Research Paper

Identification of nitrate sources in groundwater by $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ isotopes: a study of the shallow Pleistocene aquifer in the Jericho area, Palestine

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This study describes the impact of septic tanks on the groundwater quality of the shallow Pleistocene aquifer in Jericho area, Westbank, Palestine. Septic tanks are widely used for storage and disposal of sewage in the populated and agricultural city of Jericho. Routine hydrochemical tests for groundwater quality performed for several years identified the problem of a gradual nitrate increase, without pinpointing its definite sources. The geological formations of the Jericho area and the shallow nature of the Pleistocene aquifer, together with the mechanism of recharge, make the groundwater in this aquifer highly susceptible to contamination, particularly along sewers. The lithology of the Samara (high hydraulic conductivity) and the Lisan formation (low conductivity but increased infiltration along fractures) promote easy seepage of agricultural and anthropogenic inputs into the groundwater. Nitrate concentrations are elevated near septic tanks and animal farms, with nitrate values exceeding 74 mg/L. $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ signatures suggest sewage and manure as the main sources of high nitrate concentration in the groundwater. Samples taken during the end of the dry season indicate that a slight denitrification in the aquifer.

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1 Introduction

The problem of high nitrate concentrations in drinking water constitutes a major health risk to both humans and stock life. Nitrite reacts directly with haemoglobin in human blood and other warm-blooded animals to produce methemoglobin. Methemoglobin destroys the ability of red blood cells to transport oxygen. This condition is especially serious for babies under three months of age. It causes a condition known as methemoglobinemia or "blue baby" disease. Water with nitrite levels exceeding 1 mg/L should not be used for feeding babies. Also the WHO assigned the nitrate of 50 mg/L as a health significant value in drinking water [1].

For this matter of fact, the identification of the possible sources of nitrate in groundwater is very important as a first step to solve these problems. Many studies were performed using hydrochemical ratios, but they didn't identify the various possible sources. Stable isotope techniques have successfully been used for more than three decades [2]. Nitrate in the environment may have various sources, including atmospheric deposition, soil organic nitrification, fertilizer, sewage and manure. Nitrate from each source is typically characterized by a distinct isotopic signature. Typical $\delta^{15}N_{nitrate}$ values for chemical fertilizers range from −4 to +4 ‰, for human and animal waste from +7 to more than +30 ‰, and for soil nitrate from less than −10 to +4 ‰.

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$\delta^{18}O_{nitrate}$ values for atmospheric deposition exceeds +25 ‰. For chemical fertilizers they range from +18 to +22 ‰, and for human and animal waste and soil nitrate $\delta^{18}O_{nitrate}$ is −10 to +10 ‰ [3]. Hence, the isotopic composition of nitrate constitutes a useful tracer for determining its sources, provided that no alteration of isotopic ratios by biogeochemical reactions such as denitrification has occurred.

Nitrogen isotopes, mainly $\delta^{15}N$, provide information about nitrogen sources and sink. Furthermore, the nitrate $\delta^{18}O$ and $\delta^{17}O$ are promising new tools in determining nitrate sources and reactions, and complement conventional uses of $\delta^{15}N$ [4], since they provide a mean to distinguish between nitrate of atmospheric deposition from fertilizers, sewage [5], and from soil nitrification processes [6].

The objective of this study is to use the tracer isotopes values of $\delta^{15}N$ and $\delta^{18}O$ to identify the main sources of nitrate in the shallow Pleistocene wells and springs in Jericho area, Palestine.

2 Study area

Jericho is located at the eastern boundary of the West Bank. It extends from 10 km to the north of the Dead Sea, and 7 km to the west of the Jordan River (Fig. 1). While it has a desert climate its position on the eastern slope of the Jerusalem and Ramallah Mountains in the west contributes to a good catchments area with relatively abundant water resources, which make it an important agricultural area. Jericho has an area of approximately 35 330 hectares. Of this, 591 hectares are Palestinian residence area and 517 hectares are occupied by Jewish settlements. The rate of annual precipitation varies between 120 mm and 250 mm, with an annual groundwater recharge rates of about 180 Mio m^3, while the annual consumption rate is about 140 Mio m^3 distributed between domestic and agricultural use, according to ARIJ [7].

