropogenic impact, especially nitrogen contamination, have recently become evident. In this study, and for the first time, stable isotope ratios ($\delta^{15}N$ and $\delta^{18}O$) of NO_3^- were determined in groundwater to identify their origins and evaluate the presence of transformation processes. The Mount Vulture groundwaters are meteoric in origin, as demonstrated by measurements of δD and $\delta^{18}O$, and can be divided into two distinct areas based on their NO_3^- content. In the southeastern area, characterized by active agricultural land use, the high NO_3^- content and the $\delta^{15}N$–NO_3 isotopic values are due to anthropogenic contamination (inorganic fertilizer). In groundwaters from the western area, the NO_3^- contents below 4 mg/L and the $\delta^{15}N$–NO_3 values can be associated at organic soil N. Evidence for local denitrification may be assumed in a few groundwater samples of the western area showing relatively heavy $\delta^{15}N$ values and low concentrations of nitrate. Finally, the low measured $\delta^{18}O$ values indicate that nitrification occurred in both investigated areas.

Keywords Anthropogenic contamination · Groundwater · Nitrification · Nitrogen and oxygen isotopes

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Introduction

The Mount (Mt. thereafter) Vulture basin represents one of the most important aquifer systems of southern Italy. Groundwater in this aquifer is an important and valuable resource for potable and mineral water supply, and agricultural and industrial uses. Groundwater extraction, which started in the 1940s, has been gradually increased during recent years to satisfy the rising water demand. However, signs of anthropogenic impact, especially nitrogen contamination, have recently become evident (Parisi et al. 2011a; Paternoster et al. 2010). The European Union standard for drinking and mineral water quality is 50 mg/L of NO_3^- (EU directive 1998/83/EC; EU directive 2003/40/EC, respectively). The World Health Organization has set a limit of 44.3 mg/L of NO_3^- for drinking water, to protect infants from ingesting groundwater high in nitrate. The isotopic composition ($\delta^{15}N$) of dissolved nitrate has been extensively used to provide information on the origins and transformations of inorganic N in the hydrosphere (Heaton 1986). Nitrate (NO_3^-) is found naturally in moderate concentrations in many aquatic environments, but its concentration is often increased due to the use of nitrogen-containing fertilizers (Chae et al. 2009; Choi et al. 2011) and the discharge of waste water and manure (Benkovitz et al. 1996; Choi et al. 2007). Liu et al. (2006) reported that these sources produce nitrate with distinguishable $^{15}N/^{14}N$ ratios: $\delta^{15}N$ values are from -1 to $+2$ ‰ for synthetic fertilizer, from $+2$ to $+8$ ‰ for soil organic nitrogen, and from $+8$ to $+20$ ‰ for livestock waste and sewage. However, a disadvantage of the single isotope approach is its inability to identify sources and transformation of NO_3^- in groundwater due to the non-conservative behavior of nitrogen in the earth's surface (Kendall 1998). In fact, nitrogen is biologically modified through, for example,

