Nitrogen sources and denitrification potential of Cyprus aquifers, through isotopic investigation on nitrates

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Abstract Nitrates is one of the most common groundwater pollutants. Being able to identify the source(s) as well as evaluating the denitrification capacity of aquifers can help shape appropriate remedial action. This paper aims to investigate the isotopic composition of nitrates in groundwater samples in order to identify primary and secondary nitrate sources as well as to evaluate denitrification potential of aquifers in Cyprus. A total of 135 groundwater samples from 12 different Ground Water Bodies (GWB) were analyzed for $^{15}N/^{14}N$ and $^{18}O/^{16}O$. It was concluded that the dominant primary source of nitrate in rural Cyprus is fertilizers. For many samples a secondary nitrate source with an isotopic signature of organic source is contributing. This organic source is, in most cases, assumed to be manure. In 16% of the groundwater samples, manure was identified as the primary nitrate source. Finally, the potential of denitrification is seen in 21% of the samples from 7 different GWBs.

1 Introduction

There are two stable isotopes of nitrogen, ^{15}N and ^{14}N and they are both active in the nitrogen cycle participating in various nitrogen compounds. The ratio at which these two isotopes are incorporated in compounds depends on the processes and reactions that produce such compounds. Therefore, $\delta^{15}N$ in nitrates can be used in isotope hydrogeology because of such fractionation between the various nitrogen compounds, enabling tracing of nitrogen sources, sinks and fate. For example, nitrates derived from synthetic fertilizer can be distinguished from animal manure through $\delta^{15}N$ values (Hoefs 1997, Clark and Fritz 1997). The use of isotopes in hydrogeology to trace nitrogen fate gained reliability and further attention when it became possible, through advance analytical processes, to analyze $\delta^{18}O$ in nitrates. Nitrogen molecules of different origin have large oxygen isotopic difference between them. Therefore, $\delta^{18}O$ can distinguish between nitrates that originate from the atmosphere, fertilizers or manure/effluent. The combination of the isotopic composition of $\delta^{18}O$ ‰ VSMOW and $\delta^{15}N$ ‰AIR can be used not only in distinguishing nitrate sources more reliably but most importantly in, among other applications, recognizing denitrification processes (Amberger and Schmidt 1987, Bottcher et al. 1990, Durka et al. 1994). More specifically, ammonium and nitrate synthetic fertilizers have an isotopic signature of $\delta^{15}N$ ranging from -1 to 5‰ and $\delta^{18}O$ from 17 to 22‰. Nitrate originating from litter, soil and sewage/manure have similar with each other $\delta^{18}O$ values that are very close to 0‰, but their $\delta^{15}N$ vary significantly (Clark and Fritz 1997; Mook 2000; Lorence et al. 2010). Ammonia evaporation causes enrichment of $\delta^{15}N$ whereas the process of denitrification causes a simultaneous increase of both $\delta^{15}N$ and $\delta^{18}O$ values. This work aimed to use nitrate isotopes in order to investigate nitrate sources in GWB as well as denitrification potential, in order to help shape the necessary action plans within the nitrate vulnerable zones, in accordance to the European Directive 91/676/EEC. Nitrate isotopic investigations in Cyprus have been carried out earlier by a number of researches, but on a smaller scale (Constantinou 2004; Udluft et al. 2006).

2 Sampling

The sampling was carried out in two phases; groundwater samples were collected in September 2009 and September of 2010. In the 2009 campaign, 98 samples were collected from all 12 different GWBs whereas in 2010, 37 samples from the Western Mesaoria GWB; 16 of these samples were common with that of the 2009 campaign. Sampling was restricted to the area that the Republic of Cyprus exercises effective control. Sample volume varied from one to five liters, depending on the nitrate concentration. Upon sampling, field pH, conductivity, dissolved oxygen and water level were measured and recorded. One liter of sample was collected in the cases of nitrate concentration equal or above 20 mg/L, whereas in lower concentrations, up to five liters were collected. Polyethylene bottles were used and ten drops of chloroform were added upon collecting the samples. Samples were stored in a cool place until they were shipped for analysis to the lab Hydroisotop, in Germany. In addition, a second one liter sample was also collected and used in analyzing SO_4^{-2} and Cl^- with ion chromatography.

