



## Assessment of sources and fate of nitrate in shallow groundwater of an agricultural area by using a multi-tracer approach



Ernesto Pastén-Zapata<sup>a</sup>, Rogelio Ledesma-Ruiz<sup>a</sup>, Thomas Harter<sup>b</sup>, Aldo I. Ramírez<sup>a</sup>, Jürgen Mahlknecht<sup>a,\*</sup>

<sup>a</sup> Centro del Agua para América Latina y el Caribe, Tecnológico de Monterrey, Av. Eugenio Garza Sada Sur No. 2501, C.P. 64849 Monterrey, Nuevo León, Mexico

<sup>b</sup> Department of Land, Air and Water Resources, University of California, C.P. 95616 Davis, CA, USA

### HIGHLIGHTS

- A new multiple tracer approach for improved evaluation of nitrate sources and transformation processes was developed.
- Nitrate  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  isotopic compositions were completed with halide ratios.
- Water isotopes were used to assess groundwater origin and recharge.
- Groundwater chemical processes were evaluated using statistical approaches.
- It is suggested that this approach is a powerful tool with potentially wide applications.

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### ABSTRACT

Nitrate isotopic values are often used as a tool to understand sources of contamination in order to effectively manage groundwater quality. However, recent literature describes that biogeochemical reactions may modify these values. Therefore, data interpretation is difficult and often vague. We provide a discussion on this topic and complement the study using halides as comparative tracers assessing an aquifer underneath a sub-humid to humid region in NE Mexico. Hydrogeological information and stable water isotopes indicate that active groundwater recharge occurs in the 8000 km<sup>2</sup> study area under present-day climatic and hydrologic conditions. Nitrate isotopes and halide ratios indicate a diverse mix of nitrate sources and transformations. Nitrate sources include organic waste and wastewater, synthetic fertilizers and soil processes. Animal manure and sewage from septic tanks were the causes of groundwater nitrate pollution within orchards and vegetable agriculture. Dairy activities within a radius of 1000 m from a sampling point significantly contributed to nitrate pollution. Leachates from septic tanks caused nitrate pollution in residential areas. Soil nitrogen and animal waste were the sources of nitrate in groundwater under shrubland and grassland. Partial denitrification processes helped to attenuate nitrate concentration underneath agricultural lands and grassland, especially during summer months.

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### 1. Introduction

Nitrate ( $\text{NO}_3^-$ ) constitutes a widespread contamination source in shallow groundwater. High concentrations are mainly attributed to agricultural activities beginning in the mid-twentieth century (Foster and Young, 1980). However, atmospheric deposition, discharge from septic tanks and leaking sewers, the spreading of sewage sludge to land and seepage from landfills can all contribute to the pollutant load (Wakida and Lerner, 2005). Groundwater concentrations exceeding an

arbitrary threshold of 3 mg/l may be indicative of contamination of natural groundwater as a result of human activities (Burkart and Kolpin, 1993). Elevated concentrations of nitrate in groundwater represent human and environmental health risks: (i) excessive consumption of nitrate in drinking water has been associated with the risk of methemoglobinemia or 'blue baby syndrome' in humans (Fan and Steinberg, 1996), stomach cancer (Mason, 2002), and nitrate poisoning in animals (Stadler, 2012); (ii) nitrate export into adjacent surface water bodies may induce an increased level of nutrients (eutrophication) affecting adversely biodiversity, mammals, birds, and fish population by producing toxins and reducing oxygen levels (Environmental Agency, EA, 2005). Besides, denitrification processes contribute to the emission of greenhouse gases due to production of  $\text{N}_2\text{O}$  (Haag and Kaupenjohann, 2001).

In Mexico, elevated nitrate concentrations are reported in a number of aquifers that support extensive irrigation and use of fertilizers

\* Corresponding author. Tel.: +52 81 8155 2573.

E-mail address: [jurgen@itesm.mx](mailto:jurgen@itesm.mx) (J. Mahlknecht).