denitrification reactions that cause isotope fractionation and modify the isotope composition of the dissolved N species (Silva et al. 2000). Denitrification can cause enrichment in heavy isotope of nitrogen and oxygen in the residual NO_3^- (Amberger and Schmit 1987; Aravena et al. 1998; Böttcher et al. 1990; Fukada et al. 2003). The $\delta^{18}O$ of NO_3 has been used to provide more information about the nitrate cycling in groundwater (Amberger and Schmit 1987; Böttcher et al. 1990; Kendall 1998). Typical $\delta^{18}O$ values of NO_3^- from nitrification (including $\delta^{18}O$ values from microbial production of NH_4^+ in fertilizers and precipitation, NO_3^- derived from both soil N and manure plus sewage) are lower than that of NO_3^- from precipitation and NO_3^- in fertilizer (Xue et al. 2009). The $\delta^{18}O$ of microbially produced NO_3^-, NO_3^- in precipitation and NO_3^- fertilizer are regulated by different processes. During nitrification, about one-third of the oxygen of the NO_3^- ion is from the atmosphere while two-third is from the groundwater (Andersson and Hooper 1983; Anisfield et al. 2007). Nitrate derived from nitrification should theoretically have $\delta^{18}O$ values between -10 and $+10$ ‰, since environmental water typically has $\delta^{18}O$ values between -25 and $+4$ ‰ and $\delta^{18}O$ of atmospheric O_2 is $+23.5$ ‰ (Liu et al. 2006; Xue et al. 2009). The $\delta^{18}O–NO_3$ of precipitation is controlled by complex atmospheric processes, which result in large spatial and temporal variability in $\delta^{18}O–NO_3$ (from $+25$ to $+75$ ‰). Synthetic NO_3^- fertilizers have distinctive $\delta^{18}O$ values (Amberger and Schmit 1987), with a range from $+17$ to $+25$ ‰, as the O is mainly derived from atmospheric O_2 ($\delta^{18}O = +23.5$ ‰). Therefore, a dual isotope approach (combination of ^{15}N and ^{18}O) can enhance the ability to delineate nitrate sources and transformation processes in groundwater (Aravena and Robertson 1998; Aravena et al. 1993; Panno et al. 2001; Seiler 2005; Widory et al. 2004). Because the Mt. Vulture groundwater is a major source of potable and mineral water in southern Italy, defining origin of groundwater and identifying the possible sources of contamination in this aquifer is essential for determining the causes of increasing NO_3^- concentrations, and for monitoring groundwater quality in the future. Therefore, the present study has been performed with the following objectives: (1) to report for the first time, in addition to the classical δD and $\delta^{18}O$ in groundwater, the isotopic values of $\delta^{15}N$ and $\delta^{18}O$ in NO_3^-, and (2) to trace natural and anthropogenic sources of nitrate in order to identify the transformation processes.

Study area

Mt. Vulture is a Pleistocene composite volcano (1.320 m above sea level) located at the easternmost border of the Apennine compressive front (Fig. 1), at the western margin of the Apulia foreland. The volcanic products are characterized by lavas and pyroclastics ranging in composition from basanites and foidites, to phonolites, with several intermediate rock types (e.g., Beccaluva et al. 2002). The volcanic products lie over Pleistocene gravel and clay, in sub-horizontal layers that cover the intensely deformed flysch sediments of Miocene age. Various conceptual hydrogeological models have been proposed for the Mt. Vulture aquifer. Parisi et al. (2011a) recently conducted a comprehensive isotopic, hydrogeochemical, and hydraulic study that provides a better definition of the recharge and discharge patterns of the Mt. Vulture volcanic aquifer system. The flowing groundwater moves along radial flow paths of various lengths and depths toward the lowest elevations in the south and southeastern parts of the aquifer. The volcano hosts numerous springs and wells emerging from the highest to the lowest elevations around the cone. The volcanic aquifer is comprised of highly permeable units such as coarse pyroclastic layers, fissured lava flows, and fissured tuff, and to a lesser extent of low-permeability units including fine pyroclastic layers, compact tuff, and palaeosoils. The more permeable units of these various lithological units constitute a unique unconfined aquifer (Spilotro et al. 2006).

According to UNESCO/FAO (1963), the study area has a temperate Mediterranean climate and an annual average temperature of about 13 °C, with a maximum from June to August (22 °C) and a minimum between December and February (~ 5 °C). The annual average precipitation is about 750 mm, with a maximum amount of rainfall from November to January (Parisi et al. 2011a). The maximum rainfall amounts are associated with the highest elevations of the study area.

In the western area of Mt. Vulture, the soils are principally developed on pyroclastic deposits and are covered by forests, pastures, and fields uncultivated. Beech forests are widespread at higher altitudes while oak and chestnut trees are found at lower altitudes. The soils in the southeastern area of Mt. Vulture have developed mainly on pyroclastic material and colluvial, fluvial, and lacustrine deposits. This area is characterized by active agricultural land use where crops (i.e. wheat, barley, oats) are prevalent. In the southeastern area commercial fertilizers, including urea ($CO(NH_2)_2$) and N–P–K fertilizers with minor pro-portions of lime, ammonium sulfate, K and Mg sulfate and KCl, are applied on agricultural fields year-round.

