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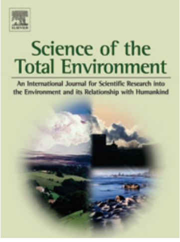

Elevated nitrate levels in the groundwater of the Gaza Strip: Distribution and sources

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ABSTRACT

Seven years of monitoring groundwater in the Gaza Strip has shown that nitrate was and still is a major groundwater pollutant. The objectives of this research were to study the distribution of NO_3^- in the groundwater of the Gaza Strip and to identify the sources of NO_3^- in the Gaza aquifer system by assessing nitrogen and oxygen isotopes. The most recent samples collected in 2007 showed 90% of the wells having NO_3^- concentrations that are several times higher than the WHO standards of 50 mg/L. Potential NO_3^- source materials in Gaza are animal manure N, synthetic NH_4 based fertilizers, and wastewater/sludge. The average concentrations of N in the sludge, manure and soil of Gaza were 2.9%, 1% and 0.08%, respectively. The range in $\delta^{15}N$ of solid manure samples was +7.5 to +11.9‰. The range in $\delta^{15}N$ of sludge samples was +4.6 to +7.4‰, while four brands of synthetic fertilizers commonly used in Gaza had $\delta^{15}N$ ranging from +0.2 to +1.0‰. Sludge amended soil had $\delta^{15}N$ ranging from +2.0 to +7.3‰. For both $\delta^{18}O$ and $\delta^{15}N$, the ranges of groundwater NO_3^- were −0.1 to +9.3‰ and +3.2 to 12.8‰, respectively. No significant bacterial denitrification is taking place in the Gaza Strip aquifer. Nitrate was predominantly derived from manure and, provided $\delta^{15}N$ of sludge represents the maximum $\delta^{15}N$ of human waste, to a lesser extent from septic effluents/sludge. Synthetic fertilizers were a minor source.

1. Introduction

Groundwater is one of the most precious natural resources in the Gaza Strip as it is the only source of drinking water for the majority of the population. The groundwater aquifer of Gaza is extremely susceptible to surface-derived contamination because of the high permeability of sands and gravels that compose the soil profile of Gaza (Shomar et al., 2005a). Several studies in Gaza reported high nitrate (NO_3^-) levels in groundwater as one of the major concerns among the public and governmental decision makers (Abu Maila et al., 2004; Shomar, 2006), but these studies did not include a scientific evaluation of source of NO_3^- nor their implications on the health of the population in Gaza.

Nitrate in contaminated water is known to cause methemoglobinemia in infants (AAP, 1970; Avery, 1999; Cynthia et al., 2002). The association of diarrhea and acidosis with methemoglobinemia is more common than previously thought and can produce dangerously high methemoglobin levels (Lebby et al., 1993; Gebara and Goetting, 1994; Kim et al., 1997; Avery, 2001; Freishtat et al., 2005; Venkateswari et al., 2007). Recent observations revealed a high positive correlation between the concentrations of NO_3^- (>80 mg/l) in groundwater of the Gaza Strip and the occurrence of methemoglobinemia in babies younger than six months of age. Among 640 babies tested in Gaza, 50% showed signs of methemoglobinemia in their blood samples (Absi and Shomar, unpublished data). Additionally, one study suggested a potential link between

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high NO_3^- in drinking water and gastrointestinal cancer (Morales-Suarez-Varela et al., 1996). Nitrates could combine with amines in the body to form N-nitroso compounds that are known cancer causing agents. However, this association is controversial (Weyer et al., 2001).

Contamination of the groundwater can occur if input of NO_3^- into soil exceeds the consumption of plants and denitrification (Mcclain et al., 1994). Shomar (2006) proposed that the excess NO_3^- in the groundwater of the Gaza Strip occurred as a result of NO_3^- leaching from irrigation, wastewater septic tanks, sewage sludge, animal manure and synthetic fertilizers.

NO_3^- and nitrite (NO_2^-) are naturally occurring inorganic ions, which are part of the nitrogen (N) cycle. Microbial action in soil or water decomposes wastes containing organic nitrogen first into ammonia, which is then oxidized to NO_2^- and NO_3^- (Mcclain et al., 1994). Because NO_2^- is easily oxidized to NO_3^-, NO_3^- is the compound predominantly found in groundwater and surface waters under oxidizing conditions. Contamination with N-containing fertilizers, including anhydrous ammonia, as well as animal or human natural organic wastes, can raise the concentration of NO_3^- in groundwater (Thorburn et al., 2003). NO_3^--containing compounds in the soil are generally soluble and readily migrate into groundwater (Rzan et al., 2001; Wakida and Lerner, 2002).

Nitrogen isotopes have been used to identify sources of NO_3^- contamination in groundwater (Brandes et al., 1996; Kendall, 1998; Ogawa et al., 2001). Different sources of NO_3^- and organic matter often have distinctive isotope “fingerprints” that can provide a better understanding of the sources of NO_3^- than more commonly used mass balance “black box models” (Kendall, 1998).

The main objectives of this study were: (1) to determine the average levels and distribution of NO_3^- in the groundwater of the Gaza Strip, and (2) to assess N and O isotopes to identify the major sources of NO_3^- that may contaminate groundwater.

2. Study area, materials and methods

2.1. Study area

The Gaza Strip is one of the most densely populated areas in the world (2638 people per km^2; PCBS, 2000). For administrative purposes, the government divides the Gaza Strip into five regions (Fig. 1): North, Gaza, Middle, Khan Younis and Rafah. Approximately 85% of the population of the Gaza Strip drink from municipal groundwater wells and 15%, mostly in agricultural areas, use private wells to supply their drinking water (Shomar, 2006).

