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ORIGINAL ARTICLE

Distribution and origin of nitrate in groundwater in an urban and suburban aquifer in Mar del Plata, Argentina

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Abstract The impact of urbanization on groundwater quality is of special concern for water managers dealing with the provision of drinking water to large urban centers. Nitrate is one of the most common contaminants found in urban aquifers. This paper presents a case study aiming at evaluating the distribution and sources of nitrate in an urban aquifer in the city of Mar del Plata, Argentina. Four study zones under different land uses, including a pristine, a semi-rural, an intermediate, and an urban area, were evaluated as a part of this study. The three latter zones are linked by the groundwater flow system. The average nitrate concentration in the pristine area is 6.7 mg/L as nitrate and is over the permissible level of 50 mg/L for drinking water in the other areas. In the semi-rural area it ranges from 39.2 to 107.1 mg/L with an average value of 38.2 mg/L and the nitrate concentration tends to decrease in the intermediate zone to an average value of 38.2 mg/L; however, values above 60 mg/L are also observed there. Then the nitrate concentration in the urban area water is higher than that in the intermediate zonewater ranging from 48.2 to 100.3 mg/L with an average value of 67.3 mg/L. Data on the stable isotopes 15N and 18O in nitrate show that the main sources of nitrate in the study area are manure associated to agriculture uses and cesspools in the semi-rural area, and leakage of the sewage distribution network in the urban area, respectively. This is supported by a previous study which found that 20 % of the water flooding many underground structures in the city came from leakage of the sewage network. No evidence of nitrate attenuation by denitrification was found in the groundwater. This study has shown that aquifers in urban areas can be affected by agricultural activity in the upstream areas and leakage of the sewage network in the urban area.

Keywords Nitrate groundwater pollution · Nitrate sources · Nitrate isotopes · Mar del Plata · Argentina

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Introduction

Nitrate is the main chemical species of nitrogen in water, participating in chemical and biological reactions in the environment. Its high solubility and non-reactive behavior under oxidizing conditions make nitrate a useful indicator of groundwater pollution. Nitrate ingestion by infants due to drinking water can cause low oxygen levels in blood (methemoglobinemia), a potentially fatal condition in special cases (Spalding and Exner 1993). Moreover, nitrate concentrations of 4 mg/L or more in water from community wells in Nebraska have been associated with increased risk of non-Hodgkin's lymphoma (Ward et al. 1996). Investigation conducted by local public health officials in Indiana implicated nitrate-contaminated drinking water as the possible cause of several miscarriages (Schubert et al. 1997). The US Environmental Protection Agency (USEPA)

(1997) has established a drinking water standard of 10 mg/L for NO_3–N, which is the same value for the Argentinian Food Code (Código Alimentario Argentino (Argentinian Food Code) 2012).

Although there are many sources of nitrogen (both natural and anthropogenic) that could potentially lead to the high level of nitrate in groundwater, anthropogenic sources raise the amount of nitrate to dangerous levels more often. These can be diffusive sources associated with excess use of fertilizers (organic and inorganic) in agricultural areas and point sources such as, "sites used for disposal of human and animal sewage; industrial wastes related to food processing, munitions, and some polyresin facilities (Vomocil 1987); and sites where mishandling may cause accidental spills and nitrogenous materials may accumulate" (Hallberg and Keeney 1993, p. 303). Septic tanks and cesspools are another example of anthropogenic point sources of nitrogen contamination of groundwater and the extent of contamination is usually related to the density of sewage systems. In densely populated areas, sewage system leakages can represent a major local source of nitrate in the groundwater. In less populated areas, however, this source does not pose a major threat to groundwater contamination (Hallberg and Keeney 1993).

The evaluation of nitrate sources in groundwater is one of the key aspects related to long-term management of groundwater resources. Identification of the origin and fate of nitrogen species in groundwater can be assessed through the application of isotopic techniques, specifically using stable isotopes of O and N in nitrate. Previous studies have demonstrated that nitrogen isotopes can be used to help to distinguish between different nitrate sources (Aravena et al. 1993; Durka et al. 1994; Wassenaar 1995; Ging et al. 1996; Kendall et al. 1997). In addition, oxygen isotopes can be used to identify processes, such as denitrification, that may alter the concentration and isotopic composition of nitrate (Amberger and Schmidt 1987; Böttcher et al. 1990). Sulfur isotopes can also be useful to provide information about the role of sulfide minerals in denitrification in groundwater (Strebel et al. 1990). Isotope data can be used more effectively when combined with additional geochemical data (Böhlke and Denver 1995). Supplemental geochemical data provide additional constraints necessary to distinguish between nitrates that are likely to be derived from residential sources as rather than agricultural land use.

The water quality of the unconfined aquifer in the southeast of Buenos Aires Province in Argentina is seriously affected by high nitrate levels; this includes urban areas such as the city of Mar del Plata (Cionchi 1994; Cionchi and Redín 2004) and neighboring towns (Martinez et al. 1997; Massone et al. 1998; Moschione 2010).