Materials and methods

Water from 29 springs and operating wells, owned by both companies and private individuals, and used for irrigation and drinking water supply, were collected during a single field trip between January and March 2009. The wells were
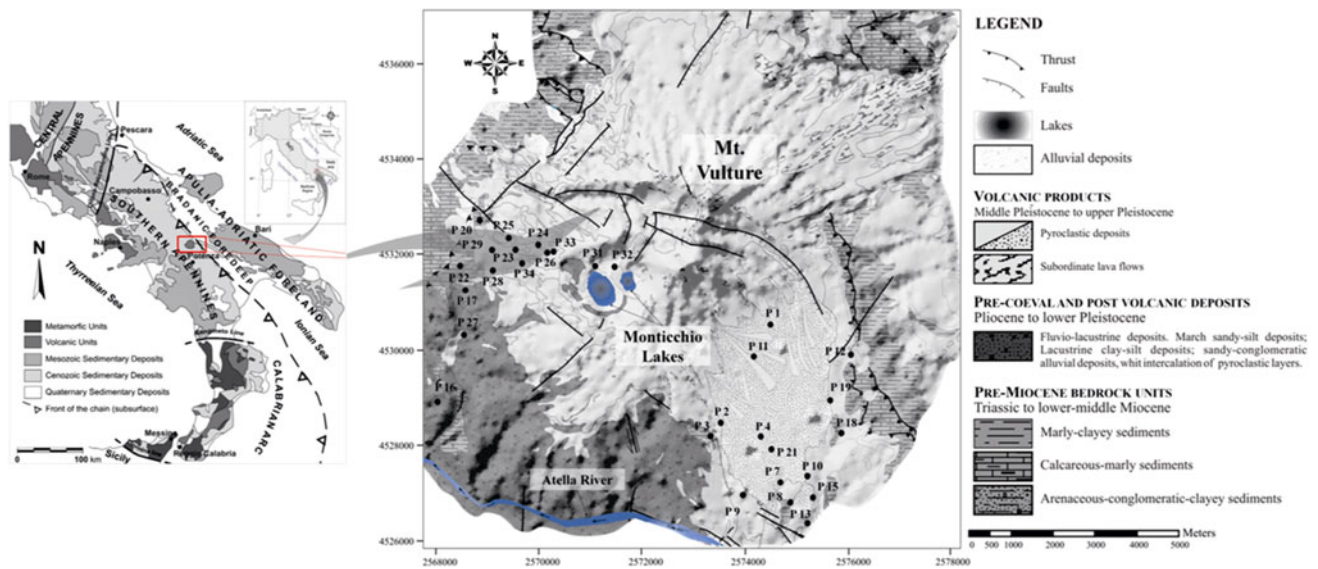
Fig. 1 On the *left* sketch geological map of the central-southern Italy (from Bonardi et al. 2009). On the *right* geological setting of Mt. Vulture area (modified from Giannandrea et al. 2004)

sunk to depths of 100–250 m, and were drilled into volcanic products (pyroclastic and effusive rocks). The sampling sites were selected based on the presence of particular hydrogeological and hydrogeochemical features found in the area, which related to the geological context. Sampling sites (Fig. 1) were located mainly in the W and S–SE sectors of the study area, and within the volcanic products. Some of the sampling sites in the SE sector were located near urban areas. The dissolved NO_3^- and NO_2^- were analyzed using ion chromatography at Actlabs Laboratories (Canada), with experimental accuracy better than ±5 %. Samples of NO_3^- for isotopic analysis were collected following the methods described by Chang et al. (1999) and were analyzed for $\delta^{15}N$ and $\delta^{18}O$ in the Isotope Science Laboratory (ISL-UofC) using the denitrifier technique (Casciotti et al. 2002; Sigman et al. 2001). The N and O isotope ratios were measured on the produced N_2O using a Finnigan Mat Delta Plus XL isotope ratio mass spectrometer. The reproducibility of duplicate analyzes was approximately ±0.5 ‰ for $\delta^{15}N$ and ±0.7 ‰ for $\delta^{18}O$. Oxygen isotope compositions were measured on triplicate samples using the CO_2–water equilibration technique (Epstein and Mayeda 1953) and hydrogen isotope analyses were performed using the zinc reduction method (Coleman et al. 1982). Stable isotope ratios were measured on a dual inlet Finnigan Delta Plus IRMS with analytical precision of better than ±0.2 ‰ for oxygen and ±1 ‰ for hydrogen. Five water samples calibrated with respect to V-SMOW and GISP International Standards were used as working standards. Stable isotope ratios (D/H and $^{18}O/^{16}O$) were provided by the Istituto Nazionale di Geofisica e Vulcanologia (INGV), section of Palermo

(Italy). All the isotope measurements were reported in delta units (δ) with respect to the V-SMOW international standard (for $\delta^{18}O$ and δD) and to atmospheric nitrogen (for $\delta^{15}N$).