The study area is a part of the coastal zone in the transitional area between the temperate Mediterranean climate to the east and north and the arid climate of the Negev and Sinai deserts to the east and south. As a result, the Gaza Strip has a characteristic semi-arid climate. The hydrogeological features of the Gaza aquifer are well known. The coastal aquifer consists primarily of Pleistocene age Kurkar Group deposits, including calcareous and silty sandstones, silts, clays, unconsolidated sands, and conglomerates. Near the coast, coastal clays extend about 2–5 km inland, and divide the aquifer sequence into three or four sub-aquifers, depending upon the location. Towards the east, the clays pinch out and the aquifer is largely unconfined (PEPA, 1994). Within the Gaza Strip, the total thickness of the Kurkar Group is about 100 m at the shore in the south, and about 200 m near Gaza city. At the eastern Gaza border, the saturated thickness is about 60–70 m in the north, and only a few meters in the south near Rafah. Local perched water conditions exist throughout the Gaza Strip due to the presence of shallow clays (MEnA, 2000).

2.2. Sampling and analyses

2.2.1. Groundwater collection

Water samples were collected 24 February–17 March 2006 and 1–20 June 2007, as the final two of seven collection periods beginning in August 2001. Samples were collected from the major 115 municipal wells and 50 private wells selected to represent the five geographical areas (Fig. 1). At the municipal wells, samples were collected from a tap along the water distribution line. Prior to sampling, chlorine or sodium hypochlorite treatment of water was stopped to minimize interference during analysis. Additional details of water collection are available in Shomar (2006).

2.2.2. Analysis of nitrate, major anions and dissolved organic carbon in groundwater

Groundwater samples were filtered through 0.45 μm (Sartorius filter); the first few milliliters were used for rinsing and were discarded. The filtrate was transferred to clean polyethylene bottles and stored at 4 °C. The sample was divided into two subsamples, the first 100 mL was analyzed in Gaza using the UV spectrophotometric screening method according to the American standard methods, APHA (1995), and the other 100 mL were shipped to the University of Heidelberg—Germany, where NO_3^- and other major anions were analyzed by ion chromatography (IC DIONEX DX-120). Two sets of standard reference materials RS1 and RS3 were used in the determination of NO_3^- in groundwater (DIN, 1997). Generally, there was a difference of ±10% between the results of the NO_3^- analyses conducted in Gaza and Germany.

2.2.3. Analysis of nitrogen and oxygen isotopes of nitrate dissolved in water

Conservation of groundwater samples for isotopic analysis of nitrate was done by cooling (<2 °C). No chemicals for the inhibition of microbiological activity were added because the samples were measured using the denitrifier method. In doing so, the isotopes of nitrogen and oxygen are measured on gaseous N_2O, which is produced under controlled conditions from microbial degradation of nitrate dissolved in the water sample (Sigman et al., 2001; Casciotti et al., 2002).

For the denitrifier method we used bacteria of the strain *Pseudomonas chlororaphis* (ATCC #13985). Because of a lacking enzyme, there is no formation of N_2 by further reduction of N_2O when using these bacteria. For the preparation of the bacteria, medium consisting of a solution of tryptic soy broth (Difco), KNO_3, Al_2SO_4 and foam blocker (Sigman et al., 2001) was autoclaved in 500 mL-bottles and inoculated with the bacterial strain. After incubation of 6–10 days at 32 °C the culture is enriched by centrifugation. About 2 mL of the concentrated culture was introduced into autoclaved vials (10 mL) and tightened with a