The city of Mar del Plata, located on the Atlantic coast of Buenos Aires Province, has a population of 700,000. Groundwater pumped from about 280 extraction wells is the sole source for domestic and industrial use. High levels of nitrate above 45 mg/L have been found in urban areas and similar concentrations have also been observed in rural areas located upstream of the city of Mar del Plata. The probable origin of nitrate in rural areas could be fertilizers used excessively and/or solid waste leachate (Massone et al. 1998). It has been proposed that the source of nitrate pollution in the urban areas could be related to leakages in the sewage network system (Bocanegra et al. 2010; Moschione 2010). An additional source in urban areas could be contaminated groundwater from rural areas.

The origin of nitrate in the aquifer used as a public drinking water supply for the city of Mar del Plata has a significant relevance to long-term groundwater management. Specifically, the selection of extraction and management strategies and the adoption of preventive and corrective measures require a certain understanding of nitrate sources in groundwater. The research approach included the use of hydrogeological, geochemical and isotopic tools with the aim to evaluate sources and processes that can affect nitrate concentration along the groundwater flow system in the aquifer of Mar del Plata.

Study area

The study area is placed in the city of Mar del Plata, which is on the Atlantic Coast of the Province of Buenos Aires, Argentina Republic, South America. Four study zones were selected (Fig. 1), representing different land uses: semi-rural (Zone A), intermediate (Zone B) and urban (Zone C), which are characterized by high nitrate levels in groundwater (Fig. 1). A non-polluted area, characterized by low nitrate levels located to the north of the Las Chacras Creek Catchment, was selected as a "Control Zone" (Fig. 1). The three polluted zones included the upper part (recharge areas) and the middle and lower part (discharge areas) of the Las Chacras Creek Catchment. The regional hydrogeology shows the existence of an "unconfined and multilayer" clastic aquifer called Pampeano Aquifer, which is composed of loess deposits more than 100 m thick, with silt and very fine sand granulometry and clay intercalations. These deposits have aeolic and fluvio-aeolic origins in the Neogene Period.

Permeability values have been estimated at 10 m/d with transmissivities between 600 and 1,400 m^2/d (Bocanegra et al. 1993; Martínez and Bocanegra 2002). The recharge in this aquifer is direct infiltration of rainwater and it is estimated to be around 150 mm/year (Bocanegra et al. 2001). The sediments that form the aquifer lie above a hydrogeological basement composed by Eopaleozoic orthoquartzites of the Balcarce Formation (Poiré et al. 2003). The

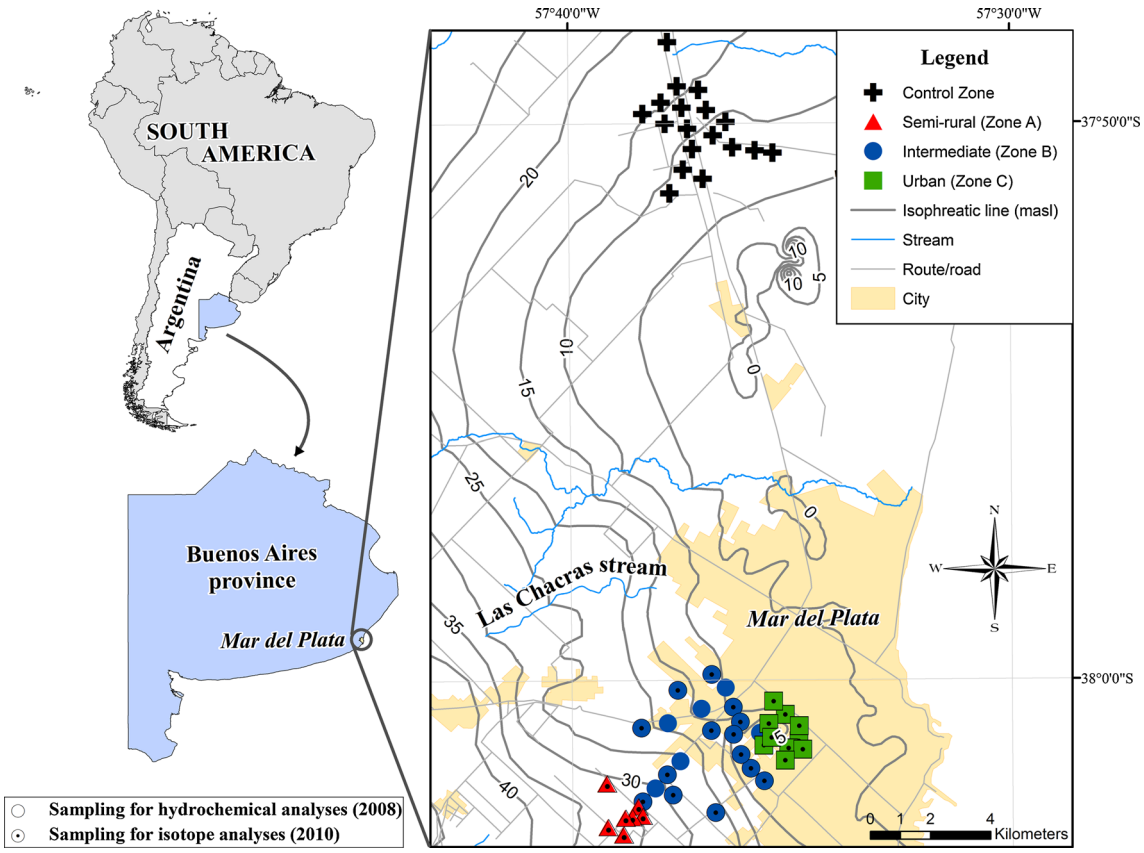

Fig. 1 Location of the four study zones and a piezometric map

piezometric contour map of the area (Fig. 1) shows a natural groundwater flow direction from west to east, which has been modified by aquifer exploitation mostly in the northern zone.