Results and discussion

Table 1 summarizes the isotopic and chemical data of the 29 groundwater samples. Groundwaters in the Mt. Vulture area range in temperature from 8.8 to 19.9 °C, pH values from 5.7 to 7.6, and electrical conductivity from 141 to 4,350 μS/cm (Parisi et al. 2011b). Much of the groundwater has a bicarbonate alkaline-earth and alkaline composition, with the exception of a few springs that are bicarbonate–sulfate–alkaline in composition and show the highest salinity values (Parisi et al. 2011a). Further details of the water chemistry and isotopic composition (δD, $\delta^{18}O$, and $\delta^{13}C$) are summarized in Caracausi et al. (2009), Parisi et al. (2011a, b); Paternoster et al. (2008, 2010). In general, the investigated groundwater not show season variations in major, minor, and trace elements. Most of the Mt. Vulture groundwaters display CO_2 partial pressure values that are 1–3 orders of magnitude higher than the atmospheric value. The CO_2 in these groundwaters is magmatic in origin (Caracausi et al. 2009; Paternoster 2005). During basalt weathering, CO_2 is converted into bicarbonate, which shows a positive correlation with the concentration of major and minor elements. The composition of bicarbonate alkaline-earth and alkaline waters is due to variability in the processes of interaction between water and volcanic rock, and to the dissolved-CO_2-rich gases within the

Table 1 Chemical and isotopic data

Sample no.	Long.(north)	Lat.(east)	Elevation (m a.s.l.)	Type	Well depth (m)	T^a (°C)	Electric conductivity^a 25° C (µS/cm)	pH^a	$\delta^{18}O$ (‰)	δD (‰)	NO_2^- (mg/L)	NO_3^- (mg/L)	$\delta^{15}N$–NO_3 (‰)	$\delta^{18}O$–NO_3 (‰)
P1	4,531,210	555,380	545	W	150	13.0	350	6.6	−8.5	−54	<0.1	43.2	7.3	−1.9
P2	4,528,490	554,302	544	W	96	15.2	237	6.8	−8.7	−54	<0.1	30.8	3.7	1.0
P3	4,528,250	554,060	600	W	132	17.2	233	7.5	−8.9	−55	<0.1	23.1	4.1	1.4
P4	4,528,240	555,360	545	W	128	15.0	304	6.1	−9.0	−55	<0.1	15.5	4.2	1.9
P7	4,526,900	556,320	490	W	n.m.	15.3	607	6.1	−9.4	−57	<0.1	16.9	4.2	0.5
P8	4,526,817	556,303	490	W	n.m.	14.1	478	6.9	−8.8	−55	<0.1	26.6	4.8	2.1
P9	4,526,707	556,342	490	W	n.m.	13.8	430	6.9	−8.5	−54	<0.1	28.5	3.5	−0.5
P10	4,526,605	556,340	483	W	120	16.0	291	7.0	−8.3	−52	<0.1	40.7	6.1	3.2
P11	4,531,235	555467	555	W	150	13.1	234	6.2	−9.3	−55	<0.1	16.4	4.3	−0.8
P12	4,534,820	557,160	519	W	133	15.7	265	6.5	−8.6	−53	<0.1	11.1	5.0	−1.0
P13	4,525,820	555,300	474	S	–	15.7	763	5.9	−8.6	−54	<0.1	12.8	6.2	1.0
P15	4,526,955	556,359	487	W	130	14.7	896	5.9	−9.1	−57	<0.1	22.2	3.2	1.7
P18	4,527,726	556,960	550	W	180	15.0	370	5.9	−8.6	−55	<0.1	33.2	7.6	2.5
P19	4,527,739	556,970	552	W	132	16.1	362	6.3	−9.3	−58	<0.1	8.0	3.8	−1.9
P21	4,526,870	556,607	493	W	160	16.1	435	6.1	−9.3	−57	<0.1	7.9	3.3	2.1
P20	4,527,726	555,196	554	W	250	18.5	1,717	6.3	−9.8	−60	<0.1	2.2	9.7	n.m.
P17	4,526,867	552,828	449	S	–	17.0	4,350	6.5	−8.5	−53	<0.1	3.1	11.9	n.m.
P22	4,532,983	547,976	547	S	–	17.4	2,149	6.2	−9.4	−56	<0.1	0.9	6.5	3.1
P23	4,533,314	549,828	566	W	183	16.8	750	5.9	−9.5	−57	<0.1	3.5	6.7	2.8
P26	4,532,938	551,154	690	W	157	19.5	1,147	6.0	−9.6	−57	<0.1	2.1	7.0	4.1
P28	4,532,832	549,658	650	W	96	19.9	1,346	6.1	−9.6	−58	<0.1	1.9	11.3	3.9
P29	4,533,100	549,100	644	W	202	19.5	918	5.9	−8.3	−52	<0.1	3.1	6.1	0.4
P24	4,533,306	550,031	565	W	208	18.1	1,480	6.0	−9.6	−57	<0.1	0.9	4.2	4.1
P25	4,533,379	549,532	657	W	643	14.0	351	6.1	−9.1	−53	<0.1	1.3	2.5	2.9
P27	4,530,603	547,666	682	W	144	18.9	698	5.9	−9.4	−55	<0.1	1.9	4.3	0.3
P31	4,532,900	551,950	885	S	–	9.6	206	7.6	−9.7	−60	<0.1	0.6	4.3	1.7
P32	4,533,066	552,194	960	S	–	8.8	141	7.0	−9.6	−59	<0.1	2.9	2.4	0.6
P33	4,532,966	551,315	780	W	251	15.8	369	5.9	−9.3	−55	<0.1	1.8	4.6	0.9
P34	4,532,930	550,040	735	W	202	16.5	448	5.7	−9.2	−57	<0.1	2.6	3.6	0.8

