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The isotopic composition of nitrates from underground and surficial waters of Italy: a valuable tool for benefiting in the fight against pollution

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Abstract

A review of isotopic data of nitrates in groundwater mainly from wells located in northern and central Italy has been carried out. A subordinate number of data refers to surface waters from the Po plain area. Most of the sampling areas, that are located in the proximity of important human settlements, are devoted to intensive agriculture and, thus, isotopic data indicate that the nitrogen source is mainly represented by mineralized synthetic fertilizers. A subordinate source is composed of either the soil organic fraction and animal manure used as a fertilizer. Only for a few water samples, the origin from sewage seep is suggested. Denitrification can occur in many aquifers, contributing to abate significantly nitrate concentrations in waters. Lastly, the absence of isotopic data for the waters from uppermost Regions of southern Italy and Sicily represents a major handicap in the fight against nitrate pollution, making the maps of nitrate risk in those areas not fully useful.

Key words: N isotopes; nitrates; surface/ground water; pollution; Italy.

Introduction

The concern about the potential pollution of surface and ground water because of increasing human pressure on the environment, has recently spurred environmental geochemists to focus on the isotopic characteristics of nitrates, that represent a major source of risk to human health when present in high concentrations (see for instance Carpenter et al., 1998). Both the 91/676 and 2006/118 Directives issued by EEC for the protection of waters from nitrates of agricultural origin, have been implemented in Italy. In particular, the Regional Administrations are now responsible for the identification of vulnerable areas, as well as the layout and implementation of protocols of control and monitoring in those areas. Therefore, vulnerability maps at a square-kilometer scale have been so far drafted by each Region, letting us know that northern Italy is by far the most affected area by nitrate pollution. This is not surprising as the Padan-Venetian plain is by far the most productive agricultural area of Italy. However, the coastal areas of central-southern Italy also exhibit remarkably high nitrate concentrations (Capri et al., 2009).

In the last decade, a number of isotopic techniques have been developed aimed at defining the nitrate origin in waters. Such techniques are based on the systematics of N and O isotopes of the nitrate ion (Clark and Fritz, 1997). In Italy, the application of these systematics is still far from to be routinely; however, a number of data have been published, but several are still unpublished. In this context, the most of papers on nitrates refer to northern Italy (Arduini et al., 2008; Aquanet, 2004, Chahoud et al., 2002; Dadomo et al., 2005; Debernardi et al., 2008; Del Conte et al., 2010; Guffanti et al., 2010; Lasagna et al., 2005; Patrizi, 2002; Pilla et al., 2005; 2007; Sacchi et al., 2007, 2011), and only a few exhibit data from central Italy (Arpa Sardegna, 2009, d'Antona et al., 2009; Petitta et al., 2009; Nisi et al., 2007), and Campania (Corniello and Ducci, 2009; D'Antonio et al., 2009). Lacking so far a comprehensive review of all data available, thus, we present this paper aimed at providing the users with a useful tool. In fact, the knowledge of isotopic compositions of nitrates in waters allows for predicting the potential sources of nitrogen and, thus, provides basic information to the Administrations and other Authorities responsible for the environmental protection, in their daily struggle against pollution.

The uppermost of isotopic data here reported refer to groundwater samples from wells located in alluvial plains, mainly of the Quaternary. These plains may host simple or multi-layer aquifers, and all devoted to the agriculture, including a few areas also hosting livestock breeding farms. Therefore, the source of the nitrates present in waters is generally represented by mainly synthetic fertilizers used in the agriculture. Livestock manure and effluents from septic tanks can locally represent subordinate sources of nitrogen. Lastly, some areas located in the proximity of urban settlements can provide nitrogen from leakage of sewage network.

Isotopic compositions of nitrates

The isotopic data of N and O of nitrates presented in this paper are expressed in δ units permil against AIR and SMOW international standards, respectively. Figure 1 shows the sampling locations relative to the provinces