The four study zones were selected with reference to land use conditions to evaluate the relationship between land use and nitrate level and the origin of the nitrate.

Zone A, defined as "semi-rural," corresponds to a sector located to the west, outside the urban space. The area is dominated by private houses with farm and horticulture activities for self use, with the probable application of pesticides at a low scale and manure generation from domestic animals. This region is the main area of vegetable production and uses groundwater for irrigation. There is no sanitary service in Zone A and each house or establishment has its own cesspool for sewage disposal.

Zone B (Intermediate) corresponds to the intermediate area between Zones A and C, and represents an area with agricultural and farm activities and a low population, representing a transition to an urban area with a sanitary service.

Zone C is an urban area placed about 3 km from downtown, with residential use, sport, and commercial and educational activities. There are private houses, small companies, university infrastructure and main sports centers of the city.

All these zones are part of the Las Chacras Creek Catchment, one of the low flow streams which naturally drain the region from southwest to northeast. This stream flows through an agricultural area in the upper basin, entering the city downstream, and is piped underground with its final outfall to the sea. Zone A is located in the upper basin, while Zones B and C are downstream in that order.

The Control Zone is a rural area with sparse anthropogenic activity. The population density is almost zero with land use for occasional cattle grazing.

Materials and methods

Sampling network

The sampling network for hydrochemical analyses consisted of 11 wells in Zone A, 20 wells in Zone B, 10 wells in Zone C and 18 wells in the Control Zone. From these locations a set of 5 wells from Zone A, 14 wells from Zone B and 10 wells from Zone C were selected

for isotope analysis. The nitrate concentrations in the control zone, with an average value of 6.5 mg/L as nitrate were too low for the analytical method used in the study.

Selected wells in Zone A are private wells for domestic use with depths ranging from 34 to 65 m. The wells sampled in Zones B, C and Control Zone corresponds to extraction wells constructed for the public Water Supply and Sanitation Company of Mar del Plata. The wells' depths range from 76 to 106 m for zones B and C and from 93 to 105 m for the Control Zone.

A first groundwater sampling campaign for chemical analysis was carried out in 2008. A new sampling campaign was performed in 2010 to collect samples for isotope analysis and new chemical analysis in selected points. All sampling points were located by GPS for later use in maps and graphics.

Analytical methodology

Chemical analyses were carried out in the Mar del Plata's Water Supply and Sanitation Company Laboratory, after the arrival of the sample at the laboratory. Charge balance error for the analysis was below 5 %. N species were analyzed immediately after sampling. The major ion composition, including sodium, potassium, calcium, magnesium, chloride, sulfate and bicarbonate, and the concentration of minor species like fluoride, total manganese and total iron, was obtained using standardized test methods as described in Table 1. No specific preservation was used for major ion samples, taking into account that the analyses were done in the same sampling day. A 250 ml fraction, acidified with HCl to pH <2, was taken for N species determination. Samples for stable isotopes analysis in water were collected in 50 ml bottles and preserved in a dark container. For nitrogen and sulfate isotope analysis one liter fraction was taken, preserved in a cooler in the field and frozen at −20 °C when arrived to the laboratory. Frozen samples were sent to the analytical laboratory into refrigerated boxes.

Stable isotopes (^{2}H and ^{18}O) were analyzed for using a laser spectroscopy DLT-100 Liquid–Water Isotope Analyzer, Automated Injection, designed by Los Gatos Research, at the Hydrogeochemical and Isotopic Hydrology Laboratory (National University of Mar del Plata). The results are reported in δ (‰), defined as:

$\delta = 1{,}000\ [(R_{sample} - R_{standard})/R_{standard})]$ ‰, where R is the isotopic ratio, R_{sample} and $R_{standard}$ are the isotope ratio ($^{2}H/^{1}H$, $^{18}O/^{16}O$) for the sample and the international reference standard, respectively. The standard is Vienna Standard Mean Ocean Water (VSMOW; Gonfiantini 1978). The analytical uncertainties were ±0.3 and ±2.0 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively.

Table 1 Analytical methods for chemical analyses

Parameter	Test method
pH	SM 4500-pH. Electrometric Test. Instrument: HACH EC10
Conductivity	SM 2510. Instrument: Conductímeter HACH CO150
Total solids	OSN Test method
Hardness	SM 2340 C. EDTA titulometric method
Alkalinity	SM 2320 B. Titulometric method
Sodium and potassium	SM 3500-Na y K B. Flame emission
Calcium	SM 3500-Ca B. EDTA titulometric method
Magnesium	SM 3500-Mg B
Fluoride	SM 4500- F- B y D
Chloride	SM 4500-Cl B Argentometric method
Nitrate	SM 4500- NO3 B. UV screening method
Nitrite	SM 4500- F- B y D
Ammonia	Nessler method
Sulfate	Turbidimetry, SM 4500- E
Total iron	SM 3500 Fe–B
Manganese	Method HACH 8034 y 8149
Silica	Method HACH N° 10047

SM: standard Methods for the examination of water and wastewater (APHA et al. 1998)