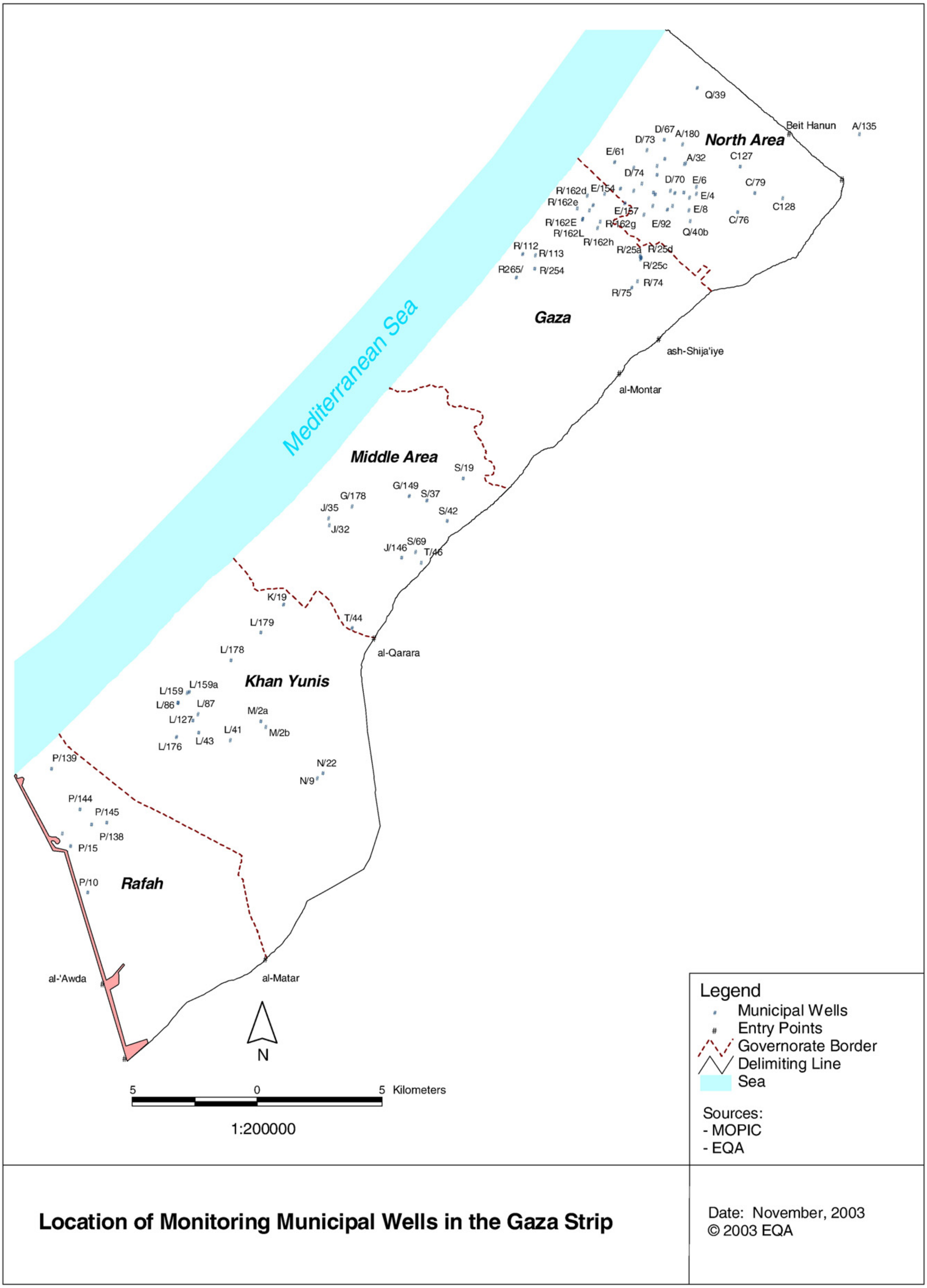

Fig. 1 – Five regions of the Gaza Strip and location of investigated groundwater wells.

septum. After flushing the vials with He for 20 min to remove residual N_2O, about 2 mL of sample water is injected into the vials. Incubation of the sample vials was performed at 30 to 34 °C for about 24 to 48 h. Immediately after incubation; 0.1 mL of 10 N NaOH was added to each sample vial to remove CO_2 from the headspace and to inhibit further microbial activity.

For the measurement of the isotopic composition of the produced N_2O we used a modified gasbench II-system connected to a mass spectrometer V plus (Thermo). The N_2O present in the headspace of the sample vials is transported with He carrier gas (about 50 mL/min) over a sequence of water and CO_2 traps and is subsequently adsorbed on a cool trap operated at the temperature of liquid nitrogen. Subsequently N_2O is remobilized using a He flow of 5 mL/min and transported into the gasbench with open split into the mass spectrometer. Details of the procedure are given in Silva et al. (2000) and Casciotti et al. (2002).

All sample measurements were performed in duplicate. Calibration and normalization were done by concurrent measurements of samples and international nitrate references USGS34, USGS 35 and IAEA NO_3, which were treated identical to the water samples. Isotopic measurements of nitrogen are given as $\delta^{15}N$ values relative to the international reference AIR with an analytical uncertainty of ±0.2‰. The $\delta^{18}O$ values are related to the international reference VSMOW (Vienna Standard Mean Ocean Water). The analytical uncertainty is in the range of ±0.5‰.

2.2.4. *Soil*

Soil samples were collected during the final water collection period, 1–20 June 2007. The soil collection was according to the European soil sampling guidelines (Theocharopoulos et al., 2001). Fifty-seven sites (Table 2) were selected to represent all types of soil in Gaza (Shomar et al., 2005b). The depth of sampling varied between 0–10 cm for the open and grass soils; 20 cm for the vegetable soils; and up to 30 cm for the ploughed soils.

At each sampling station, a circle of 2–5-m diameter was identified and 10 sub-samples were collected within the perimeter and mixed to form a composite sample. Composite samples (weighing about 0.5 kg) placed into dark polyethylene cups and transported to Germany for analysis. Samples were freeze-dried until complete dryness; then sieved through a 2-mm sieve and ground to a powder by using a ring mill (FRITSCH-Labor Planeten Mühle, pulverisette 5). The total N, carbon (C) and sulfur (S) contents were determined in dried samples by using a CNS analyzer (Leco CNS-2000). Additional details are available in Shomar et al. (2005b).

2.2.5. *Sludge, manure and synthetic fertilizers*

Twenty composite sewage sludge samples were collected during the last sampling campaign, 10 from Beit Lahia wastewater treatment plant and 10 from Gaza wastewater treatment plant. Samples were collected in polyethylene containers from the different drying lagoons of the two treatment plants and from the accumulated piles in the surrounding areas. After collection, samples were freeze-dried until complete dryness; then they were ground and homogenized in an agate mortar and sieved through a 2-mm pore size (Shomar et al., 2004). The most common manure applied in the agriculture of Gaza is poultry and cow manure. Many farmers use both for the same land. They mix them or apply them one after the other depending on the availability. Five composite samples were collected from the most agricultural areas of Gaza using the same method as described for the soil samples. Manure samples were processed using the same method used for the sludge samples.