In general, the per capita water consumption for domestic use in the West Bank is between 50 L/d and 90 L/d. The quantity of generated wastewater in Jericho district was around 2 Mio m^3 for 1996 [8]. Wastewater collection network is totally lacking in Jericho. Septic tanks are in common use for wastewater disposal, serving normally one or a cluster of houses.

The soil in Jericho developed mainly on top of the Samara formation which has a thickness of 20 m, and is composed of silts, clay, gravels and conglomerates. The Samara formation possesses a good hydraulic conductivity and serves as a good groundwater reservoir. In contrast, the interfingering Lisan formation has a finer structure with a thickness of 30 to several hundred meters, and is composed of clay and silt, marl, chalk, gypsum and aragonites. The permeability of the Lisan formation

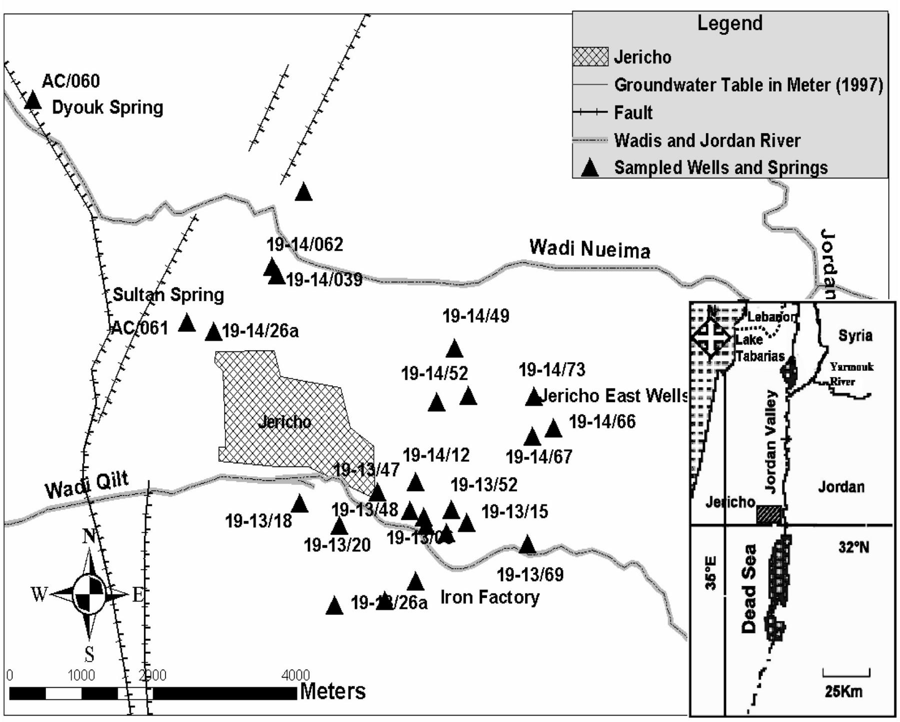

Figure 1. Location of the study area with sampled wells and springs.