Isotopes of nitrate (^{15}N and ^{18}O) and sulfate dissolved species (^{34}S) were analyzed at the Environmental Isotope Laboratory of the University of Waterloo (Canada), using VC 602 and VG 903 mass spectrometers. The analyses are expressed in δ units defined by:

$$\delta^{15}N \text{ or } \delta^{18}O \text{ or } \delta^{34}S = \left[\left(R_{sample} - R_{standard}\right)/R_{standard}\right].1000$$

where R_{sample} and $R_{standard}$ are the $^{15}N/^{14}N$ or $^{18}O/^{16}O$ or $^{34}S/^{32}S$ ratios for the sample and the standard, respectively. The standards for ^{15}N and ^{18}O are atmospheric nitrogen and VSMOW, respectively, and the troilite phase of the Canyon Diablo meteorite for ^{34}S.

Results

Hydrogeochemistry and nitrate concentrations

Data from the Control Zone are from 18 deep wells (between 93 and 105 m deep). Groundwater composition from these wells is sodium bicarbonate water (Fig. 2), with average total dissolved solids (TDS) of 778 mg/L. Nitrate concentrations in this area range from 2.0 to 11.3 mg/L with an average value of 6.7 mg/L. This average value is considered to be the regional background value for the aquifer. The Control Zone includes an important

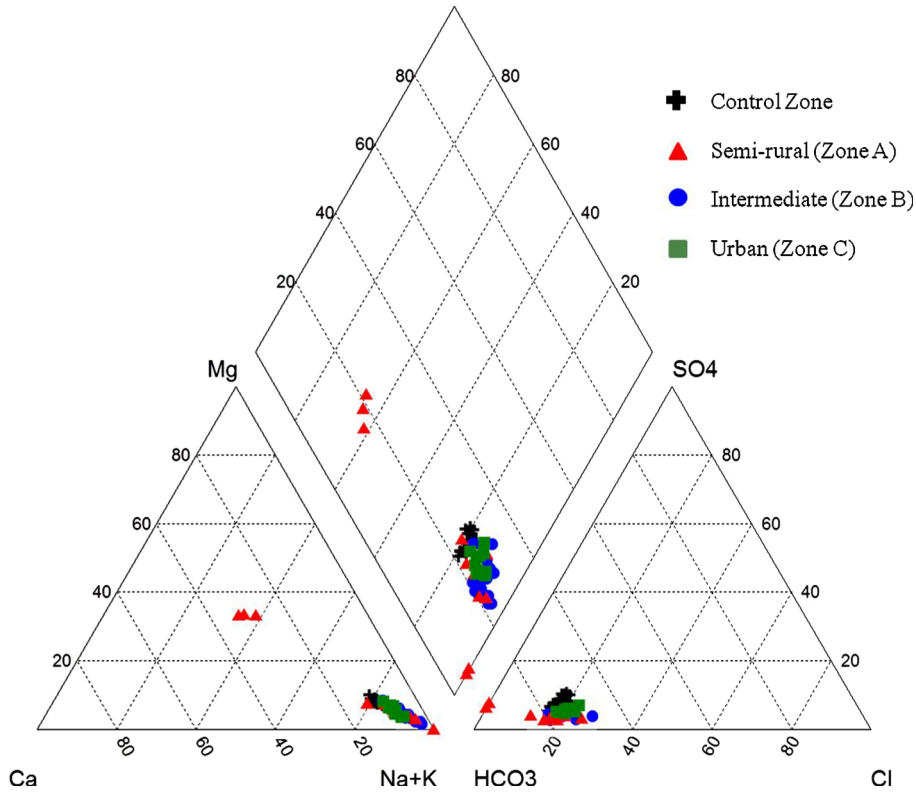

Fig. 2 Piper diagram showing the ionic composition of the groundwater in the four study zones

groundwater exploitation area, as it provides an important source of drinking water to the city.

In Zone A, the semi-rural area, groundwater types vary from calcium bicarbonate to sodium bicarbonate facies (Fig. 2). TDS values are lower than in the other study areas, with a mean value of 579 mg/L. Nitrate concentrations range from 39.2 to 107.1 mg/L with an average value of 72.9 mg/L.

The intermediate Zone B is characterized by sodium bicarbonate water type (Fig. 2), with TDS concentrations from 619 to 876 mg/L with an average value of 757 mg/L. The nitrate concentration range from 16.6 to 73.2 mg/L and the average value is 38.2 mg/L. 5 of the 20 sampled wells in the zone exceed the admissible level of nitrate for drinking water. The nitrate levels in Zone B tend to be lower than those in Zone A.

In Zone C the dominant hydrochemical facies is sodium bicarbonate (Fig. 2), with TDS concentrations from 788 to 1,081 mg/L (average 940 mg/L), which are higher than Zones A and B. Nitrate concentrations range from 48.2 to 100.3 mg/L with an average of 67.3 mg/L. All the nitrate concentrations in the wells specifically selected for this study are above the admissible national drinking water regulation limits, which specify a maximum of 45 mg/L NO_3^- (Código Alimentario Argentino (Argentinian Food Code) 2012). The nitrate values in Zone C are higher than in Zone B and similar to those in Zone A.