The location of sampling point are provided in UTM Zone 33 coordinates using the European Datum of 1950

n.m. not measured, *S* spring, *W* well

^{a} Data from Parisi et al. (2011b)

flowing groundwaters. In contrast, the bicarbonate–sulfate–alkaline waters showing the highest salinity values are related to prolonged water circulation in alkali and feldspathoid-rich pyroclastic layers.

The samples had δD and $\delta^{18}O$ isotopic compositions ranging between −8.3 and −9.7 ‰ for oxygen, and −62 and −52 ‰ for deuterium. In the binary diagram δD–$\delta^{18}O$ (Fig. 2), the investigated groundwater samples lie close to the local meteoric water line (LMWL; Paternoster et al. 2008), indicating that samples was not affected by secondary processes after rainfall (e.g., evaporation, evapotranspiration). Consequently, the water samples are retained as meteoric in origin. The measured isotopic data are in the range of the values reported by Parisi et al.

(2011a) and Paternoster et al. (2008), which excluded any significant seasonal variation. The nitrate concentration ranged from 0.6 to 43.2 mg/L, with an average value of 12.6 mg/L. However, substantial differences in NO_3^- concentration were found between the western and southeastern areas of the Mt. Vulture aquifer. In the southeastern area, groundwaters had higher NO_3^- concentrations ($NO_3^- > 8$ mg/L) than in the western part ($NO_3^- < 4$ mg/L). NO_2^- concentrations were below the detection limit (0.1 mg/L) in almost all waters. The values of $\delta^{15}N$–NO_3 ranged from +2.4 to +11.9 ‰, and $\delta^{18}O$–NO_3 from −1.9 to +4.1 ‰. In the southeastern area, $\delta^{15}N$–NO_3 values range between +3.2 and +7.6 ‰ while $\delta^{18}O$–NO_3 data between −1.9 and +3.2 ‰. The $\delta^{15}N$–NO_3 and $\delta^{18}O$–NO_3
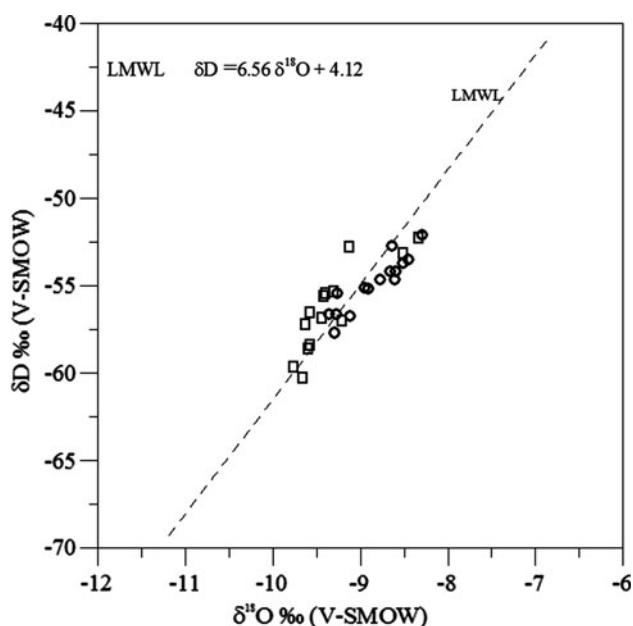
Fig. 2 $\delta^{18}O$ and δD plot of groundwater samples. *Circle* and *square* represent groundwaters from southeastern and western area, respectively
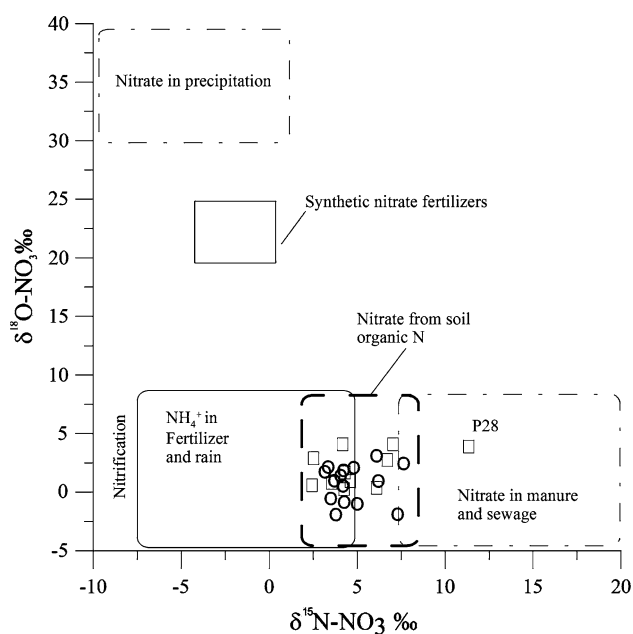
Fig. 3 Pattern of typical ranges of $\delta^{18}O$ and $\delta^{15}N$ for different nitrate sources (after Choi et al. 2011) and values measured in Mt. Vulture area

values of groundwater in the western area ranged from +2.4 to +11.9 ‰ and between 0.3 and +4.1 ‰, respectively. For two groundwaters (P20 and P17 samples), the $\delta^{18}O$ values were not reported because of high uncertainty.

Source of nitrate and its behavior

The dual-isotope approach ($\delta^{15}N$–NO_3 and $\delta^{18}O$–NO_3) provide a useful method for identifying the origin of NO_3^-