(Pacheco and Cabrera, 1997; Steinich et al., 1998; Downs et al., 1999; Pacheco et al., 2001; Cardona et al., 2004; Horst et al., 2008; Daesslé et al., 2009; Horst et al., 2011; among others). Typically these agricultural lands support also other land uses which might contribute to contamination.

Zona Citrícola (8000 km<sup>2</sup>) is an example of an agricultural area which is characterized by an increase in concentrations of NO<sub>3</sub><sup>-</sup> in a local flow system caused by multiple sources. The area produces 10% of the national citrus production (Agronevoleón, 2008). Instituto del Agua de Nuevo León (IANL) (2007) reported that 25% of 248 sampled wells in the area exceeded the Mexican drinking water standard (10 mg/l NO<sub>3</sub>-N). The use of irrigation and fertilizers on vegetable fields and in citricultural orchards is suspected to be the major source of contamination. However other potential point and non-point sources such as farm activities, landfills leachate, septic tanks, urban wastewater and to a lesser extent, industry, may contribute to increased groundwater nitrate (Dávila-Pórcel et al., 2012). Because groundwater is the major source of potable water in Zona Citrícola and provides base flow to surface water used to supply drinking water to the Monterrey metropolitan area (~4 million inhabitants), the identification of contamination sources is essential for effectively managing groundwater quality.

Stable isotope ratios of nitrogen ( $\delta^{15}\text{N-NO}_3^-$ ) have been widely used for identification of nitrate sources in groundwater under the assumption that nitrate is behaving conservatively in sub-surface environments (Kreitler, 1979; Mariotti et al., 1998; Böhlke and Denver, 1995). However, its ratios may be modified by volatilization, nitrification and denitrification, and thus not be conclusive for the identification of nitrate sources (Clark and Fritz, 1997; Kendall et al., 2007; Aravena and Mayer, 2010). The combined use of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate has allowed evaluating nitrate transformation processes in a groundwater system with microbial denitrification, since not only  $\delta^{15}\text{N}$  but also  $\delta^{18}\text{O}$  values of nitrate increase during denitrification, while reducing nitrate concentration (Böttcher et al., 1990; Wassenaar, 1995). The combination of stable isotopes of nitrate with other tracers can further enhance the ability to delineate nitrate sources and

transformation processes in groundwater (Böhlke and Denver, 1995; Einsiedl and Mayer, 2006; Moore et al., 2006; Wassenaar et al., 2006). One challenging issue is that nitrate isotopes do not distinguish manure from sewage-derived nitrates, since these sources have overlapping signatures (Kendall et al., 2007; Aravena and Mayer, 2010). Other researchers used nitrate isotopes in combination with chloride (Cl)/bromide (Br) ratio, manganese (Mn) and iron (Fe) concentration or boron isotope (<sup>11</sup>B) as a proxy for sources identification (Showers et al., 2008; Koh et al., 2010; Widory et al., 2005; Sacchi et al., 2013).

In this study, nitrate contamination of the shallow aquifer system beneath an agricultural area was investigated using a multi-tracer approach considering water chemistry, stable water and nitrate isotopes, tritium, and halide ratios. The objective was to identify sources and processes controlling nitrate concentration in the shallow aquifer. The aims were: (1) to identify most likely sources of NO<sub>3</sub><sup>-</sup> in sampled wells, (2) to detect the existence of denitrification processes; and (3) to revise and discuss the isotopic ratios of the distinct nitrate sources.

## 2. Study area

### 2.1. General settings

The study area was located in Zona Citrícola, a hilly landscape covering an area of approximately 8000 km<sup>2</sup> within the State of Nuevo León, northeastern Mexico, with elevations decreasing from 430 to 300 m above sea level (masl) towards NE. This area is home of several cities (Linares, Montemorelos, Santiago, Hualahuises and Allende) and a significant rural population spread throughout the region, totaling about 200,000 inhabitants (Instituto Nacional de Estadística y Geografía, INEGI, 2011). To the W it is bordered by mountain ranges up to 2200 masl in elevation that are part of the Sierra Madre Oriental (SMO), a Mesozoic–Cenozoic sedimentary belt of carbonate, siliclastic and evaporative rocks (Fig. 1).