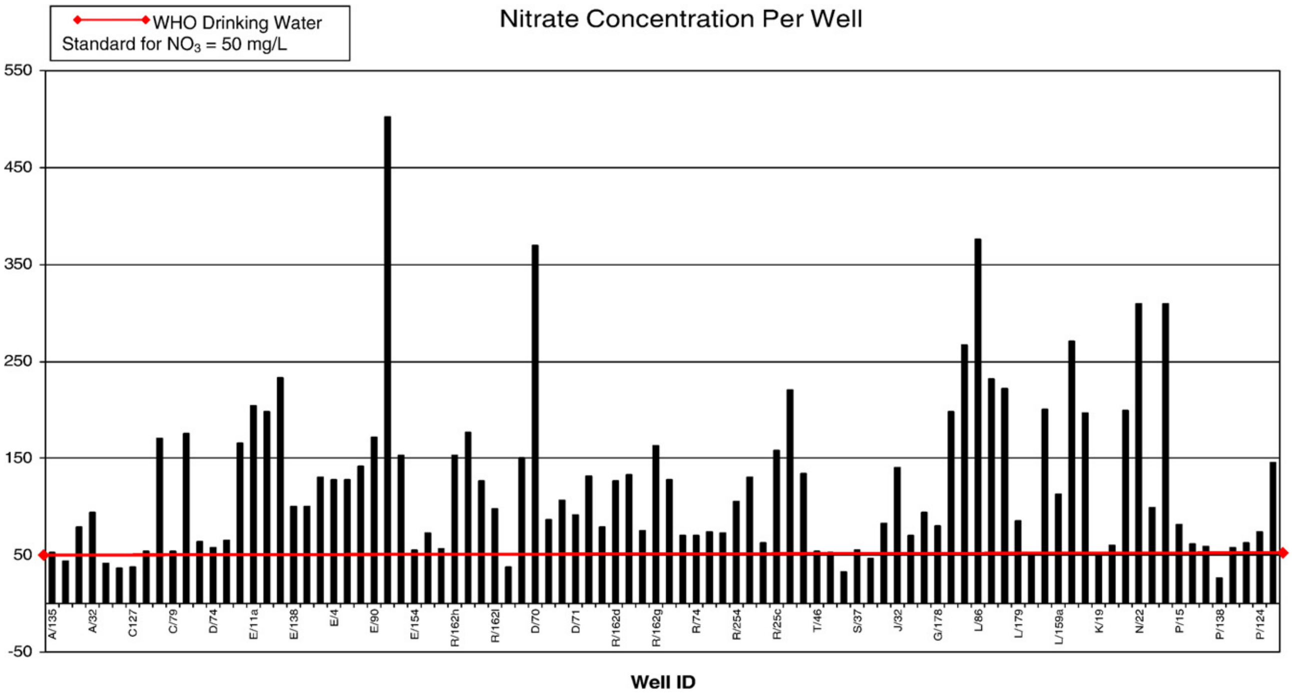

Fig. 2 – Variation of NO_3^- concentrations in the groundwater wells of the Gaza Strip, going from north on the left to south on the right.

The amount of agricultural fertilizers used for vegetables in the Gaza Strip obtained from a field survey during April to November 2005 reached 12000 tons, of which 3500 tons are chemical fertilizers and the rest are organic fertilizers from cattle and poultry (Shomar et al., 2005b). Based on discussion with the Ministry of Agriculture in Gaza, four major fertilizers were chosen for determination of total N and δ^{15}N. These fertilizers are: (i) Ethylenediamine-di(*o*-hydroxyphenylacetic acid) abbreviated as Fe (EDDHA), (ii) NO_2, Fe, Mn (iii) 2-(thiazol-4yl) benzimidazole ($C_{10}H_7N_3S$) known as Thiabendazole, and (iv) $N+P_2O_5+KO$ known as Dzmocote. The total N, C and S contents in dried ground samples of sludge, manure and synthetic fertilizers were determined using a CNS analyzer (Leco CNS-2000). For total C, N, and S in soil, sludge, manure and fertilizers, two sets of standard reference materials were used (NIST, 2000). Precision was estimated evaluating the reproducibility between duplicates and a coefficient of variation of lower than 5% was found.

2.2.6. *Analysis of nitrogen isotopes of soil, manure and sludge*

The samples were analyzed in the faculty of geology, University of Utrecht, the Netherlands. The δ^{15}N-values in soil, sludge, manure and fertilizers were measured by combusting the bulk sample of soil, manure, sludge and fertilizer in an elemental analyzer (EA-NA1500 NCS — Finnegan Delta) coupled to isotope ratio mass spectrometry (IRMS).

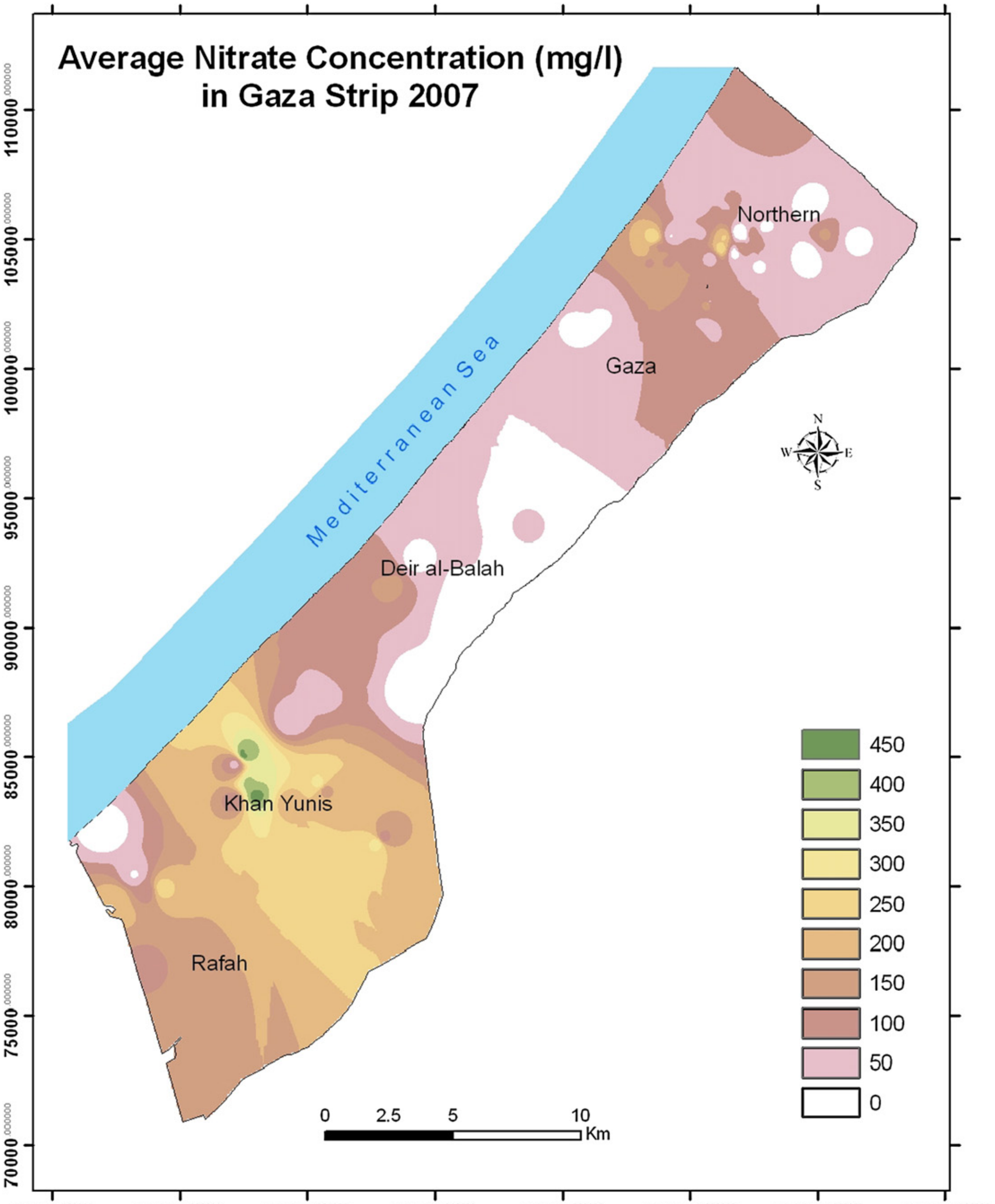

Fig. 3 – Distribution of NO_3^- concentrations in the groundwater of the Gaza Strip.