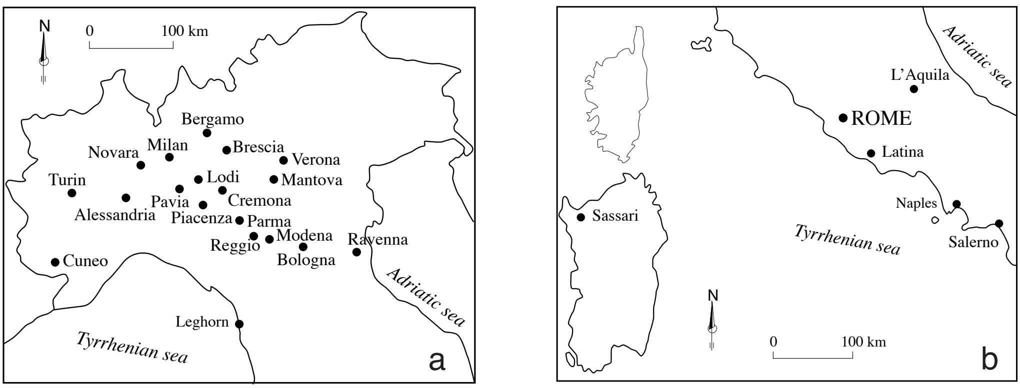

Figure 1. The Italian provinces from which isotopic data of nitrates are available: a) northern Italy; b) central and southern Italy.

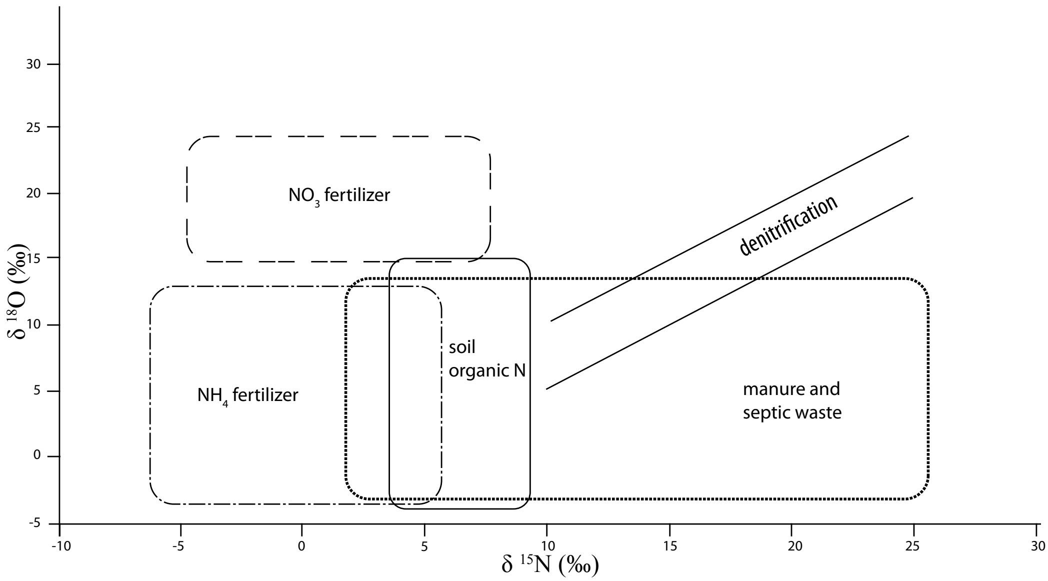

Figure 2. The $\delta^{15}N$ versus $\delta^{18}O$ plot (Silva et al., 2002) and the main sources of nitrogen in waters and soils (modified).

concerned by this study. Figure 2 depicts the plot of $\delta^{15}N$ versus $\delta^{18}O$ of nitrates with respect to the main organic and inorganic sources of nitrogen according to Silva et al. (2002). This graph also shows the denitrification line, that depicts the variations of $\delta^{15}N$ and $\delta^{18}O$ in the process affecting nitrates under reduced environmental conditions.

Piedmont

Lasagna et al. (2005) studied groundwater samples from two areas of the Turin and Cuneo provinces: the Poirino highland and the Racconigi plain, respectively. These areas are intensively cultivated with cereals and host animal breeding farms, so that manure, organic waste and leakage from sewage tanks are the potential main sources of nitrogen pollution. The waters collected from 6 wells in either area, display significantly high nitrate concentrations. In particular, in the Poirino area, groundwater has concentrations between 32.5 and 206 mg/L, increasing from the highland to the plain, and $\delta^{15}N$ and $\delta^{18}O$ ranging from 5.9 to 16.7, and from 8.8 to 14.7 permil, respectively. In contrast, groundwater from the Racconigi area, that lay in the Po river plain, shows more homogeneous (81-132.5 mg/L) concentrations, and $\delta^{15}N$ and $\delta^{18}O$ ranging from 7.6 to 11.3, and from 6.5 to 12.2 permil, respectively. The isotopic data suggest origin of nitrates from mineralized synthetic fertilizers and organic matter /septic tank effluents. Denitrification leading to nitrate abatement of 25 and 45% relative to the original concentrations, has been observed in 2 wells from the Poirino area. One sample from Racconigi exhibits comparatively lower denitrification (15%).