The area comprises a warm, sub-humid to humid climate with an annual mean temperature of 22 °C and extreme minimum and

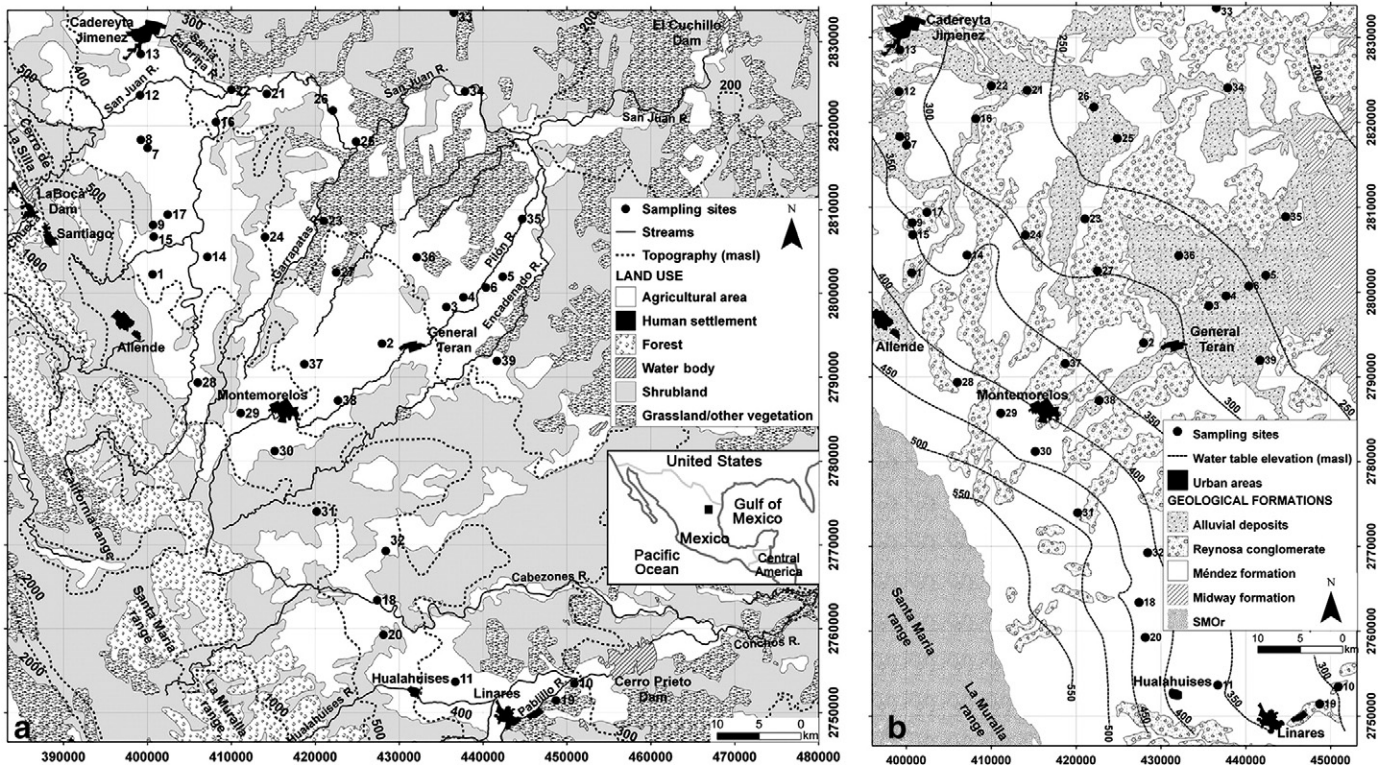


Fig. 1. Map of Zona Citrícola with major cities and sampling points for reference: (a) land use and vegetation, topography and surface waters; (b) surficial geology and hydraulic head.