The samples were put in an AS128 autosampler, dropped in the oxidation tube at 1020 °C with oxygen pulse in a Helium flow of 80 mL/min. Oxygen was removed and nitrogen oxides reduced to nitrogen over pure copper at 650 °C and the gas flow was dried over a $MgClO_4$ water trap. The nitrogen was separated from the carbon dioxide over a 2 m Porapack QS chromatographic column. The gas flow was led into the open split ConFlo-II interface (Conflo is the interface between the EA and the MS). 0.3% of the gas from the EA was led into the mass spec via a capillary in the open split. In the ConFlo refgas pulses of the labeled gases nitrogen and carbon dioxide were added to ease calculation of isotope ratios. Nitrogen and carbon contents were calculated to compare area of peak 28 respective 44 of the sample to areas of a standard. About 40 µg N for one EA-CFIRMS technique was used. Approximately 40 to 80 mg soil weight were used per analysis. The maximum capacity of the tin cup (5 mm diameter and 8 mm long) is about 4 mg. Dried pure acetanilide was used as a standard for the determination of the percentages of C and N. Ammonium sulfate standard was used for nitrogen isotopes and ^{15}N was calibrated with isotope standards IAEA-N-1 and IAEA-N-2.

3. Results

3.1. *Nitrate in groundwater*

The detailed results of general groundwater geochemical characteristics are given in Shomar (2006), whereas NO_3^- concentrations and related parameters from samples collected

Table 1 – Nitrate concentration (mg/L) and N, O isotopic composition of groundwater

No.	Area	Well ID	Purpose	Depth (m)	NO_3^- [mg/l]	$\delta^{15}N_{nitrate}$ [‰] (±0.3‰)	$\delta^{18}O_{nitrate}$ [‰] (±0.6‰)
1	North area	A/185	Municipal	90	96	+12.4	+5
2		D/2	Municipal	54	255	+12.3	+3.3
3		E/10	Municipal	90	155	+11.1	+4.2
4		E/11b	Municipal	93	26	+6.2	+2.3
5		A-19	Private	95	130	+9.6	+3.9
6	Gaza area	E/142	Municipal	55	101	+9.0	+0.4
7		E/4	Municipal	60	85	+11.4	+1.9
8		R/162e	Municipal	100	218	+12.4	+0.5
9		R/162c	Municipal	110	147	+10.3	+1.8
10		Q/68	Municipal	55	47	+8.3	+1.6
11		R/162h	Municipal	100	215	+11.9	+1.6
12		R/162ha	Municipal	95	177	+12.6	+2.1
13		R/254	Municipal	72	56	+10.4	+1.5
14		R/75	Municipal	80	130	+12.4	+2.7
15		F/203	Municipal	52	43	+9.0	+4.4
16	Middle area	FI/85	Private	50	146	+10.3	+4.4
17		FI/87	Private	65	136	+9.9	+2.9
18	Khan Younis area	L/87	Municipal	90	358	+11.2	+0.9
19		unknown	Municipal	90	55	+9.1	+3.7
20		L/43	Municipal	90	428	+12.5	+1.3
21		L/41	Municipal	105	212	+12.3	+3.5
22		L/179 a	Municipal	110	92	+7.4	+7.5
23		L/127	Municipal	120	397	+12.4	+1.3
24		unknown	Municipal	75	104	+9.8	+2.1
25		L/190	Municipal	95	112	+11.7	+4
26		unknown	Municipal	78	134	+11	+2
27		M/11	Municipal	70	82	+9.9	+2.8
28		L/181	Municipal	67	60	+4.9	+8.1
29		P/146	Municipal	90	59	+3.2	+9.3
30		unknown	Private	95	245	+11.9	+1.4
31		unknown	Private	85	201	+12.6	+2.5
32		unknown	Private	100	59	+12.2	+3.6
33		unknown	Private	90	429	+11.3	+2.1
34		LI/12	Private	80	422	+12.8	+1.8
35		L/159a	Municipal	72	380	+9.6	ND
36		L/127	Municipal	83	434	+9.7	ND
37		L/43	Municipal	89	445	+10.4	ND
38		L/87	Municipal	90	370	+9.6	ND
39	Rafah area	P/10	Municipal	100	147	+11.7	+1
40		P/145	Municipal	90	258	+9	+2
41		P/138	Municipal	85	127	+9.7	+1
42		P/15	Municipal	82	201	+10.9	+0.1
43		P/148	Municipal	90	110	+9.3	+0.8
44		P/147	Municipal	90	35	+5.9	−0.1

Unknown: new or private well with no official number.
ND: no data.