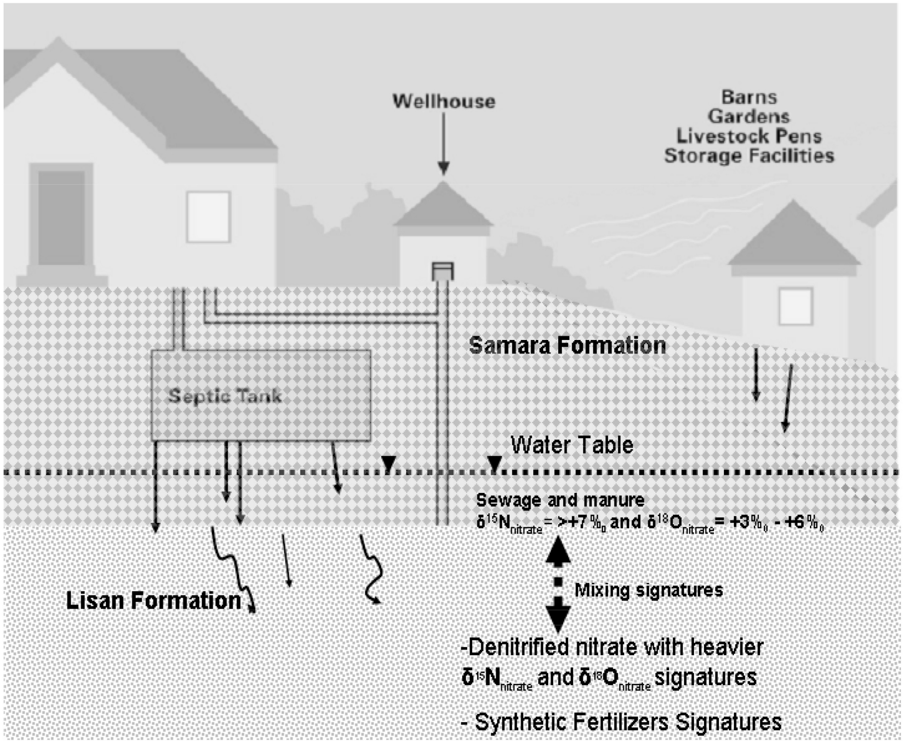

Figure 2. Groundwater pollution by nitrate sources in Jericho area.

is very low and the formation is considered an aquiclude ($K \approx 4.6 \cdot 10^{-9}$ m/s). However, because the unit contains thin sand and silt beds of 20 to 30 cm thickness and because of its high salt content, the water has developed pathways, resulting in relatively more porosity and permeability [9]. The septic tanks built mainly in the top few meters within the Samara layer are usually lined by concrete walls, sealing the four sides of the tanks but not the bottom [7]. Besides the possibility of waste seepage through the bottom, the concrete walls, especially in old tanks, may be fractured with time and, thus, wastewater seeps through these fractures (Fig. 2).

Jericho is considered to be an important agricultural area; it is the food basket of Palestine. High amount of fertilizers, up to about 82.697 t/a are used [8]. This amount which is mainly distributed on a seasonal basis does not reflect the application of nitrogen fertilizers, which comprises only a small part of the total fertilizer load. This applications lead to a fertilizer accumulation in the soil, percolating with the irrigation flow to the groundwater in the transmissive Samara formation.

3 Methods

In November 2003, water samples were collected from 19 working wells and 2 springs in the Jericho area (Fig. 1). The sampling covered most of the area surrounding Jericho city. The samples for nitrate analyses were collected in 60-mL bottles, preserved by $HgCl_2$, and kept in refrigerator. Nitrate was extracted by ion exchange from 1.5 L of water and converted to $AgNO_3$, as described in Silva et al. [10]. Collection of nitrate on an anion-exchange resin eliminates the need for sending large quantities of chilled water back to the laboratory, eliminates the need for hazardous preservatives, makes it easier to archive samples, and enables analysis of water with extremely low nitrate. Nitrogen and oxygen isotope measurements were performed by continuous flow isotope ratio mass spectrometry (CF-IRMS) with an overall analytical precision of ±0.1 ‰ for $\delta^{15}N$ and ±0.3 ‰ for $\delta^{18}O$ values.

CF-IRMS separates the ions of the element ($^{14}N/^{15}N$) on the basis of their different mass/charge ratio. Sample preparation consists of converting solid or liquid material to nitrogen gas (N_2) and isolating the particular gas for analysis.

All analyses were carried out in the Environmental Isotope Laboratory of the UFZ-Environmental Research Centre in Leipzig-Halle, Germany.

4 Results

Nitrate concentrations, $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ for groundwater sampled taken from 21 wells and springs are shown in Table 1. All of the wells are of the Pleistocene

Table 1. Nitrate concentrations, $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ for groundwater samples of the Jericho area.