3 Nitrate Isotope Analysis and Methodology

The dissolved nitrate was separated using cation exchange and neutralization with KOH. After elimination of sulfate and phosphate by precipitation with $BaCl_2$ the water samples were evaporated to dryness. The samples were heated to 570 °C together with graphite under vacuum and conversed to N_2 and CO_2. After cryogenic separation these two gases were analyzed in an isotope ratio mass spectrometer. The isotope ratio analysis was done using mass spectrometer "MAT-251" with double inlet system. The mass spectrometer was daily calibrated with international standards (N-3, SDGS 34, USGS 35) (Lorence et al. 2009, Lorence et al. 2010). The analyzed isotope ratios are reported in delta notations ($\delta^{18}ONO_3$, $\delta^{15}NNO_3$ in ‰) relative to standard mean ocean water or to air nitrogen as the standards as defined bellow:

$$\delta^{15}NNO_3 = (Rs/Rst - 1)*1000 \text{ and } \delta^{18}ONO_3 = (Rs/Rst - 1)*1000$$

Where Rs and Rst is the $^{15}NNO_3/^{14}NNO_3$ and $^{18}ONO_3/^{16}ONO_3$ ratio(s) of the sample and standard.

4 Results and Interpretation

A total of 135 samples from 12 Aquifers (Table 1) were analyzed for conductivity, chlorites, sulfates, dissolved oxygen, $\delta^{18}ONO_3$ and $\delta^{15}NNO_3$. Figure 1 shows the samples' spatial distribution as well as nitrate concentration. Nitrate concentration ranges from 1.7 to 408 mg/L with mean and median values being 64 and 29 mg/L, respectively. Nitrate concentrations are rather inhomogeneous even within the same GWBs and it is related to a number of factors such as the complexity of certain GWBs and the variations of land use within a single aquifer area.

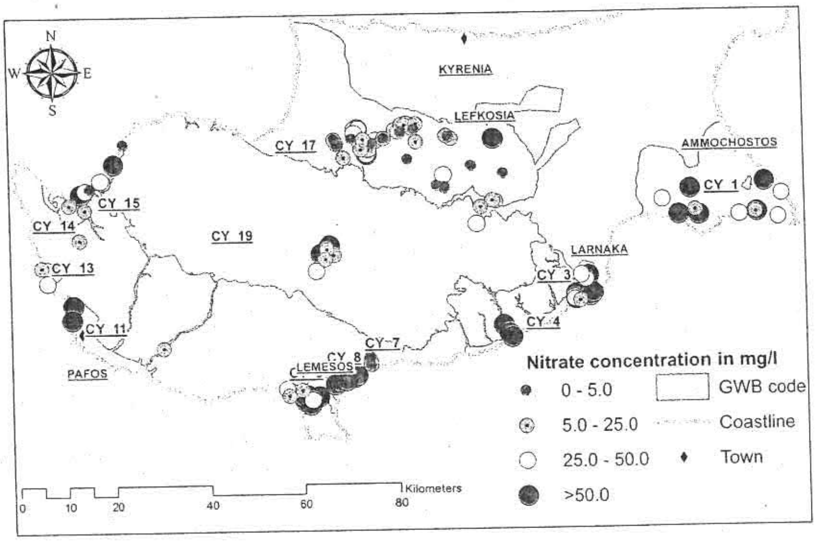

Fig. 1. Sample distribution and nitrate concentration in groundwater samples.

Table 1. Primary nitrate source and denitrification potential as number of samples per GWB.