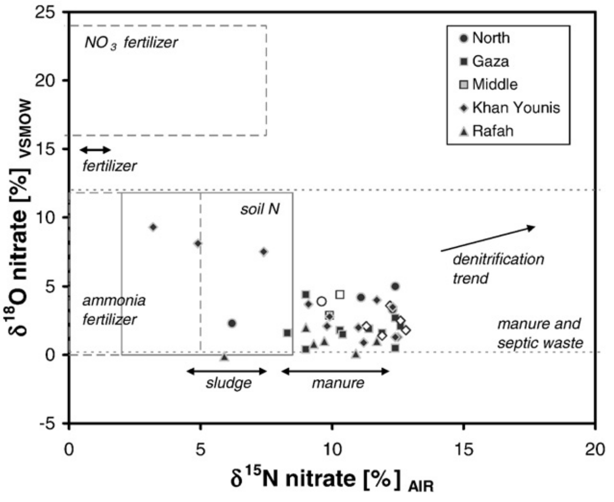

Fig. 4 – $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3$ in groundwater of the Gaza strip. The range of measured $\delta^{15}N$ values of potential N sources are indicated by arrows. Ranges for potential sources as given by literature are indicated by dashed boxes and were taken from Kendall (1998).

from 2006 to 2007 are presented in this study. NO_3^- concentrations in the Gaza aquifer ranged from 31 to 452 mg NO_3/L. Almost 90% of the sampled wells had levels of NO_3^- above the World Health Organization's (WHO) standard of 50 mg/L and only 10 of the 115 sampled wells were at or below the WHO standard. These nitrate concentrations are consistent with those from samples collected from 2001 to 2005 (Shomar, 2006). The highest levels of NO_3^- were in Khan Younis (south) and Jabalia (north). These regions showed average NO_3^- concentrations of 191 and 151 mg/L, respectively. The average NO_3^- concentrations in Gaza, Rafah and middle area were 135, 141 and 125 mg/L, respectively (Figs. 2 and 3). All private wells except three showed NO_3^- concentrations five to seven times higher than the WHO standard. There is a weak negative relationship between NO_3^- and well depth, but it is not statistically significant ($r = -0.168$, P-value $= 0.276$).

Table 2 – Average soil samples concentrations of N, C and S

Soil of agricultural land	N (%)	C (%)	S (%)
Vegetable farm uses manure (north, $n=5$)	0.07	2.2	0.02
Vegetable farm uses manure (Gaza, $n=5$)	0.08	1.1	0.02
Vegetable farm uses manure (middle, $n=5$)	0.07	0.9	0.01
Vegetable farm uses manure (Khan Younis, $n=10$)	0.13	1.9	0.02
Citrus farm uses manure (north, $n=5$)	0.10	2.5	0.02
Olive farm uses manure near Gaza SWDS ($n=2$)	0.06	2.1	0.01
Vegetable farm uses manure near Gaza SWDS ($n=2$)	0.07	1.6	0.02
Guava farm uses manure near Gaza SWDS ($n=2$)	0.09	1.8	0.02
Guava farm uses manure near Gaza WWTP ($n=2$)	0.08	1.5	0.02
Strawberry — greenhouse (north, $n=5$)	0.15	1.8	0.02
Vegetable farm — greenhouse (north, $n=5$)	0.07	2.7	0.02
Vegetable farm — greenhouse (middle, $n=5$)	0.07	2.4	0.02
Vegetable farm — greenhouse (Khan Younis, $n=4$)	0.10	1.1	0.02

Table 3 – N isotopic composition of soil, sludge manure and synthetic fertilizers

No.	Wastewater treatment plant	%N	$\delta^{15}N$-average [‰ air]
1	Soil irrigated by WW	0.024	+7.3
2	Soil beside dry sludge	0.007	+5.7
3	Soil beside plant effluent	0.08	+5.5
4	Soil behind drying lagoons	0.07	+2.7
5	Soil beside plant entrance	0.02	+4.0
1	Sludge	0.65	+5.0
2	Sludge	1.12	+6.3
3	Sludge	0.13	+5.3
4	Sludge	2.55	+4.6
5	Sludge	1.17	+7.0
6	Sludge	0.43	+4.9
7	Sludge	0.96	+4.6
8	Sludge	1.72	+5.7
9	Sludge	2.54	+4.7
10	Sludge	1.59	+4.7
11	Dried sludge 3 months old	2.21	+5.2
12	Dried sludge 3 months old	1.91	+7.4
13	Sludge	2.6	+5.3
14	Sludge	2.5	+4.9
15	Sludge	2.7	+4.6
16	Sludge	2.4	+4.8
17	Sludge	2.3	+4.3
1	Manure	0.2	+11.7
2	Manure	0.6	+11.9
3	Manure	0.7	+11.8
4	Manure	0.6	+7.5
1	Fertilizer EDDHA	3.9	+1.0
2	Fertilizer NO_2, Fe, Mn	1.0	+1.0
3	Fertilizer Thiabendazol	14.3	+0.1
4	Fertilizer Dzmocote	14.5	+0.2

3.2. *Nitrogen and oxygen isotopes of nitrate*

Table 1 shows the values of $\delta^{15}N$ and $\delta^{18}O$ for the 44 groundwater samples collected in 2007. The $\delta^{15}N$ values for dissolved NO_3^- in groundwater ranged between +3.2 and +12.8‰, the $\delta^{18}O–NO_3^-$ ranged between −0.1 and +9.3‰. Fig. 4 shows the relationship of $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3$ in groundwater. To compare the $\delta^{15}N$ of the dissolved NO_3^- to possible NO_3^- from anthropogenic sources, the ranges of the measured $\delta^{15}N$ values for manure, sludge and fertilizers are shown as arrows parallel to the x-axis. Manure had the highest $\delta^{15}N$ values (average +10.7‰), followed by sludge (average +4.8‰), and synthetic fertilizers (average +0.6‰). In Gaza, the majority of $\delta^{15}N–NO_3^-$ values in groundwater closely resemble those from the manure samples (Fig. 4). There is no evidence for the presence of denitrification processes which should have resulted in a shift of the samples along the given denitrification trend in Fig. 4. The ranges of $\delta^{15}N$ in manure and synthetic fertilizers are in accordance with isotopic compositions of manure and synthetic fertilizers from other studies (e.g. Böhlke, 2002). In contrast, the $\delta^{15}N$ values of sludge are unusually low considering that both nitrate from human septic wastes and animal wastes commonly have much higher $\delta^{15}N$ values (Kendall and Aravena, 2000). However, Fogg et al. (1998) reported comparably low $\delta^{15}N$ values of septic waste effluents in a study from California, which could be used to distinguish between NO_3^- from septic waste and from manure.