maximum values of  $-10$  and  $+45^{\circ}\text{C}$  in winter (December to February) and summer (June to August), respectively. Precipitation is produced by warm air masses originating from the Gulf of Mexico, convectively raised by the SMO just to the west of the study area, thus generating higher precipitations at its flanks (1100 mm/year) and reduced precipitation within the study area, ranging from 900 to 600 mm/year. The most rainfall is concentrated between the months of May to October (77%), with the driest months being November, December, February and March (~3% each) (García, 1998; Comisión Nacional del Agua, CONAGUA, 2002a, 2002b).

Natural vegetation within the region varies accordingly with rainfall spatial distribution. Forests of *pinaceae* and *fagaceae* families mainly cover the southwestern portion of the region where precipitation is higher. Towards the foothills and plains, *cupressaceae* shrublands prevail (Universidad Autónoma Agraria "Antonio Narro", UAAAN, 2007). Agricultural zones have been developed over the plain dominating the production of citrus fruits. Other crops grown in the area are grass, sorghum, wheat, avocado, corn, and walnuts (Fidicritus, 2007) (Fig. 1a).

Surface waters in the region are perennial and flow in a SW-NE to W-E direction to the Gulf of Mexico (Fig. 1a). In the northern and central part, the main waterway is the San Juan river which originates as La Chueca creek in the SMO at an altitude of ~2000 masl, has as tributary streams the Santa Catarina, Garrapatas and Pilon rivers, and ends up in the El Cuchillo dam flowing ultimately to the Rio Grande/Bravo river (Comisión Nacional del Agua, CONAGUA, 2002a). On the southern portion of the study area, the El Pablillo, Cabezones and Hualahuises rivers merge and flow via the Cerro Prieto dam to the San Fernando river (Comisión Nacional del Agua, CONAGUA, 2002b) (Fig. 1a).

The Cerro Prieto, El Cuchillo and La Boca dams are the main surface water reservoirs used for local agriculture and for drinking water supply in Monterrey's metropolitan area 20 km north of the study area. Monterrey is the third most populated metropolis of Mexico (~4.2 million inhabitants) and the most important urbanized area in northern Mexico (Instituto Nacional de Estadística y Geografía, INEGI, 2010).

## 2.2. Geology and hydrogeology

The region is bound by two geological provinces: SMO and Coastal Plain of the Gulf of Mexico (CPGM), ranging in age from Upper Jurassic to Quaternary. This study area is within the CPGM province. The three identified formations in the study area, from oldest to youngest, are: (a) Méndez Formation, sequences of shale, calcareous shale and stratified calcareous marl, assigned to Campanian to Maastrichtian with a thickness of 1500 to 2800 m (Padilla y Sánchez, 1982; Dávila-Pórcel et al., 2012), with low permeability, increasing notably in zones where fractures and faults are present (Comisión Nacional del Agua, CONAGUA, 2002a); (b) Reynosa conglomerate formation, a sandy Tertiary matrix consolidated by caliche with a maximum thickness of 60 m, representing isolated plateaus and hills overlying the Late Cretaceous formations and owing a mainly interstitial permeability (Comisión Nacional del Agua, CONAGUA, 2002a); and (c) Alluvium formation, which consists of fluvial terraces and lacustrine sediments from Tertiary to Quaternary age with a variable thickness of up to 25 m (Padilla y Sánchez, 1982), from mountain canyons of the SMO (De Cserna, 1956; De León-Gómez, 1993; Ruiz and Werner, 1997; Padilla y Sánchez, 1982; Dávila-Pórcel et al., 2012), and a medium to high permeability (Comisión Nacional del Agua, CONAGUA, 2002a) (Fig. 1b).