and fractionation processes that nitrate has undergone in aquifer system (Panno et al. 2001). The boxes in Fig. 3 show typical ranges of $\delta^{15}N$ and $\delta^{18}O$ deriving from various natural and anthropogenic sources of NO_3^- (after Choi et al. 2011). NO_3^- originating from both precipitation and synthetic NO_3^- fertilizer has much higher $\delta^{18}O$ values than that resulting from nitrification of reduced N sources (i.e. fertilizer applied as NH_4^+ and urea, soil organic N, and NH_4^+ from sewage and manure). The nitrate deriving from these forms of reduced N can be distinguished by its $\delta^{15}N$–NO_3 value, although a some degree of overlap. The investigated water samples have $\delta^{15}N$–NO_3 and $\delta^{18}O$–NO_3 values within the observed range of both soil organic N and inorganic fertilizer (Choi et al. 2011; Kendall 1998). Only one water (P28 sample) has high $\delta^{15}N$–NO_3 values and overlap the range of nitrate from manure and septic waste (Kendall 1998; Xue et al. 2009). More in general, a negative correlation between $\delta^{15}N$ (and $\delta^{18}O$) and NO_3^- concentrations is not observed (Fig. 4a, b, respectively). Although there are no baseline data on the level of natural NO_3^- concentrations in this area, nitrate values above 4 mg/L may be retained as due to anthropogenic contamination, according to Babiker et al. (2004) and Burkart and Kolpin (1993). Therefore, the NO_3^- concentrations of 8–43 mg/L of groundwater from southeastern area are too high to assume that the source of NO_3^- is natural soil nitrogen. We postulate that the high NO_3^- concentrations and the measured $\delta^{15}N$ values are due to anthropogenic contamination (inorganic fertilizers). This interpretation is consistent with the fact that the southeastern area contains crop farming. The most of samples from the western area are characterized by $\delta^{15}N$-NO_3 values in the range from +2.4 to +7.0 ‰ and NO_3^- concentrations lower than 4 mg/L, highlighting that the source of nitrate is soil organic N. The anomalously heavy $\delta^{15}N$ values observed