3.3. Soil, sludge, manure and synthetic fertilizers

The concentration of total N in soil samples is shown in Table 2. The highest concentrations of N were observed in agricultural soil samples of Khan Younis (south) and Beit Lahia (north) where manure and synthetic fertilizers are intensively used. Table 2 indicates that there was no relationship between the values of C, N and S in the soil samples. Sludge and manure samples had higher concentrations of total N than did soil (Table 3). The Kruskal–Wallis test (*H*) was used to determine the relationship of different potential sources to NO_3^- in groundwater via N/O isotopes. The Kruskal–Wallis test showed a significant difference among the three sources of nitrate (*H*=9.25; *DF*=2; *P*=0.010).

4. Discussion

The findings of this study are consistent with earlier surveys conducted by the Palestinian water authority (PWA, 2001) where 90% of the wells had NO_3^- concentrations exceeding the WHO's maximum permissible drinking water limit of 50 mg/L NO_3^-. Since 2001, four of the groundwater sampling campaigns spanned the summer months of August–September and three in winter (January–March). The average concentration of nitrate in domestic wells is 128 mg/L in summer and 118 mg/L in winter, and for the agricultural wells, the average is 100 mg/L in summer and 96 mg/L for winter. There was greater seasonal variation in nitrate concentration in municipal wells than in the agricultural wells. In the municipal wells, NO_3^- concentrations were 10–15 mg/L lower by the end of the rainy winter months of February and March. However, this seasonal variation did not reduce NO_3^- concentrations to levels complying with the WHO standards (Abu Maila et al., 2004; Shomar, 2006). This variation could be explained by groundwater recharge from rainfall (320 mm per year) which averaged about 43 million cubic meters (m^3) per year in 2005 (Baalousha, 2005).

The accordance between $\delta^{15}N$ values of NO_3^- in groundwater and of N in manure in Fig. 4 indicates that for the Gaza groundwater samples manure (and possibly human waste) is the main NO_3^- source when compared to synthetic fertilizers.

Fig. 5 shows the $\delta^{15}N$–NO_3^- values in relation to the reciprocal of the nitrate concentration. In such a scaling, two component mixings can be identified as straight lines. The figure shows that nitrate in groundwater of the Gaza Strip is due to mixing of more than two different NO_3^- sources. At least three end members can be identified according to the linear trends: (1) a source of low NO_3^- content and low $\delta^{15}N$–NO_3^- values, (2) a source with comparably low $\delta^{15}N$–NO_3^- values but moderate NO_3^- contents, and (3) one or more (dominating) sources with high NO_3^- content and high $\delta^{15}N$–NO_3^- values. The samples close to the low and moderate NO_3^- end members can be further distinguished by their $\delta^{18}O$–NO_3^- values, which are high (+7 to +9‰) in case of the moderate NO_3^- contents and low (−0.1 to +2.3‰) for the low NO_3^- containing end member. According to these isotopic signatures, these end members might be related to the application of inorganic fertilizer and to natural (or low fertilized) soil nitrogen, respectively.

A distinction between manure and human waste (sludge and septic effluents) based on the isotopic composition of NO_3^- is often difficult because NO_3^- from manure and human waste usually shows similar ranges of $\delta^{15}N$ values (Kendall and Aravena, 2000; Seiler, 2005). In this study, the isotopic composition of N in sludge shows significantly lower values than those of N in manure throughout the study area (Fig. 2 and Table 3). Thus, nitrate stable isotopes can be used at least as a qualitative tool to identify the origin of nitrate. However, due to the lack of $\delta^{15}N$ values of effluents from septic tanks, conclusions on the relative importance of NO_3^- from human waste will only be valid if the $\delta^{15}N$ value of NO_3^- derived from septic tanks or cesspools effluents is the same or higher than that of sludge. Differences between $\delta^{15}N$ in sludge and septic effluents might be expected because of spatial variations in the $\delta^{15}N$ values of the septic wastes or the presence of isotope effects due to isotope fractionation. Such isotope fractionation might be related to volatilization of ammonia from soils or to the nitrification of ammonia where the oxidation of ammonia is the rate-limiting step. Except for denitrification, these processes usually lead to an enrichment of $\delta^{15}N$ of the residual N in sludge and depletion in the mobile compounds like NH_3 and NO_3^- (Kendall, 1998; Kendall and Aravena, 2000). Hence, assuming that all N compounds in human waste were well mixed before separation of sludge and septic effluents, and if denitrification is minor or absent (see discussion below), the $\delta^{15}N$ of total N in sludge should represent the maximum value for NO_3^- related to sludge or septic effluents. The collected sludge samples from the two existing sewage treatment plants of Gaza were composite samples. These sludges also include human wastes from a large number of septic tanks not connected to the sewer system, which are transported to the inlet of the treatment plants by tankers. Therefore, the sludge samples should be representative of Gaza. In addition, the measured $\delta^{15}N$ values of sludge N show a narrow distribution and deviations from this range in areas without wastewater collection system seem unlikely due to similar living conditions and similar nutrition in the Gaza area. Hence, provided that the reasonable assumption of well mixed human waste is

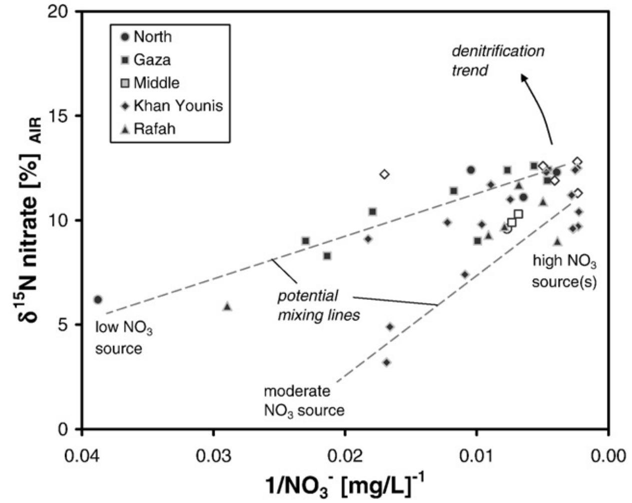

Fig. 5 – Relationship between $\delta^{15}N$ NO_3^- and NO_3^- concentration in groundwater of the Gaza Strip. Note the reciprocal scaling of NO_3^- concentrations.

accurate, the isotopic composition of the dissolved NO_3^- in groundwater (median $\delta^{15}N$ of 10.4‰) provides evidence that manure is the primary source of NO_3^- in the Gaza aquifer. Sludge and most probably also septic effluents are less important sources of groundwater NO_3^- than manure in spite of the widespread lack of wastewater collection in Gaza. A conservative estimate of the contribution from human waste can be obtained by comparing the median $\delta^{15}N$ of sludge and the maximum $\delta^{15}N$ value of manure. The results show, that NO_3^- from human waste contributes less than 50% for all, and less than 20% for the majority of samples, to the nitrate load found in the groundwater of Gaza. However, further investigations on effluents from septic tanks are needed to verify these results and rule out an influence of septic effluents with isotopic compositions similar to that of manure.