Debernardi et al. (2008) carried out a study of groundwater from a large part of the Piedmont plain, analyzing about 500 samples from the unconfined aquifer. About 20% of these samples display nitrate concentrations higher than 50 mg/L (this value represents the maximum concentration allowed by Italian law in potable waters, Dr. Lgs. 152 11/05/1999); in particular, in the shallower (as down as 20 m deep) part of the aquifer, the values range widely from 1 to 160 mg/L. Higher concentrations have been generally measured in the urban areas of Alessandria, north Cuneo and south-east Turin. Moreover, 6 waters from the agricultural land near Turin, displaying concentrations between 32.5 and 206.4 mg/L, have been analyzed for the isotopic composition, showing $\delta^{15}N$ and $\delta^{18}O$ from 5.9 to 16.7, and from 8.8 to 14.7 permil, respectively. In particular, for 4 out of 6 samples, the isotopic composition suggests a nitrogen source from soil organic matter. For the remainder, different sources have been proposed, ranging from synthetic fertilizers to livestock manure or septic tank effluents. These latter samples are also significantly affected by denitrification, proving that this process takes place not only at depth, but also in shallow aquifers.

Piedmont-Lombardy border

Pilla et al. (2005) and Sacchi et al. (2007a; 2007b) measured concentrations of nitrates in nearly 100 samples from wells and natural outflows of a N-S elongated transect crossing the alluvial Po river plain, in the Alessandria, Novara and Pavia provinces. Isotopic compositions were determined in selected samples. The sources of nitrates in the Po river plain, that hosts a multilayer aquifer of variable thickness, are represented by synthetic fertilizers, exceedingly used for crop raising and, locally, leakage from sewage network. Moreover, irrigation practices influence significantly the distribution of pollution in groundwater. In the Novara province, nitrate concentrations rarely exceed 50 mg/L, and the $\delta^{15}N$ and $\delta^{18}O$ display approximate ranges from 1 to 13, and from 4 to 19 permil, respectively. These isotopic values suggest a typical nitrogen origin from mineralized synthetic fertilizers. Little denitrification has been observed in deeper portions of the aquifer or experiencing high withdrawal rates. In contrast, the highest concentrations (from 10 to 160 mg/L) have been registered in groundwater from the Alessandria province, particularly in the area located east of the town and characterized by a thick gravel-sand aquifer. It is possible to distinguish the Casale sector from the Alessandria plain, as the $\delta^{15}N$ and $\delta^{18}O$ range approximately from 5.5 to 19, and from 4 to 22 permil, respectively, in the former area, and from 1 to 12.5, and from 2.5 to 12.5 permil, respectively, in the latter area. These values suggest two different sources of pollution, i.e. mineralized synthetic fertilizers and livestock manure. Moreover, denitrification occurs in the Casale sector, where the waterlogged practice for rice cultivation may favor this process, and in the sector east of Alessandria, where there are suitable hydrogeological conditions. Lastly, in the Pavia province, groundwater displays the lowermost nitrate concentrations of the three provinces, and different characteristics in the Lomellina-Pavese plain and the Oltrepò sector because of the varied soil use and hydrogeological conditions. In particular, in the Lomellina plain, that is intensively cultivated with rice and corn fields and hosts a multilayer aquifer thick up to 200 m, Pilla et al. (2006) studied the shallower aquifer, displaying high (between 10 and 50 mg/L) nitrate concentrations, and $\delta^{15}N$ and $\delta^{18}O$ ranging from -7.4 to 1 permil, and from 3.4 to 17 permil, respectively. These isotopic values suggest for the most of waters the provenance of nitrogen from agricultural sources due to nitrification of synthetic fertilizers. Moreover, two samples display concentrations between 34 and 50 mg/L, and strongly negative $\delta^{15}N$, likely because of the presence of oxidized biogenic ammonium in the undersatured zone of the aquifer. Moreover, there is a correlation of the isotopic composition with nitrate concentrations, probably due to continuous addition of nitrates from the fields to groundwater. Sacchi et al. (2007a) analyzed 11 water samples from shallow wells for a period of 11 months, measuring generally high concentrations, ranging from some to more than 100 mg/L. The authors have distinguished the waters into 2 groups of different concentrations and isotopic values. In particular, the Group 1, that represents the waters after soil flooding for agricultural practices, is characterized by low nitrate concentrations, and $\delta^{15}N$ and $\delta^{18}O$ ranging from 4 to 13, and from 1 to 11 permil, respectively. Such isotopic composition suggests denitrification because of oxidation of organic matter. The samples of highest concentrations display $\delta^{15}N$ typical of nitrogen supplied by soil organic matter. The Group II, that is composed of samples taken after waterlogging and showing seasonal evolution, is characterized by higher nitrate concentrations, and $\delta^{15}N$ and $\delta^{18}O$ ranging from 13 to 28, and from 7 to 17 permil, respectively. These samples plot parallel to the denitrification line in the $\delta^{15}N$-$\delta^{18}O$ graph (Figure 2), but trending in the opposite direction. This pattern likely results from mixing of residual and fresh nitrates. The samples with the highest concentrations, exhibit $\delta^{15}N = 12.5$ and $\delta^{18}O = 10.5$ permil, respectively; these values cannot be readily ascribed to any definite source. As a whole, the isotopic compositions support the agricultural origin of nitrogen due to nitrification of synthetic fertilizers. A seasonal effect due to soil flooding, causes strong denitrification. In particular, the $\delta^{15}N$ and $\delta^{18}O$ ranged approximately from -8 to 2, and from 3 to 17 permil, respectively, in autumn, and from 3 to 11.5, and from 2 and 13.5 permil, respectively, in summer. In contrast, groundwater from the lowland of the Oltrepò sector (Sacchi et al., 2007) generally displays low nitrate concentrations, probably reflecting low agricultural input and denitrification because of anoxic conditions of the local monolayer confined aquifer. However, there are also waters of high (more than 90 mg/L) concentration, attributed to leakage from the sewage network. The $\delta^{15}N$ and $\delta^{18}O$ range from 4 to 28, and from 4 to 18 permil, respectively. Occasional denitrification has been observed in this latter area. Pilla et al. (2007) extended the investigation to areas adjacent to those taken into account by Pilla et al. (2006). The uppermost of groundwater samples exhibit nitrate concentrations lower than 50 mg/L. The isotopic compositions show that the nitrogen source is essentially represented by synthetic fertilizers. Significant denitrification, affecting usually 50% but achieving up to 80% of dissolved nitrates, takes places, favoured by the clayey-silty cover present in the area, and probably by mixing of groundwater with reduced deep brines. This latter occurs in the proximity of Voghera's Fault. Only a sample of high (~ 150 mg/L) concentration, exhibits the $\delta^{15}N$ typical of organic matter, likely because of sewage seep.