Table 2 Average values for the main chemical parameters analyzed in each zone

Zone	Control	Zone A	Zone B	Zone C
pH	7.40	7.42	7.73	7.49
Total solids mg/L	778	579	757	940
Total hardness (en CO_3Ca) mg/L	128	155	64	102
Total alkalinity (en CO_3Ca) mg/L	502	364	454	544
Bicarbonate (mg $CaCO_3$/L)	612	444	554	663
Chloride (Cl^-) mg/L	85	62	88	108
Sulfate (SO_4^{2-}) mg/L	52	18	23	38
Nitrate (NO_3^-) mg/L	6.7	72.9	38.2	67.3
Nitrite (NO_2^-) mg/L	0.01	0.06	0.01	<0.01
Ammonium (NH_4^+) mg/L	0.06	0.06	<0.05	0.09
Fluoride (F^-) mg/L	0.52	0.87	1.27	0.86
Calcium (Ca^{2+}) mg/L	29	30	15	23
Magnesium (Mg^{2+}) mg/L	14	18	7	11
Sodium (Na^+) mg/L	251	174	264	305
Potassium (K^+) mg/L	10	9	8	11
Electrical conductivity (μmhos/cm 20° C)	1,255	992	1,171	1,486
Iron (total) mg/L	0.02	0.10	0.22	0.05
Manganese mg/L	0.04	0.04	0.03	0.03

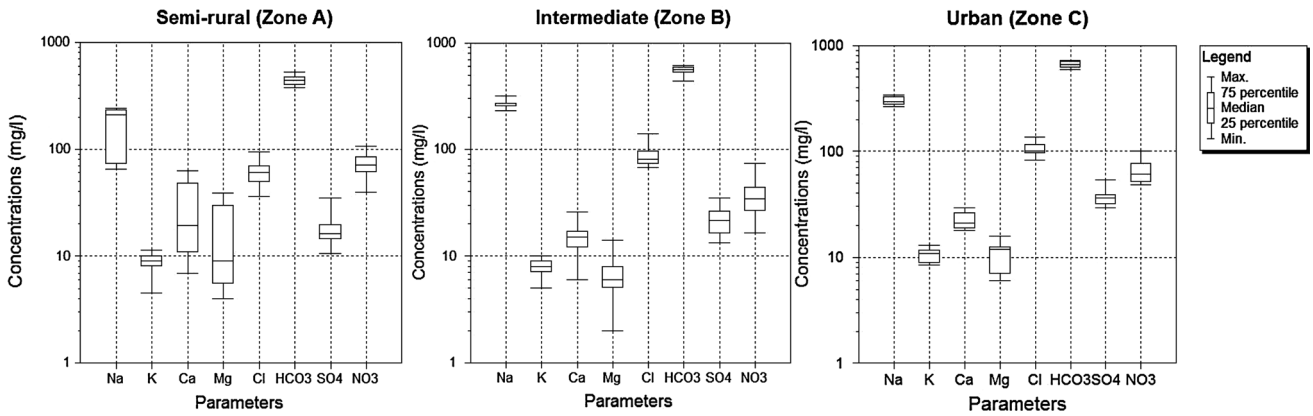

Fig. 3 *Box plots* showing major ion concentrations (mg/L) for A, B and C zones

A synthesis of the average values of the main chemical parameters analyzed for each zone is presented in Table 2. Moreover, a comparison of the major ion concentrations between the three polluted study zones is presented by the box plots in Fig. 3, where the variation in NO_3^- concentrations from recharge to discharge zone is showed.

^{18}O and ^{2}H in water and nitrate and sulfate isotope analyses

The stable isotope compositions, $\delta^{18}O$ and $\delta^{2}H$, in water were determined in five samples from the urban zone and four samples from the intermediate zone. Mean values for the urban well waters are $\delta^{18}O = -5.4$ ‰ and $\delta^{2}H = -29$ ‰, and for the intermediate zone waters $\delta^{18}O = -5.6$ ‰ and $\delta^{2}H = -29$ ‰ (Table 3). These data show a very narrow range, with all the samples grouped around the average values. This range of values corresponds to a deuterium excess "d" around 15 which is typical for groundwater in the study area (Romanelli et al. 2013). The local meteoric water line for Mar del Plata area obtained from precipitation collected in a gage installed at the University of Mar del Plata, for the period 2008–2013, is $\delta^{2}H = 8.52\ \delta^{18}O + 16.8$, which fits very well with groundwater data (Fig. 4).

The $\delta^{15}N$ and $\delta^{18}O$ in nitrate and $\delta^{34}S$ in sulfate results are also shown in Table 3. The data show a range from 7.7 to 13.5 ‰ for $\delta^{15}N$ and from 4 to 7.4 ‰ for $\delta^{18}O$. Assuming that 2/3 of the oxygen could be derived from the water ($\delta^{18}O = -5.5$ ‰) and 1/3 from the atmosphere ($\delta^{18}O = 23.5$ ‰), the $\delta^{18}O$ values for nitrate formed by nitrification should be around +4.3 ‰ in the study area. The field results are slightly higher than the calculated value. Such enrichment has also been observed in other studies (Silva et al. 2002; Fukada et al. 2004). The results for $\delta^{15}N$ and $\delta^{18}O$ are shown in a graph, which also shows

Table 3 Isotope composition: $\delta^{18}O$ and $\delta^{2}H$ in water; $\delta^{15}N$ and $\delta^{18}O$ in nitrate, $\delta^{34}S$ in sulfate