The groundwater of Gaza is shallow and oxygenated (Shomar et al., 2005a). The interaction of N compounds in the soil with the surrounding media leads to oxidation of N compounds and the formation of NO_3^-. The NO_3^- is normally not strongly adsorbed by the soil particles and/or matrix (Abu Maila et al., 2005), but rather percolates into the groundwater.

The presence of denitrification seems unlikely because of the hydrochemical characteristics of the groundwater aquifer in Gaza. Several works have identified methods to determine denitrification processes in groundwater (Mariotti et al., 1988; Mosier and Schimel, 1993; Aravena and Robertson, 1998). The apparently unaltered isotopic composition of NO_3^- in Figs. 4 and 5 provides no evidence for denitrification, which usually is accompanied by a substantial enrichment of $\delta^{15}N$ of NO_3^- along the characteristic trend lines. Isotope fractionation would also affect $\delta^{18}O$, although to a lesser extent. The low $\delta^{18}O$–NO_3^- values in groundwater support that denitrification is not of importance for the investigated groundwater samples. If denitrification is present in some parts of the soil, e.g. in oxygen poor or anoxic zones in the shallow soil zone from spreading of manure or wastewater, this either leads to complete conversion of NO_3^- or the residual nitrate only makes a minor contribution to nitrate dissolved in recharging groundwater. Most commonly, the presence of a redox gradient that generates a series of oxidation–reduction reactions, including the reduction of NO_3^- at the appropriate position in the sequence, provides evidence for denitrification in groundwater (Kendall, 1998). Conditions needed for denitrification do not exist in the groundwater of Gaza. The average dissolved oxygen (DO) is 7.8 mgO_2/L (Shomar, 2006) and microbial denitrification does not occur in the presence of significant amounts of oxygen (Koba et al., 1997). Anaerobic microorganisms can perform denitrification at O_2 levels of less than about 0.5 mg/L (Hübner, 1986). Additionally, the average HCO_3^- is 310 mg/L, the dissolved organic carbon (DOC) is less than 0.2 mg/L, the Fe is in the oxidized form of Fe^{3+} and the average pH is 8. The lack of denitrification is likely due to the lack of labile or sufficient supplies of electron donors. As the dissolved organic carbon (DOC) of the sampled groundwater of Gaza was less than 0.2 mg/L, this level could not support microbial denitrification in the Gaza aquifer (Starr and Gillham, 1993).

According to Kendall (1998), the $\delta^{18}O$ of NO_3^- can be used to distinguish between synthetic fertilizers and organic NO_3^- sources if nitrate directly enters the groundwater without being incorporated into the soil nitrogen cycle. The measured $\delta^{18}O$–NO_3^- values suggest that most NO_3^- in groundwater is due to nitrification of N compounds mineralized from soil organic material. The $\delta^{18}O$ value of microbial NO_3^- produced by nitrification of ammonia depends on the $\delta^{18}O$ values of atmospheric oxygen ($\delta^{18}O$ value of 23.5‰) and the available soil water (Hollocher, 1981; Anderson and Hooper, 1983). Due to the lack of soil water data, we used the $\delta^{18}O$ of rain water from monitoring stations of the Global Network of Isotopes in Precipitation (GNIP) as a reasonable estimate of the soil water $\delta^{18}O$ value, although this neglects isotope effects due to evaporation processes from soil. The closest stations to the Gaza Strip were Beer Sheva (Israel) and Alexandria (Egypt) with a range of −1.8 to −5.9‰ for the weighted monthly $\delta^{18}O$ values in rain (IAEA/WMO, 2004). Provided that two of the three oxygens in NO_3^- stem from soil water, the expected $\delta^{18}O$ of NO_3^- is about +4 to +7‰. Hence, most of the measured $\delta^{18}O$–NO_3^- values in Gaza's groundwater fall into the expected range or below, which indicates that most of NO_3^- is produced by microbial oxidation from ammonia or mineralized nitrogen.

In summary, the $\delta^{18}O$ and $\delta^{15}N$ isotopic composition, as well as the correlation between application of manure and levels of NO_3^- in groundwater indicates that NO_3^- in the aquifer is predominantly derived from manure N compounds, human waste and to a lesser extent from NH_4 fertilizers. Most of the NO_3^- in the aquifer is produced by nitrification of manure which is subsequently flushed into the groundwater during fall recharge.

5. Conclusions

1. Almost 90% of the groundwater wells of the Gaza Strip sampled between 2001 and 2007 showed NO_3^- concentrations two to eight times higher than the WHO standards.
2. The $\delta^{18}O$ and $\delta^{15}N$ isotopic composition of NO_3^- revealed that manure and septic effluents are the main sources of NO_3^- in the groundwater of Gaza followed by sludge and synthetic fertilizers. Provided N compounds were well mixed in human waste before separation of sludge and septic effluents, the low $\delta^{15}N$ values of sludge indicate that nitrate in groundwater was predominantly derived from manure.
3. Because of the potential for NO_3^- in groundwater to cause methemoglobinemia in babies younger than six months of age, governmental and nongovernmental sectors should take immediate actions to solve the nitrate problem by groundwater quality management and to offer the greatest protection to infants. Babies younger than six months should not drink water (or formula made with water) that exceeds the WHO NO_3^- standard.

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