The aquifer system is shallow and unconfined and consists of two hydrological layers: (a) a highly permeable and porous aquifer in the Alluvium-Conglomerate formation, and (b) a fractured and weathered aquifer in the Méndez formation. The main recharge mechanisms in the study area are rainwater infiltration through the valleys and plateaus, infiltration along rivers and streams, and infiltration of excess

irrigation in agricultural plots. The shallow aquifer system is highly vulnerable to contamination due to local infiltration (Instituto del Agua de Nuevo León, IANL, 2007). Hydraulic conductivity, from pumping tests in the southern study area varies from  $2.28 \times 10^{-6}$  to  $3.4 \times 10^{-4}$  m/s (De la Garza-González, 2000; Dávila-Pórcel, 2011; Dávila-Pórcel et al., 2012).

Depth to groundwater varies from 5 to 25 m, with shallowest levels located in the surroundings of the Cerro Prieto dam, and deepest levels in isolated areas to the SE of Allende, E of General Teran and NW of Hualahuises. The water table elevation varies between 200 and 550 masl with highest values in the SW portion of the study area near the foothills of SMO, showing a SW-NE groundwater direction in the central and northern portion and W-E direction in the southern portion of the study area (Fig. 1b).

Wastewater from urban zones and industrial areas that is not treated by wastewater treatment plants is discharged into rivers that, contaminating both, surface water and groundwater resources. Other contamination sources within the study area are: municipal wastes that are land applied, livestock farms lacking good sanitation practices, industrial raw materials stored in leaking surface storage impoundments, and septic tank and latrine leach fields in rural zones of the study area (Lizárraga-Mendiola et al., 2006; Dávila-Pórcel et al., 2012).

## 3. Materials and methods

### 3.1. Previous studies

An earlier investigation of 52 study area wells reported that  $\text{NO}_3\text{-N}$  in groundwater varies between 0.2 and 36.1 mg/l (average = 9.0 mg/l), with 15 wells (29%) exceeding the drinking water standard (10 mg/l  $\text{NO}_3\text{-N}$ ) (Antares, 1997). Unpublished records from state water authority for 2005 indicate that  $\text{NO}_3\text{-N}$  concentrations in groundwater range from 0.2 to 45 mg/l (average = 6.9 mg/l), with 31 samples (20%) above the drinking water standard. Another groundwater quality study from 2006 revealed that  $\text{NO}_3\text{-N}$  concentration range from 0.0 to 30.6 mg/l (average 8.2 mg/l), with 6 wells (19%) exceeding the water drinking standard (Instituto del Agua de Nuevo León, IANL, 2007).

Monthly analyses of a one-year rain water study 20 km NW from this study area yielded mean values of 1.2 mg/l for  $\text{Na}^+$ , 0.8 mg/l for  $\text{NH}_4^+$ , 0.7 mg/l for  $\text{K}^+$ , 4.9 mg/l for  $\text{Ca}^{2+}$ , 0.7 for  $\text{Mg}^{2+}$ , 1.8 mg/l for  $\text{Cl}^-$ , 1.6 mg/l for  $\text{NO}_3^-$ , and 3.4 mg/l  $\text{SO}_4^{2-}$  (Ramírez-Lara et al., 2010). It is estimated that the combined input of precipitation-derived  $\text{NO}_3^-$  and  $\text{NH}_4^+$  yields a final  $\text{NO}_3^-$  concentration in groundwater (after nitrification of  $\text{NH}_4^+$ ) < 3 mg/l.

Zona Citricola's agriculture applies chemical and manure fertilizers to 90% of its area to improve plant growth. Most commonly applied products include Urea,  $\text{CO}(\text{NH}_2)_2$ , applied in 57% of orchards, ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$  (48%), manure (28%), and ammonium nitrate,  $\text{NH}_4\text{NO}_3$  (21%) (Agronuevoleón, 2008). Detailed application rates are not documented.