Lombardy

Arduini et al. (2008) studied mainly calcium-bicarbonate waters from 90 wells of the alluvial plain of the Milan province. The isotopic composition was determined for 37 samples. Groundwater, taken from each of the three layers of the local aquifer thick between 20 and 200 m, displays nitrate concentrations generally higher than 50 mg/L. In particular, nitrates are present in the waters from the north sector of the province, where the sources of nitrogen are represented by town sewage, cattle breeding and inorganic fertilizers widely used in agriculture. The $\delta^{15}N$, that range from -4.5 to 10 permil, suggest an organic origin of nitrogen.

Guffanti et al. (2010) carried out a study of 111 samples of calcium-bicarbonate groundwater from the alluvial plain of the Lodi province. Nitrate concentrations are lower than 50 mg/L, but higher values characterize groundwater from the northern part of the province where coarse sediments occur. The $\delta^{15}N$ and $\delta^{18}O$ of 7 samples displaying nitrate concentrations between 10 and 36 mg/L, vary from 6.7 to 12.7, and from not detected to 13.4 permil, respectively. These ranges suggest an origin of nitrate from synthetic fertilizers and livestock manure. Denitrification affects groundwater due to locally redox conditions; in particular, significant decrease of nitrate concentrations has been observed in one sample showing residual concentrations as large as 80% if nitrates derive from both synthetic fertilizers and organic matter, or about 50% if they are only synthetic. Three other samples display weak denitrification. In general, there is a positive correlation between the denitrification rate and the aquifer depth, as deeper waters exhibit higher rate. Such self-depuration of deeper aquifer is essentially correlated with reduced conditions determined by the local runoff irrigation system, that lowers soil oxygen concentrations.