in three samples (P20, P17, and P28) may suggest that a significant contribution of NO_3^- from an isotopically heavy $\delta^{15}N$ source is present. Since these samples have low NO_3^- concentrations and relatively high values of $\delta^{15}N$ they could be affected by denitrification. Kendall (1998) suggested that denitrification is usually associated with both a significant increase in alkalinity, resulting from the oxidation of organic matter, and the presence of dissolved Mn and Fe, due to the dissolution of Fe- and Mn-minerals. The P20, P17, and P28 samples are characterized by very high contents of dissolved Mn and Fe due to the redox reactions occurring in the system (Parisi et al. 2011b). Overall this points toward the existence of a redox gradient involving a placed nitrate reduction.

Values of $\delta^{18}O$–NO_3 provided a further indication of sources and transformation of nitrate in groundwater. The $\delta^{18}O$ values of NO_3^- in groundwater (Fig. 4b) range from −1.9 to +4.1 ‰. It is known, that NH_4^+ and NO_3^- from

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Fig. 4 **a** $\delta^{15}N$ composition of dissolved NO_3^- versus NO_3^- concentrations. The *box* shows $\delta^{15}N–NO_3$ values of soil source of nitrate (Kendall 1998); **b** $\delta^{18}O$ composition of dissolved NO_3^- versus NO_3^- concentrations. The estimated range of $\delta^{18}O$ values for nitrate derived from nitrification is shown. *Symbols* as in Fig. 2
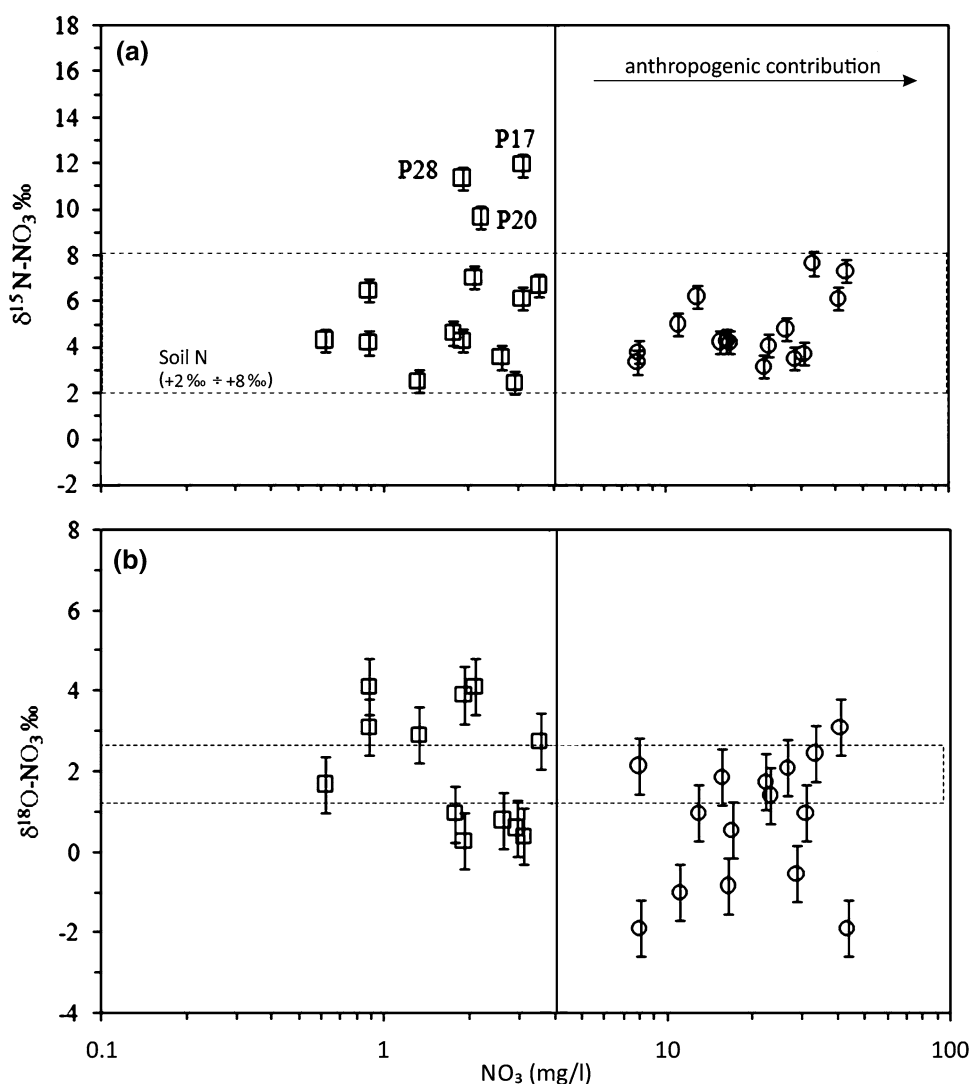
chemical fertilizers are rapidly immobilized as organic N in agricultural soils (Mengis et al. 2001). Based on experimental studies, it is suggested that NO_3^- produced during nitrification should contain two-third of the oxygen from soil water and one-third of the oxygen from atmospheric oxygen (Anisfield et al. 2007; Aravena et al. 1993; Liu et al. 2006; Wassenaar 1995). Assuming the oxygen from these sources is incorporated without isotope fractionation (Mayer et al. 2001), the $\delta^{18}O–NO_3$ value of the newly formed NO_3 can be calculated as shown below (Fukada et al. 2004):