### 3.2. Sampling and analytical procedure

Initially, seventeen (17) wells were sampled for chemical and isotopic analyses in December 2009. The sampling campaign was repeated in June 2010 on the same 17 wells and on an additional 22 wells (Fig. 1a,b). All 39 wells were equipped with pre-installed pumps. Temperature, pH, electrical conductivity and dissolved oxygen were measured in the field using measurement meters (Thermo, Orion). Alkalinity was determined in the field by volumetric titration (0.02 N  $\text{H}_2\text{SO}_4$ ) to pH 4.3 of filtered water samples. At each sampling site, two pre-rinsed low density polyethylene bottles were filled with filtered (0.45  $\mu\text{m}$ ) sample water for 250-ml bottle for cations and one 1-liter bottle for  $^{15}\text{N}$ , respectively. The samples were acidified with HCl to pH < 2. Additionally, four pre-rinsed low density polyethylene bottles were filled with untreated water as follows: one 500-ml bottle for

tritium, one 250-ml bottle for deuterium and oxygen-18, one 250-ml bottle for anions, and one 250 ml bottle as blank sample. Bottles were filled with sample water avoiding bubbles and stored at a constant temperature of 4 °C.

Dissolved cations and anions were determined in Activation Laboratories Ltd., Ancaster, Ontario, by inductive-coupled plasma mass spectrometry (ICP-MS) and ion chromatography, respectively. Duplicates of selected samples were analyzed using inductive-coupled plasma optical emission spectrometry (ICP-OES) and ion chromatography.

Deuterium and  $^{18}\text{O}$ ,  $^3\text{H}$  and  $^{15}\text{N}$  were analyzed at the Environmental Isotope Laboratory (EIL) of University of Waterloo at Ontario, Canada, by isotope-ratio mass spectrometry. The results of  $^2\text{H}$  or  $^{18}\text{O}$  analyses were reported as  $\delta$ -values with respect to Vienna Standard Mean Ocean Water (VSMOW). Tritium analysis was performed by scintillation counting (enriched  $^3\text{H}$ ) and reported as Tritium Unit (T.U.). Nitrogen-15 results are reported as  $\delta^{15}\text{N}$  with respect to atmospheric  $\text{N}_2$  (AIR).

### 3.3. Statistical treatment

A correlation matrix was established to evaluate bivariate relationships. The degree of correlation was measured with the Spearman rank correlation coefficient (Siegel, 1956). Spearman is usually used when variables are not normal and linear distributed. In this case, for each of the variables X and Y separately, the observations are sorted into ascending order and replaced by their ranks. The correlation coefficients and level of significance (p-value) were inspected to evaluate the level of significance.

Nonparametric tests (Mann–Whitney and Kruskal–Wallis) were used to evaluate chemical and isotopic datasets, by comparing the means of two independent samples (subgroups). These tests are used because several datasets are not following a normal distribution. The null hypothesis stated that the two or more samples taken from a single population would have no consistent differences between the two or more sets of ranking. When the calculated p-value is less than 0.05, two groups are significantly different.

Hierarchical cluster analysis (HCA) was applied for classification using Ward's linkage rule which iteratively linked nearby points (samples) through a similarity matrix, and performed an ANOVA to evaluate the distance between clusters (Ward, 1963). The squared Euclidian distance was selected as the similarity measurement. All variables were first standardized (z-scores). All statistical calculations were performed using SPSS 20.0 (IBM, 2011).