Zone	Sample	H_2O		NO_3		SO_4
		$\delta^{18}O$	$\delta^{2}H$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{34}S$
A	R1	nd	nd	13.17	7.08	13.21
	R2	nd	nd	11.82	6.66	13.39
	R4	nd	nd	9.61	6.92	14.09
	R8	nd	nd	12.81	6.71	13.19
	R11	nd	nd	9.95	7.19	13.95
B	I2	nd	nd	11.84	7.43	11.10
	I3	nd	nd	12.04	6.30	13.13
	I4	nd	nd	7.69	6.90	14.99
	I6	nd	nd	11.46	7.01	12.07
	I7	nd	nd	10.86	4.94	12.48
	I9	nd	nd	7.9	6.20	13.96
	I12	nd	nd	11.6	nd	12.07
	I13	−5.72	−29.8	9.06	nd	12.20
	I14	nd	nd	11.02	6.71	12.69
	I15	−5.59	−27.4	10.98	5.96	13.13
	I16	nd	nd	12	7.10	11.41
	I17	nd	nd	9.31	6.29	13.49
	I18	−5.77	−27.8	10.53	6.65	13.59
	I19	−5.19	−29.5	10.65	7.43	14.31
C	U1	nd	nd	13.52	7.04	12.17
	U2	nd	nd	10.79	4.04	14.59
	U3	−5.43	−28.7	11.99	nd	13.56
	U4	−5.23	−27.7	11.27	4.92	13.54
	U5	−5.7	−28.7	12.54	6.65	13.25
	U6	−5.19	−29	11.79	6.01	14.02
	U7	nd	nd	12.95	6.30	12.12
	U8	nd	nd	13.44	8.96	12.68
	U9	−5.25	−28.3	13.43	6.23	12.91
	U10	nd	nd	13.06	7.40	12.26

nd no data

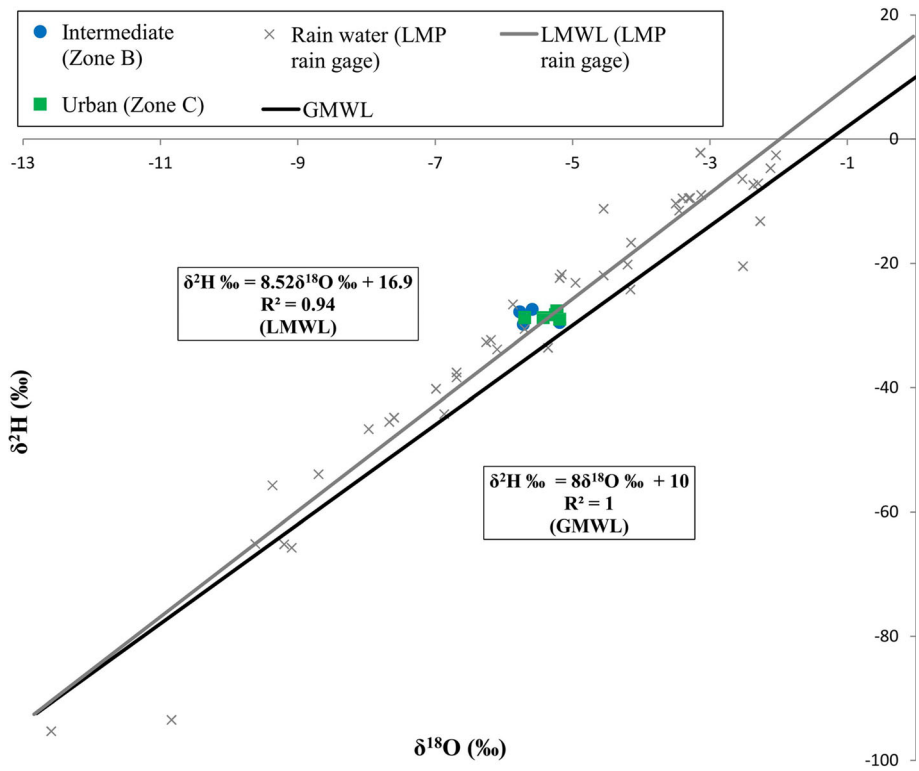

Fig. 4 Plot δ^2H vs. $\delta^{18}O$ showing the Global Meteoric Water Line (GMWL), the Local Meteoric Water Line (LMWL) of Mar del Plata city (data from 2008 to 2013 period), and the groundwater data for B and C zones

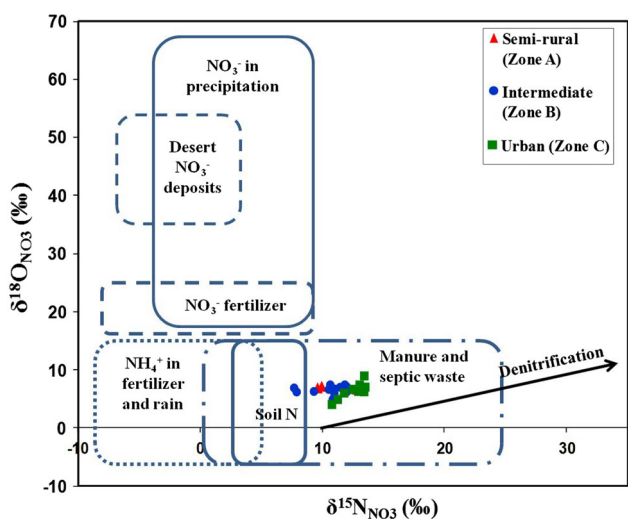

Fig. 5 Graph of $\delta^{18}O_{NO_3}$ vs. $\delta^{15}N_{NO_3}$ for A, B and C zones. It includes the areas of the isotopic composition of various NO_3^- sources (source: Kendall 1998)

ranges of the isotope composition for various NO_3^- sources (Kendall 1998) (Fig. 5). All the samples from the study area fall within the area of the isotope composition for nitrate associated with manure and sewage.