$$\delta^{18}O–NO_3 = (2/3)(\delta^{18}O–H_2O) + (13)(\delta^{18}O–O_2) \quad (1)$$

Since the measured $\delta^{18}O$ values of groundwater in the study area range between −8.3 and −9.8 ‰ and the $\delta^{18}O–O_2$ for molecular oxygen is +23.5 ‰ (Liu et al. 2006; Xue et al. 2009), the expected $\delta^{18}O–NO_3$ values for nitrate derived from nitrification would then be from +1.3 to +2.3 ‰. However, it has to be stressed that this

expected local nitrate $\delta^{18}O$ range is rather simplified, because the relative contribution of ambient O from surrounding water and O_2 has been found not always keeping the rule of 2:1 (Mayer et al. 2001). Bearing in mind the uncertainties and assumptions in the use of Eq. (1), it is worth of note that these theoretically expected values correspond exactly to the middle of the range of values measured for nitrate in groundwater ($\delta^{18}O–NO_3$ from −1.9 to +4.1 ‰). Thus, we believe that the low measured $\delta^{18}O$ values indicate that nitrification occurred in both the investigated areas.

Conclusion

The isotopic data ($\delta^{18}O$ and δD) of the investigated groundwater indicate that are meteoric in origin. NO_3^- contents allowed us to discriminate the western area from the southeastern areas. In water samples from the

southeastern area, NO_3^- contents above 8 mg/L were detected, $\delta^{15}N$–NO_3 isotopic values suggest that NO_3^- originated from anthropogenic contamination (inorganic fertilizers). The measured low $\delta^{18}O$ values indicate that groundwater nitrate derived from nitrification of inorganic fertilizers in an area affected by active agricultural land use. In groundwater from the western area, the NO_3^- content was lower, and the $\delta^{15}N$–NO_3 values generally suggest a natural NO_3^- origin from organic soil N. In addition, the low $\delta^{18}O$ values indicate that groundwater nitrate derives from nitrification of organic soil N. However, for a few samples located in this area showing relatively heavy $\delta^{15}N$ values and low concentrations of nitrate a placed nitrate reduction could not be excluded.

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