In different months of 2009 and 2010, Del Conte et al. (2011) took more than 200 samples from a variety of water bodies, including the Oglio river and its tributaries as well as the effluents of both a sewage treatment plant and two fisheries. Although the Oglio river watershed is an agricultural area, the river water displays a low (from 0.15 to 7.6 mg/L) range of nitrate concentrations, that increase downstream. The $\delta^{15}N$ and $\delta^{18}O$ ranged approximately from 9.5 to 14, and from 7.5 to 10 permil, respectively, in August 2009 and February 2010, suggesting a typical origin of nitrogen from organic matter of both natural and anthropogenic origin. Such an origin is also characteristic of the nitrates taken in December 2009; however, the large ranges of $\delta^{15}N$ and $\delta^{18}O$, approximately from 2 to 14, and from 2 to 12 permil, respectively, measured in the low-nitrate samples from the upstream area, suggest contributions from either atmospheric deposition or mineralized synthetic fertilizers. Mixing of the river water with highly denitrified groundwater could explain the isotopic variation observed upstream. In the lower watershed, the isotopic data of the Oglio river water do not evidence clear denitrification, except for a limited number of cases in summer. The waters from the sewage treatment plant display isotopic composition rather similar to the Oglio river and its tributaries with typical signature of anthropogenic organic matter. Moreover, one sample shows evidence of denitrification. The samples from the tributaries of the Oglio river, that do not always cluster isotopically with the river samples, are characterized by isotopic composition of organic nitrates. Lastly, one sample of springwater from the upper watershed displays a high nitrate concentration and isotopic composition referred to anthropogenic organic matter.

Lastly, Sacchi et al. (2011) carried out a wide study on groundwater from the provinces of Milan, Cremona, Bergamo, Brescia and Mantua, integrating their results with the data obtained since 2005 on groundwater from the provinces of Pavia, Novara and Alessandria (see above). As a whole, these authors analyzed more than 300 samples, measuring a wide range of nitrate concentrations from 10 to 180 mg/L (average about 30 mg/L). The $\delta^{15}N$ and $\delta^{18}O$ vary widely from -10 to 28, and from 2 to 23 permil, respectively. In particular, the isotopic composition of the samples displaying concentrations higher than 10 mg/L, suggests a nitrogen origin from soil organic matter, likely resulting from mixing of both synthetic fertilizers and anthropogenic organic matter. Some samples exhibit significant isotopic enrichment by denitrification, that achieves up to 80% reduction of the original nitrate concentration. Considering the data of the different areas, it appears that in the northern part of the Milan province (and the Alessandria-Novara provinces), the isotopic signature is generally characterized by synthetic fertilizers. In Milan's urban area, the isotopic composition of the water indicates mixed sources or anthropogenic organic pollution, likely from obsolete and leaking sewage network. In the Lomellina plain from the Pavia province, nitrate concentrations in groundwater are highly reduced by denitrification. In the provinces of Bergamo, Brescia and Mantua, although pollution is also organic, the main source of nitrogen is represented by manure downpoured on fields for agricultural practices. Lastly, denitrification is also important in the south-eastern part of the Po plain, characterized by clayey soils and exhibiting low nitrate concentrations in groundwater.

Veneto

Patrizi (2002) conducted a study of the waters from the Lessini Mts. and the adjacent plain, in the Verona province. The samples from the plain and some localities of the lower part of the Lessini Mts. valleys display high (up to 100 mg/L) nitrate concentrations, while the samples from the upper valleys exhibit values between 10 and 20 mg/L. The measured $\delta^{15}N$ and $\delta^{18}O$ are high, indicating that the uppermost of the waters are polluted by nitrate of both human and animal origin. However, in the Montorio and Lessini Mts. foothill areas, the waters, also from springs, exhibit lower isotopic composition, typical of nitrogen contributions from synthetic fertilizers.

Emilia-Romagna

Chahoud et al. (2002) and Aquanet (2004) reported the results of a project carried out in 2001-2002 by the Administration of Emilia-Romagna Region, concerning nitrate concentrations in groundwater from 7 provinces. 72 samples collected in the spring and fall of 2003 showed concentrations ranging from 1.5 to 67.6 mg/L, and $\delta^{15}N$ from 3.5 to 8.14 permil. No significant isotopic difference was found between the samples of May and October 2003, indicating that the composition is independent of both the sampling season and nitrate concentrations. Moreover, groundwater from the Piacenza province displays lower (average about 5.5 permil) $\delta^{15}N$ than groundwater from the provinces of Parma, Reggio-Emilia and Modena (average $\delta^{15}N$ ranging from 7 to 9.5 permil). In particular, groundwater from these latter provinces is characterized by a mainly organic origin of nitrogen, probably because of dilution of nitrate from chemical fertilizers with manure and farm waste correlated with the industries manufacturing the Parmigiano-Reggiano cheese. In contrast, the large diffusion of maize cultivation in the central sector of the Piacenza province, that is a crop not used to feed milk cows grown for the production of Parmigiano-Reggiano cheese, requires fertilization with inorganic nitrogen. Therefore, the lower $\delta^{15}N$ of Piacenza waters probably reflect intensive use of inorganic nitrogen. In this context, it has been ascertained that $\delta^{15}N$ lower than 4 are typical of surface waters and natural biological activity of soils of the Piacenza province and, thus, $\delta^{15}N$ higher than 4 indicate anthropogenic pollution. Moreover, the joint use of chemical fertilizers characterized by $\delta^{15}N$ between -5 and +5 permil, and groundwater yields mixing of surficial and deep waters, favouring the homogenization of aquifers. This leads to significant decrease of the $\delta^{15}N$ of nitrates, in that distinguishing the Piacenza province from the other Emilian provinces. Lastly, groundwater from the provinces of Forlì-Cesena, Bologna and Ravenna exhibit average $\delta^{15}N$ from 7 to 9 permil, i.e. similar to the values of the other provinces of Emilia-Romagna, except that of Piacenza.