GWB CODE	Ground Water Body (GWB) Name and Type	Samples/ GWB	Significant denitrification	Primary source of nitrates			
				Fertilizer	Organic	Industr.	Mixin
CY1	Kokkinochoria (Clastic, unconfined / confined)	11	4	11	-	-	5
CY3	Kiti-Perivolia & Tremithios Riverbed (Alluvial, unconfined)	13	3	12	1	-	3
CY4	Softades-Vasilikos coastal plain & riverbeds (Alluvial, unconfined)	3	-	3	-	-	1
CY7	Germasogia Riverbed (Alluvial, unconfined)	5	4	4	1	-	-
CY8	Lemesos (Alluvial, unconfined)	9	3	1	8	-	8
CY9	Arkotiri (Alluvial, unconfined)	10	-	9	1	-	4
CY11	Pafos Coastal Plain & riverbeds (Alluvial, unconfined)	3	1	3	-	-	2
CY13	Pegeia limestones (Semiconfined)	2	-	2	-	-	1
CY14	Androlikou limestones (Semiconfined)	2	-	2	-	-	-
CY15	Chrysochou-Gialia coastal plain & riverbeds (Alluvial, unconfined)	8	1	7	1	-	2
CY17	Central-Western Mesaoria (Clastic, unconfined – confined)	62	13	53	8	1	19
CY19	Troodos area (Ophiolites –fractured)	7	-	5	2		4
Total		135	29	112	22	1	49

that would suggest evaporative nitrate ... GWBs of Southeastern Mesaoria (CY 1), Kiti-Pervolia (CY 3), Lemesos (CY 8) and Akrotiri (CY 9), such a correlation seems to exist. The isotopic composition of nitrates in all of the samples is presented in Figure 2. Primary and secondary sources are attributed to all samples based on nitrate isotopic composition and consequently their position within the graph. Based on the primary isotope signature, denitrification paths can be calculated and the enrichment paths modeled. Such paths, using published fractionation ratios, are sketched in Figure 2 (Lorenz 2010; Amberger and Schmidt 1987; Bottcher et al. 1990).

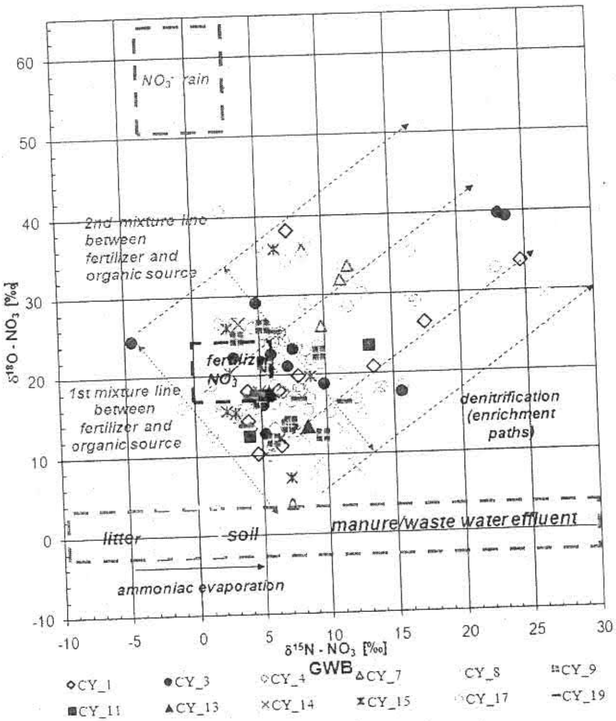

Fig. 2. Isotopic composition of NO_3 in all groundwater samples.

Samples that have isotopic signatures to the right of the first mixing line are already going through some degree of denitrification. However, in this paper, a more conservative approach is adapted and only the samples positioned far to the right of the second mixing line were considered as having significant denitrification potential. The majority of the samples, 112 samples (83%), from all aquifers, show nitrate isotopic composition very similar to that of mineral fertilizers. This indicates that the dominant, primary contributing source of nitrates in groundwater, for these samples is mineral fertilizers. Twenty-nine of these samples (21%) fall along the mixing lines of mineral fertilizers and manure/waste water effluent.