Location	Well Name	Well Code	Nitrate mg/L	$\delta^{15}N_{nitrate}$	$\delta^{18}O_{nitrate}$
West Springs Area	Ein Dyouk (Spring)	AC/060	29.07	10.48 ‰	3.9 ‰
West spring Area	Ein Sultan (Spring)	AC/061	42.46	10.08 ‰	3.3 ‰
Jericho North	Saeed Aladeen	19-14/062	5.18	10.12 ‰	13.9 ‰
Jericho North	Mohammed Masri	19-14/038	7.5	2.99 ‰	14.7 ‰
Jericho North	Samed	19-14/26a	15.97	15.78 ‰	8.5 ‰
Jericho East	Abdallah Araikat	19-14/049	30.58	8.14 ‰	3.4 ‰
Jericho East	Awni Hijazi	19-14/052	34.07	9.99 ‰	4.9 ‰
Qilt West	Basil Husaini	19-13/018	29.08	8.29 ‰	5.2 ‰
Qilt West	Basil Husaini	19-13/020	49.38	6.89 ‰	3.4 ‰
Qilt West	Fahmi Nahas	19-13/047	43.73	6.94 ‰	3.8 ‰
Qilt West	Fahmi Nahas	19-13/048	41.67	7.42 ‰	3.8 ‰
Qilt West	Salah Arouri	19-14/012	40.54	8.47 ‰	4.3 ‰
Qilt West	Sabiru Rantizi	19-13/006	72.71	9.29 ‰	2.3 ‰
Qilt East	Zuhdi Hashwa	19-13/052	46.55	7.7 ‰	4.3 ‰
Qilt East	Fahed Hishmi	19-13/015	33.24	8.5 ‰	4.8 ‰
Jericho East	Arab Project	19-13/069	24.51	10.9 ‰	7.3 ‰
Qilt East	Iron Factory	19-13/26a	70.13	9.64 ‰	5.2 ‰
Qilt East	Ibrahim Daek	NW	29.68	6.59 ‰	4.9 ‰
Jericho East	Arab Project	19-14/067	38.86	7.42 ‰	4.5 ‰
Jericho East	Arab Project	19-14/073	40.41	7.37 ‰	3.9 ‰
Jericho East	Arab Project	19-14/066	29.69	9.25 ‰	5.7 ‰

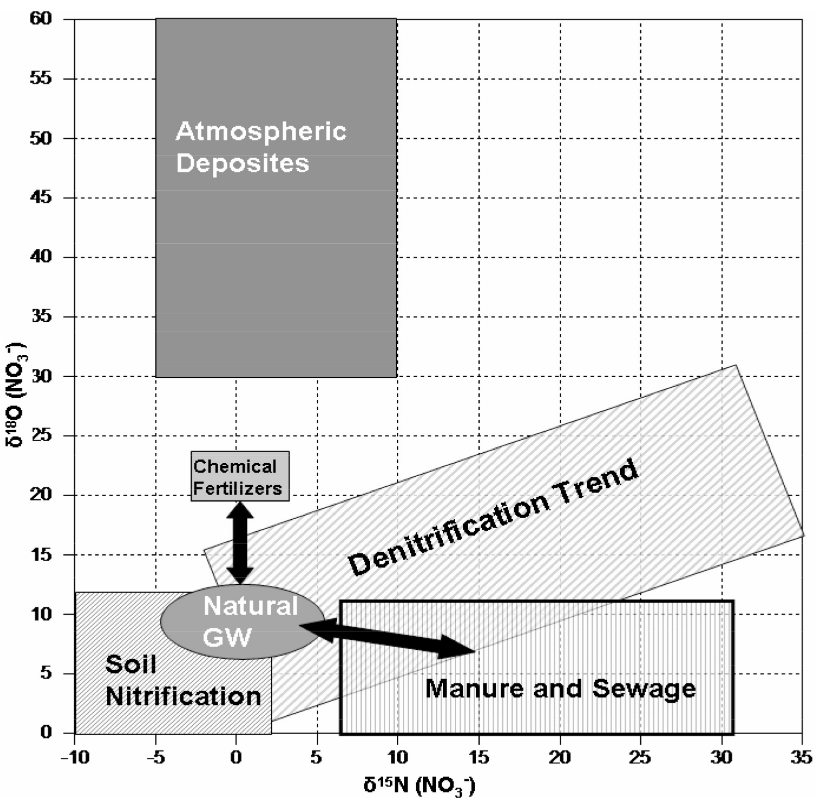

Figure 3. $\delta^{18}O_{nitrate}$ vs. $\delta^{15}N_{nitrate}$ isotopic composition of major nitrate sources [3].

aquifer, while the springs are mainly draining from the mountain's cretaceous aquifer through the fault system to the west. The nitrate concentrations varied depending on the well location and surrounding activities, the values were between 5.2 mg/L in the well (19-14/062) to the north-west of Jericho city and 72.7 mg/L in (19-13/006) which located within an area with extensive agriculture and green houses.