## 4. Results and discussion

### 4.1. Groundwater origin and recharge

Stable water isotopes may provide a fingerprint of the origin of groundwater and an indication of recharge processes (Clark and Fritz, 1997). The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values vary from  $-24.5$  to  $-48.8\%$  and from  $-7.3$  to  $-3.2\%$ , respectively (Table 2). Fig. 2 compares groundwater with global (Rozanski et al., 1993) and a regional, Mexican (Cortés et al., 1997; Wassenaar et al., 2009) meteoric water lines (GMWL and RMWL, respectively). Groundwater samples with lower  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values (group A in Fig. 2) plotted closer to RMWL. These samples were collected from the NW portion of the study area (Cadereyta Jimenez–Allende–Montemorelos). Groundwater with higher  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values (group B) were obtained from the W and S part of the study area. The similar signature of samples from higher and lower altitude shows that contributions from upper areas are significant. Also, most samples plot below meteoric lines indicating evaporational effects.

A direct indicator of migration of contaminants is groundwater age. According to Table 2, tritium values in groundwater ranged from 1.1 to 2.7 TU (average  $1.9 \pm 0.4$  TU) indicating the presence of post-1960

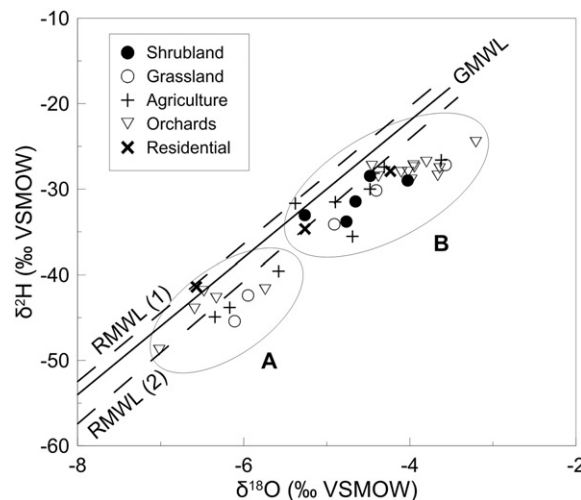


Fig. 2. Relationship between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  with respect to Global Meteoric Water Line (GMWL; Rozanski et al., 1993) and Regional Meteoric Water Line (RMWL) according to Cortés et al. (1997) and Wassenaar et al. (2009).

groundwater and a relatively rapid and homogenous groundwater recharge throughout the area. This confirms that solutes are carried from the root zone to groundwater under present-day climatic and hydrologic conditions.

The shallow aquifer is considered to be a two-layer aquifer system with local recharge: (a) piston flow conditions in alluvial and conglomerate formations, and (b) dual porosity conditions in the fractured and weathered Mendez formation. A rough calculation of groundwater recharge rate via the chloride mass balance method (Wood, 1999; Mahlkecht et al., 2004) results in recharge estimates between 200 and 360 mm/year. This estimate is based on precipitation (ranging from 600 to 1100 mm/year),  $\text{Cl}^-$  concentration in rainwater (1.8 mg/l; according to Ramírez-Lara et al., 2010), and  $\text{Cl}^-$  concentration in groundwater under recharge conditions (5.5 mg/l). The recharge rate is consistent with other studies performed in the Linares area, suggesting that ~18 to 35% of annual precipitation is converted to recharge (Dávila-Pórcel, 2011).

### 4.2. Groundwater geochemistry

Carbonate-rich marine sediments such as limestone and dolomite, as well as sulfate containing sediments such as gypsum and anhydrite are major constituents of Sierra Madre Oriental. Mendez formation is the result of a series of deposition of carbonate-rich lites and marls, occasionally intercalated with sandstones and argillaceous limestones. Furthermore alluvial deposits developed caliche (calcrete) nodules (Mahlkecht et al., 2013). As expected from the carbonate-rich substrate, groundwater is dominated by a  $\text{Ca-HCO}_3$  to  $\text{Ca-SO}_4$ -chemistry (Table 1), with moderate to high EC values ranging from 515 to 2641  $\mu\text{S}/\text{cm}$ , temperature values between 20 and 32 °C (average  $26.5 \pm 0.7$ ), and neutral to moderately alkaline pHs from 6.8 to 8.5 (average  $7.5 \pm 0.1$ ). According to a Mann–Whitney U-test, there was no significant difference ( $p = 0.05$ ) in dissolved oxygen (DO), electrical conductance (EC),  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , total dissolved solids (TDS) and isotope values from the 17 sites with two consecutive samples (December 2009 and June 2010). On the other hand, groundwater temperature is significantly lower in the winter (23.9 °C) than in summer (26.9 °C) samples, while  $\text{Na}^+$  and  $\text{HCO}_3^-$  concentrations experience the opposite: an average decrease from 68.4 to 42.9 and from 406.5 to 352.2 mg/l, respectively, indicating a higher weathering rate in winter, associated with the rainfall season, than in the dry summer.