The ^{34}S isotope composition was primarily determined (Table 3) to evaluate the role of denitrification mediated by sulfide minerals as an attenuation mechanism for nitrate in the aquifer. If denitrification is mediated by sulfide oxidation, the sulfate from this reaction will tend to have $\delta^{34}S$ values <3–4 ‰ (Aravena and Robertson 1998). The data show $\delta^{34}S$ values ranging from 11.1 to 14.9 ‰, which correspond to marine and atmospheric sulfur sources (Krouse 1980).

Discussion

An analysis of the geochemical evolution along the groundwater flow system offers a first approximation for evaluating the differences among Zones A, B and C in the study area. On a regional scale, most of the chemical differences in the study area have been explained by Martínez and Bocanegra (2002) as a consequence of the combination of the natural evolution along the groundwater flow system plus the effect of seawater intrusion in the lower part of the urban area.

The chemical data show a hydrogeochemical evolution from calcium bicarbonate waters in the semi-rural zone, which is near the recharge zone, to sodium waters toward the intermediate and urban zones (discharge area) (Fig. 2). The TDS and the major ion, chloride and sodium concentrations increase along the flow system, according to the normal evolution of natural waters (Chebotarev 1955). The concentration of other ionic species (calcium, magnesium,

sulfate) slightly decreases in the intermediate zone and increases again when groundwater flow enters into the urban zone. Nitrate is the only ion that shows a relatively large decrease in the intermediate zone (Fig. 3). The average nitrate concentration in the semi-rural zone is 72.9, 38.2 mg/L in the intermediate zone, and 67.3 mg/L in the more distal urban zone. The background value obtained in the Control Zone is around 6.7 mg/L. It is clear that the semi-rural, intermediate and urban zones evidence the effect of nitrate contamination due to anthropogenic activities.

The ^{18}O and ^{2}H isotope composition of groundwater does not differ among intermediate and urban zones. This is a pattern also observed in the Pampeano Aquifer in southeast Buenos Aires Province (Martínez et al. 2007; Quiroz Londoño et al. 2008). The isotope values in the groundwater correspond to the average value for precipitation, which is the result of a well-mixed system. Groundwater in the three zones has the same isotopic fingerprint, indicating a flow system with a recharge source, rain infiltration and no other recharge sources or mixing of waters. Although the urban zone was partially affected by seawater intrusion (Bocanegra et al. 1993; Martínez and Bocanegra 2002), the isotopic data does not show evidence of mixing with seawater for the selected wells. The Water Supply and Sanitation Company designated the most salinized wells as being out of service and they were not included in the sampling for this study.

Based on the information on land use and potential nitrate sources in each zone, and taking into account the groundwater flow system (Fig. 1), it is possible to postulate that the nitrate dynamic in the study area is controlled by nitrate input in near recharge areas (semi-rural area) and its transport by the groundwater flow system toward the discharge area (urban area). Additional sources along the groundwater flow system are nitrate input from cesspools in the intermediate area and leakage of the sewage distribution network in the urban area.

The nitrate concentration in the semi-rural area ranges from 39.2 to 107.1 mg/L with an average value of 72.9 mg/L. It tends to decrease in the intermediate zone to an average value of 38.2 mg/L, but values over 60 mg/L are also observed in this area. Then, the nitrate concentration in the urban area is higher than in the intermediate zone, ranging from 48.2 to 100.3 mg/L with an average value of 67.3 mg/L. The lower nitrate concentrations in Zone B compared to those in Zone A could be related to the sampling depth of the wells. The wells in the intermediate zone (Zone B) are deeper than those in Zone A. Thus, it is possible that the nitrate contents in the deepest part of the aquifer are relatively lower than those in the shallow part of the aquifer. The high nitrate concentration observed in Zone C could be explained in part by an input of sewage into the urban area. This is supported by a study by Bocanegra et al. (2010), which found a sewage contribution of around 20 % for the water flooding underground parking structures in downtown Mar del Plata city.

The $\delta^{15}N$ and $\delta^{18}O$ data in nitrate provide additional information to evaluate the origin of nitrate and processes that affect nitrate along the groundwater flow system in the study area. The $\delta^{18}O$ data show that the nitrate was formed by nitrification of ammonium in the study area. Concerning the $\delta^{15}N$ pattern, and starting with the semi-rural area near the recharge area, the $\delta^{15}N$ values vary from 9.6 to 13 ‰, which is in the interval of manure and septic waste nitrate and can be attributed to the use of organic fertilizers (manure and guano) in the horticultural land plots of the area and some contributions from cesspools. The isotopic fingerprint of nitrate in the intermediate zone shows a group of samples with $\delta^{15}N$ values similar to those for the nitrate in the semi-rural area, but some of the samples tend to be more depleted in ^{15}N than that in the semi-rural zone. The nitrate in these samples could be related to a relatively major contribution from cesspools. Nitrate from septic systems can be in the range of 8–10 ‰ in $\delta^{15}N$ values (Aravena et al. 1993; Fukada et al. 2004). The transport of dissolved nitrate in groundwater from the semi-rural area is considered to be the main source of nitrate in the intermediate area. This is also supported by chemical data. The average concentration of the conservative ions (chloride, sulfate and sodium) increases while that of nitrate decreases. The increase in major ion concentrations is a consequence of the dissolution of salts during natural groundwater evolution (Martínez and Bocanegra 2002).