Dadomo et al. (2005) analyzed calcium-bicarbonate water samples from 81 wells of the alluvial plain of the Piacenza province in 2003. Nitrate concentrations (from several to more than 50 mg/L) have resulted to be strongly controlled by pollution from synthetic fertilizers and livestock manure. In particular, although higher concentrations occur in areas next to pig husbandry farms, however, high concentrations are also characteristic of pig-farm free areas. The $\delta^{15}N$, that have been determined in selected wells, range from 3.5 and 8.5 permil. The lowest values, that are associated with higher nitrate concentrations, have been measured in the shallower aquifer of the central sector of the plain. In contrast, higher $\delta^{15}N$ have been recorded in both the eastern and western sectors; in particular, in the latter sector, they are associated with high nitrate concentrations, while in the former sector, they correlate with high NH_4^+ (up to 1.2 mg/L) and low nitrate concentrations. In both sectors, the isotopic composition mainly suggests an organic origin of nitrogen, that is, in contrast, inorganic in the water from the central sector, likely resulting from mineralized synthetic fertilizers. However, unlike in the eastern sector, in the western sector, the source of nitrogen cannot be referred to pig farms, that lack locally, but likely to leakage of sewage network. A well from the central sector exhibiting a higher value than the others, has been monitored through time, showing no significant variation of isotopic composition, suggestive of an organic source of nitrogen.

Tuscany

Nisi et al. (2007) measured nitrate concentrations and isotopic compositions in groundwater from the coastal plain of the Leghorn province between the settlements of Rosignano and San Vincenzo. This area, that is devoted to agriculture and industrial activities, hosts a multilayer, 70 m thick aquifer, displaying wide permeability and characterized by a wide range of composition from calcium-bicarbonate to calcium-sulphate/chloride and sodium-chloride. Nitrate concentrations measured in 88 wells in June and October 2006, ranged widely from 0.06 to 354 mg/L; in particular, about 20 wells displayed concentrations higher than 50 mg/L in either sampling campaign. The $\delta^{15}N$ and $\delta^{18}O$ of nitrates from 10 samples collected in October, ranged from -2.8 to 14.9, and from 10.1 to 22.6 permil, respectively. For the waters of higher nitrate concentrations, the values indicate a nitrogen source from synthetic fertilizers. In contrast, for the waters of lower nitrate concentrations (14-38 mg/L), the isotopic values suggest mixing of nitrogen from sewage network, livestock manure and/or soil organic nitrogen. Lastly, some waters, although of higher nitrate concentration, exhibit isotopic composition characteristic of denitrification. The dishomogeneous distribution of isotopic values through the territory, proves that groundwater pollution is local, as it is controlled by the different location of economic activities, urban settlements and hydraulic characteristics of terrains.

Latium

d'Antona et al. (2009) studied several groundwater samples from the coastal plain of the Latina province, that is mainly devoted to intensive agriculture. The samples from the shallower phreatic aquifer, generally display high nitrate concentrations (up to 270 mg/L), and $\delta^{15}N$ and $\delta^{18}O$ ranging from 3.1 to 14.5, and from 3.1 to 11.2 permil, respectively. For groundwater of lower isotopic composition, the nitrogen source is represented by mineralized synthetic fertilizers and/or soil organic matter. In contrast, in a few waters of higher isotopic composition, nitrogen can be derived from the use of both synthetic fertilizers and livestock manure or leakage from septic tanks. Little denitrification occurs in very confined sectors of aquifers.