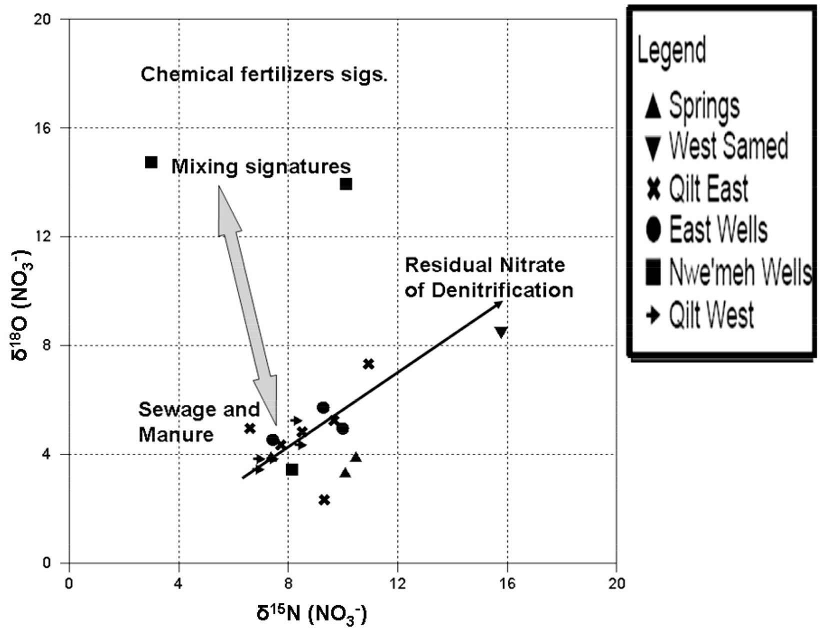

Figure 4. $\delta^{18}O_{nitrate}$ vs. $\delta^{15}N_{nitrate}$. Most of the isotopic signatures lay within the range of sewage and manure and slight denitrification process. Two wells show a mixing signature of fertilizers with other sources.

The $\delta^{15}N_{nitrate}$ values ranged from +3.0 to +15.78 ‰. Oxygen isotope ratios of nitrate were around +3.3 to +8.5 ‰ with an exception of two samples having values of 13.9 ‰. and 14.7 ‰. These two anomalous signatures belong to samples with very low nitrate contents in the wells (19-14/038) and (19-14/062) north-west of the city.

5 Discussion

The ranges of signature of nitrogen and oxygen isotopes for various sources of nitrate are illustrated in Figure 3 [3]. Comparing with the given results, most of isotopic signatures suggest sewage or manure as the main source responsible for the higher nitrate concentrations, with $\delta^{15}N$ values > +7 ‰, and $\delta^{18}O_{nitrate}$ between +3 ‰ and +6 ‰ Some samples also show a slight denitrification trend. This process was significant in the Samed well (Figs. 4, 5). This reflects the dry season sampling (end of summer), with nearly no recharge and groundwater may have persisted in the reservoir for several months.

The values in Figures 5a and 5b show slightly increasing $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ with decreasing $[NO_3^-]$. These combined trends point to slight denitrification within the aquifer, where the heavy isotopes ^{15}N and ^{18}O are preferentially retained in the remaining nitrate [11].

Sewage is the main source of nitrate because it contains a high amount of urea and other organic and inorganic nitrogenous compounds. Manure under aerobic condition in shallow aquifers is another source of nitrate originating from oxidation processes. The presence of many animal farms, especially in the east of Wadi Qilt and Ein Dyouk areas support these interpretations, in addition, practice of using animal manure as natural fertilizers.

Two wells in the north show relatively small nitrate concentrations and much higher $\delta^{18}O_{nitrate}$ values (Fig. 5b). This may indicate a different (non-continuous) nitrate source, where nitrate may persist for a long time in the groundwater. The isotopic signature of these wells bears the isotopic signature of chemical fertilizers. The signatures are more isotopically depleted due to mixing with nitrate with different signatures of other sources such as sewage. The source that yields such lower nitrate concentrations also represents the residual nitrate from bacterial denitrification for sewage or manure and gives the high $\delta^{18}O$ values, above +12 ‰.