This is interpreted as having an additional, less significant, secondary, organic source that is also contributing to the concentration of nitrates in these groundwater samples. The organic source of mixing can be either manure that is used as fertilizer in the fields or direct infiltrates from animal manure and/or animal waste water. The isotopic composition of animal waste water does not differ from that of the urban waste water therefore in theory the organic source could also be urban waste water. A total of 22 samples from 7 different GWB (16%) show organic as the primary nitrate source; 20 of them indicate mineral fertilizers as a secondary contributing source. Most of these samples however come mainly from Central-Western Mesaoria (CY 17) and Lemesos (CY 8) GWBs. It is also clear that 29 samples from 7 different GWBs (21%) show significant denitrification potential. Most of these samples come from Central–Western Mesaoria (CY 17) GWB, suggesting a significant denitrification potential of this aquifer. It should also be noted that, the majority of the denitrifying samples tend to have lower nitrate concentrations than those with insignificant denitrification thus supporting the scenario of denitrification. The spatial distribution of the samples, their denitrification potential and primary source are presented in Figure 3 and tabulated in Table 1. For presentation purposes, only the two end sources are presented as primary source and the rest of the samples are presented as mixing samples. No further classification is made for the mixing samples, in terms of which of the two sources is the prevailing one.

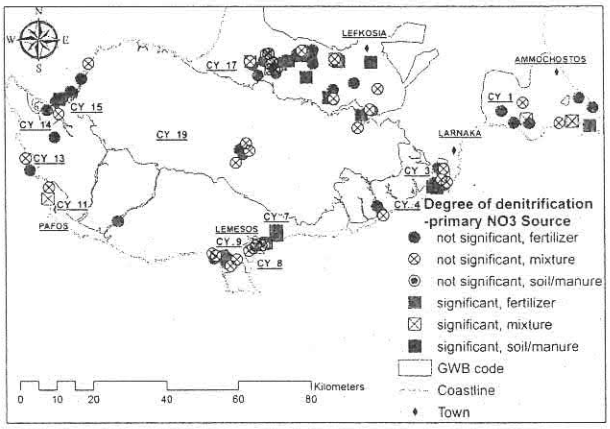

Fig. 3. Sample spatial distribution, denitrification potential and primary nitrate source.

A more detail presentation of the results pertaining to the GWBs of Germasogia river bed (CY 7), Lemesos (CY 8) and Akrotiri (CY 9) is undertaken bellow. Germasogia, Lemesos and Akrotiri are alluvial GWBs that develop along the south central coast of the island. The Germasogia GWB (CY 7) is a river alluvial aquifer that develops along its channel. In 1969, Germasogia dam was constructed and since

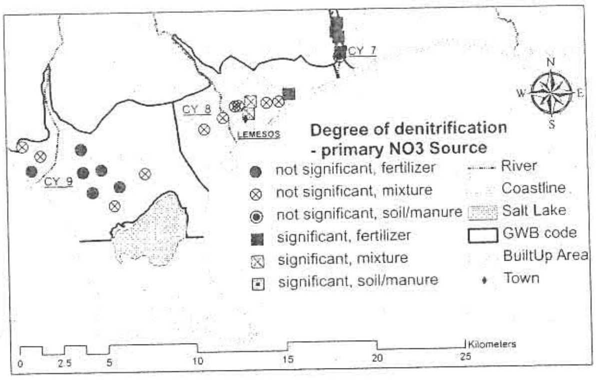

Fig. 4. Sample distribution, denitrification capacity and primary source in GWBs 7, 8 and 9.

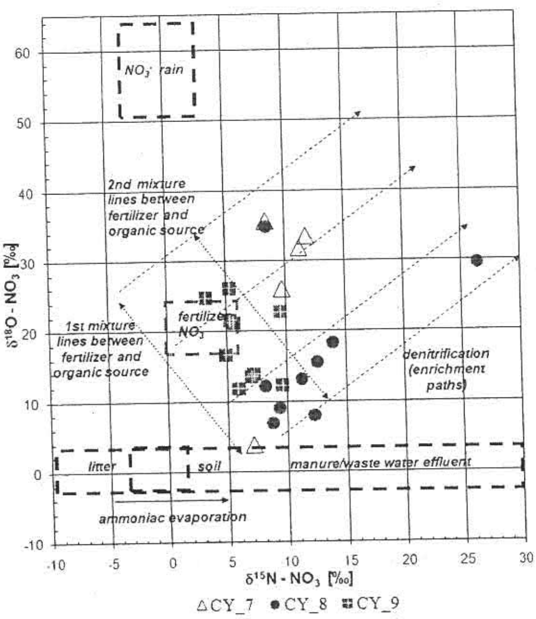

Fig. 5. Isotopic composition of nitrates in groundwater samples from GWBs 7, 8 and 9.