Abruzzo

Petitta et al. (2009) carried out a study of both surface (springs and irrigation canals) and ground waters from the Fucino plain, an intra-mountain former lake basin located in the L'Aquila province, devoted to intensive horticultural crop requiring high water demand and wide fertilizer use. The Fucino area is composed of alluvial and lacustrine sediments of variable (up to hundreds m) thickness. The water samples have been analyzed over a 11-month period composed of 4 stages, correlated with the calendar of agricultural practices. This time span included the A phase (November 2005 before the main manure application to fields), the B phase (December 2005 after the manure application), the C phase (May and June 2006 start of the irrigation season) and the D phase (October 2006 end of the irrigation season). Nitrate concentrations in waters from springs and wells of the carbonate aquifer ranged from 0.2 to 4 mg/L in the A and B phases. Higher (5-12 mg/L) concentrations were measured in the shallower aquifer of the plain in the D phase. The $\delta^{15}N$ and $\delta^{18}O$ of these overall 13 groundwater samples range widely, from 5 to 58.4, and from -0.1 to 35.8 permil, respectively. The low isotopic values fall into the range of soil organic nitrogen and mineralized inorganic fertilizers, while the intermediate values suggest a nitrogen origin from manure and, lastly, the high values could be related to denitrification. As concerns irrigation canals, their waters generally display higher $\delta^{15}N$ than groundwater. In particular, 6 samples from the carbonate aquifer exhibited mainly low $\delta^{15}N$ from 5.2 to 9.4 permil in the A and B phases. These values are similar to those measured in the C phase in 4 wells from the plain. In contrast, the $\delta^{15}N$ were much higher in groundwater from 3 wells from the plain in the D phase, ranging between 16.4 and 58.4 permil. Lastly, the waters from irrigation canals exhibited a range of $\delta^{15}N$ from 10.8 to 42.9 permil in the A phase. In the successive phases, the values ranged less widely, from 6.9 to 17.1 permil, with no significant difference through the time. In this context, two groups of values can be distinguished: the first group ranging between 8 and 11 permil, and the other group displaying values between 12 and 17 permil. This latter range suggests pollution from manure. In fact, in the B phase, leaching of the manure disposed on fields released runoff nitrates, that were thus conveyed to the canals. In the C and D phases, it is inferred the contribution of nitrogen from denitrification occurring in the shallower aquifer of the plain, where the highest $\delta^{15}N$ and $\delta^{18}O$ were recorded in the D phase. It is known that denitrification leads to enrichment in heavy isotopes of both elements in the residual nitrate. Moreover, in the D phase, no nitrate from surface sources was available to the canals, that were fed only by springwater discharge. As this latter was at its lowest value due to the rainfall lack in summer, only the nitrate input from the shallower aquifer at the end of the irrigation season, could favour higher concentrations in the canals relative to the low values measured in the C phase because of dilution with springwater.

Campania

D'Antonio et al. (2009) carried out a study of groundwater from the alluvial coastal plains of the Sarno and Sele rivers, in the Naples and Salerno provinces, respectively. The former plain, that is covered with volcanic and alluvial deposits, hosts a single aquifer. In contrast, the latter plain, that is characterized by a thick succession of continental and marine sediments, hosts a multilayered aquifer. Groundwater was collected in either plain from 5 wells and piezometers year-round since September 2006. In the Sarno river plain, the aquifer have yielded widely different nitrate concentrations (average 59 mg/L). In particular, 3 samples have displayed values from 72.6 to 148 mg/L, while the remainder have exhibited much lower concentrations, from 14 to 21 mg/L. The $\delta^{15}N$ and $\delta^{18}O$ range from 3.3 to 15.7, and from 3.7 to 20 permil, respectively, suggesting a typical origin of nitrogen from mineralized synthetic fertilizers. Only for one well, nitrogen is mainly organic, probably resulting from septic tank seepage, as no livestock breeding occurs in the area. In the Sele river plain, all samples were taken from the deeper aquifer. Nitrate concentrations range from 16.4 to 58.6 mg/L (average 37 mg/L). The $\delta^{15}N$ and $\delta^{18}O$ range from 2.5 to 14.6, and from 5.2 to 24.8 permil, respectively, suggesting a main nitrogen source from mineralized synthetic fertilizers.

Lastly, Corniello and Ducci (2009) studied the aquifer from the Acerra plain, in the Naples province. This plain is covered with pyroclastic rocks, that host either the phreatic aquifer as down as 20 m, and the deeper aquifer. This latter can also be hosted by the coarse fraction of the clayey-sandy complex underlying pyroclastic rocks. Nitrate concentrations measured in 2006 were very high, often up to more than 300 mg/L. Only 15 % of the analyzed waters have displayed concentrations higher than 50 mg/L. Although both aquifers exhibit very high concentrations, the latter are slightly lower in the deeper aquifer. The lowermost concentrations have been measured in less anthropized areas and/or sectors where Fe and Mn occur, indicating anaerobic conditions. The $\delta^{15}N$ and $\delta^{18}O$ of 9 samples mainly taken from the deeper aquifer, range from 2.4 to 10.6, and from 5.5 to 6.15 permil, respectively, independently of the studied aquifer. The data of 4 samples indicate a nitrogen origin from mineralization of soil organic matter. For other 4 samples from an agricultural area, the lower $\delta^{15}N$ are suggestive of mineralized synthetic fertilizers and, lastly, one sample is characterized by isotopic composition typical of leakage of sewage network and/or livestock waste.