6 Conclusion

- $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values show that most of the groundwater samples from the wells and springs in Jericho area were dominantly influenced by nitrate derived from septic tanks.
- Sewage and manure appears to be the cause of increased nitrate concentrations.
- The application of fertilizers nitrate is of second importance, but this may vary with seasonal applica-

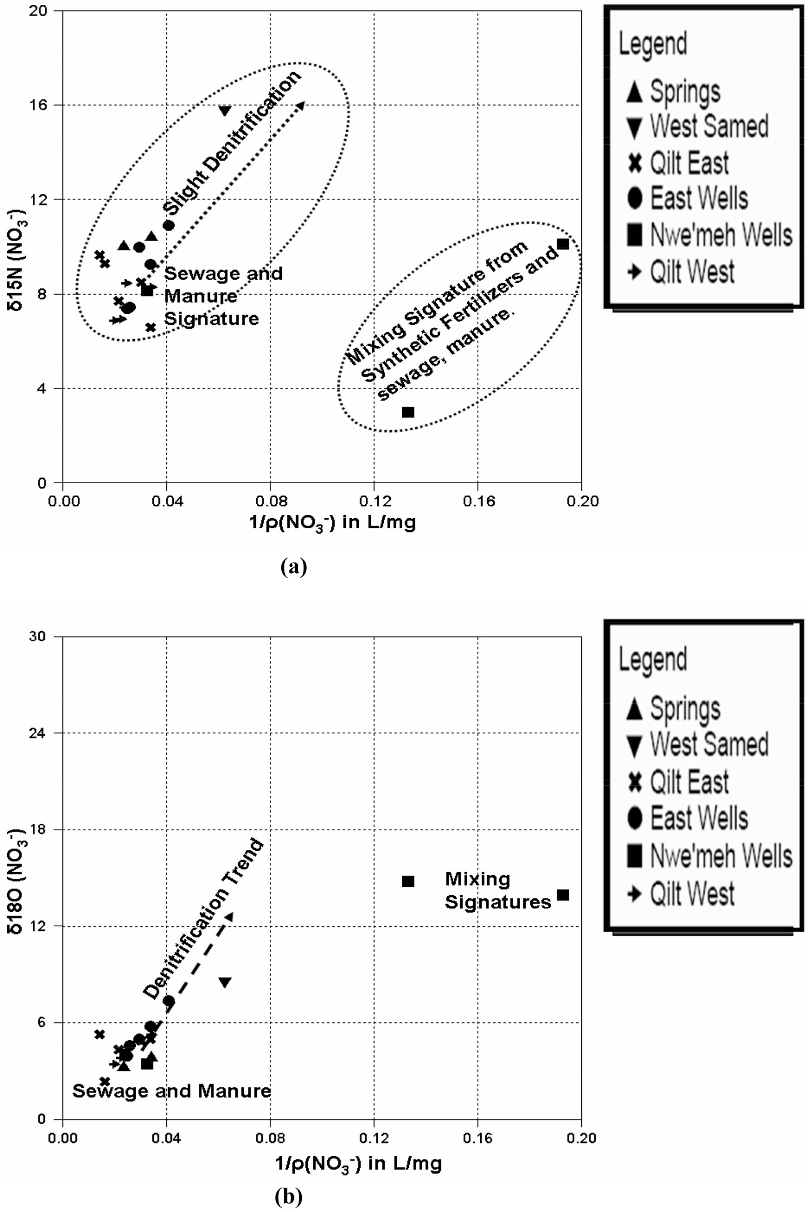

Figure 5. $\delta^{15}N_{nitrate}$ (a) and $\delta^{18}O_{nitrate}$ (b) versus 1/[NO^{-}_{3}] in L/mg. Most wells and springs show no significant differences in isotopic signatures, except for the Samed well, where its low nitrate level and enriched isotopic signature is reflecting a denitrification process. Jericho north wells show low nitrate concentration with higher $\delta^{18}O_{nitrate}$ signatures, reflecting a mixing signature from other sources.

tion of the pesticides and with chemical composition of the fertilizers.

– Long persistence of nitrate within the groundwater reservoir during the dry season (sampling time) gives a good chance for the beginning of denitrification processes within the aquifer.

– The enriched $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values in the northern wells reflect sources of nitrate other than just sewage. This signature may arise from a mixing trend between chemical fertilizers and the residual nitrate from bacterial denitrification of sewage.

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