Nitrate isotopic signatures from the collected samples is distinguished from the other two GWBs and suggest that the dominant nitrate source in CY7 groundwater is mineral fertilizers. Denitrification capacity of this aquifer appears to be high since four out of five samples show significant denitrification (Table 1 and Fig. 4 - 5). Lemesos (CY 8) and Akrotiri (CY 9) are adjacent, coastal, alluvium GWBs. The Lemesos GWB develops within the city of Lemesos and it is recharged by the Garilles River.

The area is heavily urbanized and up to 1995 sewage effluent absorption wells was constructed thus reducing recharge of this part of the aquifer which depends heavily on river flow. A total of 11 samples were collected and analyzed from the Lemesos GWB. Samples show nitrate values above 50mg/L and conductivity values above 1200μS/cm. The primary source of nitrates in groundwater is organic with minor mixing with chemical fertilizer. Samples from Lemesos GWB exhibit the heaviest influence of an organic source on the isotopic signature of the nitrates to such an extent, that they are distinguishable from all other samples. It appears that urbanization and the use of sewage effluent absorption wells in the past, remains the dominant nitrate source. In addition, a weak correlation between nitrate concentration and conductivity exists. This may suggest partial nitrate enrichment through evaporation brought about by reduced recharge. The samples that show denitrification potential tend to have lower nitrate concentration than those with insignificant denitrification. Denitrification appears to reduce nitrate concentration from about 100 - 140mg/L to about 60mg/L.

The Akrotiri GWB is adjacent to the Lemesos GWB. The major land use in this case is predominantly agriculture with a number of smaller in extent builtup areas. The Kouris River that runs from north to south intersects and recharges this part of the aquifer. It discharges to the sea to the southwest part of the aquifer. In 1987, Kouris, the biggest dam of Cyprus, was constructed on this river and changed the recharge regime of the GWB. Recharge is now limited to direct infiltration from rain, return irrigation and to the rare, controlled releases from the dam. The aquifer is pumped mostly for irrigation water and its water balance is negative. As a result, seawater intruded primarily from the west. A total of 8 samples have been collected from Akrotiri GWB. Nitrate concentration ranges from 19 to 279mg/L. The isotopic signature of the samples confirms that mineral fertilizer is the main source of nitrates in groundwater. Organic contribution is only seen near and downstream from Episkopi, Trahoni and Asomatos Villages. None of the samples shows significant denitrification capacity. This might be attributed to the relatively thin unsaturated zone, high hydraulic conductivity and most importantly to the much lower clay content in the Akrotiri GWB in comparison to that of the Lemesos GWB (U.N.D.P. 1970). Nitrate isotopic composition from the collected samples from the above three aquifers shows distinct differences between them that reflect the different status of each GWB.

5 Conclusions

From the nitrate isotopic investigation of the groundwater samples collected from 12 aquifers in Cyprus the following can be summarized:

- Nitrate sources in groundwater can be assigned through investigation of the isotopic signature of nitrates.
- The dominant primary source of nitrates in rural Cyprus is fertilizers.

- For 21% of the samples, a secondary nitrate source with an isotopic signature of organic source is contributing. This organic source is in most cases assumed to be manure.
- 16% of the samples show organic as the dominant nitrate source. The majority of these samples are from GWBs CY 17 and CY 8. Samples from CY 8 exhibit the heaviest influence of an organic source. It is thought that the organic source in this area is old sewage effluent.
- The potential of denitrification is seen in 21% of the samples in 7 different GWBs. Denitrification potential seems to be higher in GWBs CY 17 and CY 7.
- The low denitrification potential of CY 9 might be due to the low clay content and high permeability of the GWB.

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