The decrease of nitrate contents in groundwater could also be the result of a denitrification process (Korom 1992).

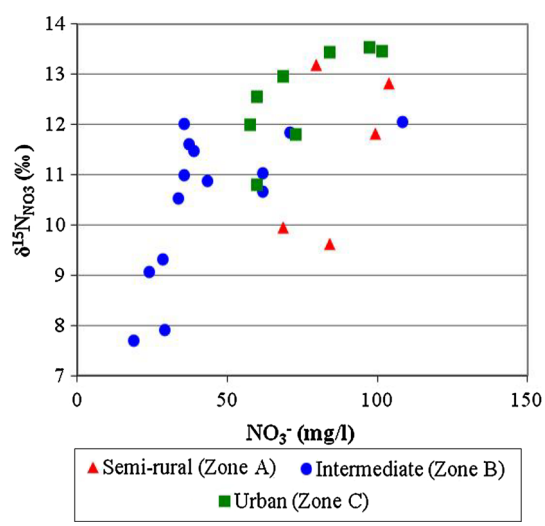

Fig. 6 Graph of $\delta^{15}N_{NO_3}$ vs. NO_3^- for A, B and C zones

During this process, the remaining nitrate becomes more enriched in ^{15}N and ^{15}O as the nitrate concentration decreases (Aravena and Robertson 1998; Fukada et al. 2004). The data reported in the graph $\delta^{18}O$ vs. $\delta^{15}N$ (Fig. 5) show no indication of the occurrence of denitrification in the study area. Furthermore, the general pattern observed in the study shows that $\delta^{15}N$ values become more enriched as the concentration of nitrate increases (Fig. 6), which is opposite to the trend expected for denitrification (Mariotti 1986). The ^{34}S values, between 11 and 14 ‰, are not in the range expected for sulfate associated with sulfide oxidation (Aravena and Robertson 1998), supporting the non-occurrence of nitrate attenuation in the aquifer associated with denitrification. Then, the $\delta^{15}N$ vs. NO_3^- relationship (Fig. 6) and the ^{34}S results are not consistent with a denitrification process, and the nitrate content in the intermediate zone is better explained by transport from the semi-rural area and local input.

In the urban area, the $\delta^{15}N$ values are >11 ‰, associated with nitrate concentrations of more than 50 mg/L. Similar to those in the semi-rural area, the more enriched $\delta^{15}N$ values tend to be associated with higher nitrate concentrations. These patterns indicate that the nitrate in the urban area can be related to manure and sewage origin, the latter being associated with city sewage system leakage. This is supported by Bocanegra et al. (2010), who found that 20 % of the water flooding many underground structures in the city came from sewage network leakage.

Conclusions

Groundwater quality in some areas of the aquifer in the city of Mar del Plata, Argentina, is highly impacted by nitrate contamination with many wells exceeding the drinking level limits of 45 mg/L NO_3^-. In the non-polluted Control Zone, the average nitrate concentration is around 6.7 mg/L; however, values as high as 100 mg/L are not unusual in polluted urban and suburban catchments in the study area.

It is common to have a variety of nitrate sources in agricultural and urban areas. Therefore, this complexity requires the use of hydrogeological, geochemical and isotope tools for evaluating nitrate sources and the behavior of nitrate in groundwater.

This multidisciplinary approach was used to evaluate sources of nitrate in the Las Chacras Creek Catchment, which included the city of Mar del Plata. This study shows that the groundwater in semi-rural, intermediate and urban areas in this watershed is highly impacted by nitrate concentrations that are much higher than the regulation nitrate level for drinking water. The $\delta^{15}N$ values indicate that the sources of nitrate in the semi-rural area are manure and sewage (cesspools). The $\delta^{15}N$ data and the chemical data indicate that the nitrate in the intermediate zone is associated with nitrate from the semi-rural area plus nitrate associated with cesspools. Finally, in the urban area located in the lower part of the groundwater flow system, the $\delta^{15}N$ data and the nitrate concentration pattern tend to indicate that the sources of nitrate are associated with upgradient sources (semi-rural and intermediate zones) and with the leakage of sewage from the public sewer system of the city of Mar del Plata. The isotope data on nitrate show that denitrification does not play a role in the nitrate concentration pattern observed along the groundwater flow system.

The results of this research have significant implications for long-term groundwater management for the aquifer that provides drinking water to the city of Mar del Plata. This study has shown the absence of attenuation processes (such as denitrification) that can reduce nitrate concentration along the groundwater system. Therefore, the strategy to reduce nitrate concentration in the aquifer is to reduce the nitrate load in the upstream semi-rural and intermediate areas. Leakage of the city sewage network should also be minimized.

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