Sardinia

The local Regional Agency for Environment Protection (ARPA) carried out an isotopic study in December 2008 on 11 groundwater samples from the alluvial plain of Nurra, in the Sassari province. The wells from different aquifers, were located on a transect perpendicular to the groundwater flux; in particular, one well was sited in an area of agriculture and livestock breeding. Nitrate concentrations ranged widely from 10.4 to 273.2 mg/L, while the $\delta^{15}N$ and $\delta^{18}O$ ranged from 3.2 to 19.1, and from 6.2 to 15.4 permil, respectively. The waters can be clustered into 4 groups on the basis of the isotopic composition. The I Group, that clusters samples of relatively low isotopic ratios, is, in turn, divided into two subgroups according to different $\delta^{15}N$ but similar (about 6 permil) $\delta^{18}O$. The Ia subgroup, that is composed of 3 samples displaying nitrate concentrations between 30.5 and 62.6 mg/L, and dissolved oxygen between 2 and 4 mg/L, is characterized by $\delta^{15}N$ (about 6-8 permil) of soil organic signature, i.e. derived from mineralized fertilizers and, subordinately, septic tank effluents and/or organic fertilizers. The Ib subgroup, that associates 2 waters containing dissolved oxygen higher than 4 mg/L, and relatively high nitrate concentrations, displays $\delta^{15}N$ (about 9.5 permil) typically of organic fertilizers and/or septic tank effluents. The II Group includes 3 waters of low (about 4.5 permil) $\delta^{15}N$ and high (about 12.5 permil) $\delta^{18}O$. In particular, 2 samples were characterized by isotopic values falling between the fields of synthetic and mineralized synthetic fertilizers in the $\delta^{15}N$ and $\delta^{18}O$ plot (Figure 2). These samples, that belong to the same aquifer, exhibit nitrate concentrations of 22.5 and 63.2 mg/L, respectively, and dissolved oxygen concentrations between 2 and 4 mg/L, in that likely reflecting feeding from two different groundwater systems. Lastly, the III Group comprises 3 waters of low concentrations of nitrates and dissolved oxygen lower than 2 mg/L, but high $\delta^{15}N$ (about 12-19 permil) and $\delta^{18}O$ (about 15.5 permil). In particular, 2 samples exhibit denitrification displaying characteristic high $\delta^{15}N$ and $\delta^{18}O$ (Figure 2). The high $\delta^{15}N$ of the third sample suggests pollution from livestock manure, in agreement with the well location downhill an area of livestock breeding farms.

Concluding remarks

The isotopic composition of groundwater from the studied areas suggests that the main source of nitrogen is by far represented by synthetic fertilizers used in agricultural practices and undergoing mineralization in the soil. In this context, field irrigation can favour abatement of nitrate concentrations as in the case of rice crops. In fact, periodical waterlogging of fields favours reduced conditions, promoting denitrification. This latter also takes place in some areas, where underground conditions are anaerobic. Supply of livestock manure to fields, that is a generally unsystematic agricultural practice, represents a minor nitrogen input to the soil and, then, to the phreatic aquifer. Lastly, there are several cases of organic pollution from leakage of sewage network near urban settlements and/or septic tanks in rural areas, due to the lack of periodic maintenance. If this latter kind of pollution can be ruled out, once Public Administrations and private owners are correctly informed about, the huge impact of agricultural practices on soils and underlying aquifers can be constrained and reduced with difficulty. In fact, as agriculture is the main source of nitrogen input into the waters, the possibility of curbing local pollution from nitrates in underground water is questionable.

So far, only a little number of samples of surface waters have been analyzed, all represented by the Oglio river in Lombardy, and irrigation canals from the Fucino plain, in Abruzzo. The former waters display isotopic composition generally typical of a nitrogen origin from organic matter of both natural and anthropogenic origin, while the latter exhibit contributions from the underground aquifer in November and from the manure of fields in May-June.

Lastly, the bulk of isotopic data so far available is related to the waters from the Po river valley. A subordinate number of data, that are sparsely distributed, refer to central Italy and Campania. This dishomogeneous territorial distribution of data may undermine the usefulness of determination of nitrate concentrations in waters, as it is known that, unlike nitrate concentrations, isotopic composition can provide information about nitrogen sources. Such a knowledge can greatly help fight successfully nitrate risk.

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