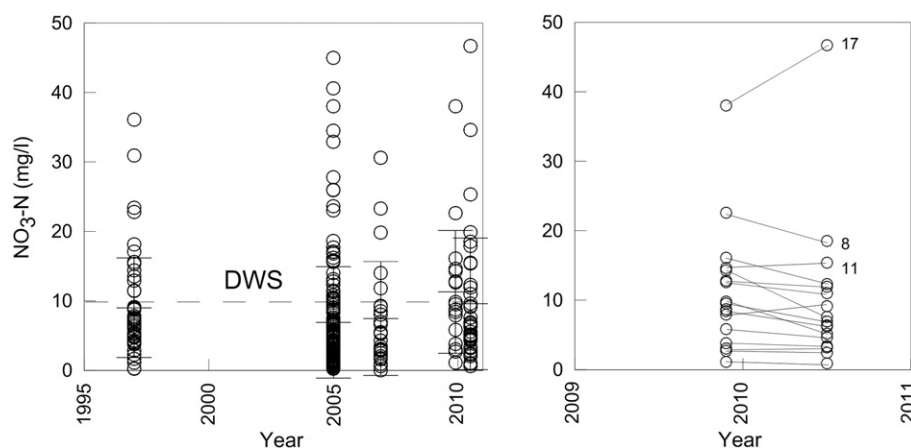
**Table 1**

Hydrochemical results from field campaign from June 2010, including measured field parameters, major dissolved constituents and hydrochemical facies.

Sample no.	Geology	pH (—)	T (°C)	O <sub>2</sub> (mg/l)	E.C. (μS/cm)	Cl <sup>-</sup> (mg/l)	HCO <sub>3</sub> <sup>-</sup> (mg/l)	SO <sub>4</sub> <sup>2-</sup> (mg/l)	NO <sub>3</sub> <sup>-</sup> (mg/l)	Na <sup>+</sup> (mg/l)	K <sup>+</sup> (mg/l)	Ca <sup>2+</sup> (mg/l)	Mg <sup>2+</sup> (mg/l)	Hydrochemical facies
1	Reynosa conglomerate	6.8	25.9	0.5	1182	22.8	566	239	7.6	34.6	0.58	215.0	28.4	Ca-HCO3
2	Reynosa conglomerate	7.4	26.3	3.8	1418	41.5	420	485	9.1	52.1	0.67	234.6	29.8	Ca-SO4
3	Alluvial deposits	7.0	27.6	1.6	1760	82.4	416	566	6.2	145.2	0.87	254.1	42.2	Ca-SO4
4	Alluvial deposits	7.1	28.8	1.8	2534	175.0	320	902	11.9	224.7	1.15	302.6	49.6	Ca-SO4
5	Alluvial deposits	7.0	25.1	2.5	1853	30.2	300	894	3.2	55.3	1.64	265.0	60.2	Ca-SO4
6	Alluvial deposits	7.0	24.6	2.6	1444	28.2	308	611	2.4	32.2	1.18	275.0	53.7	Ca-SO4
7	Alluvial deposits	7.1	26.2	2.2	798	14.1	306	58	11.0	50.8	0.41	104.6	5.6	Ca-HCO3
8	Alluvial deposits	7.2	27.1	0.4	1060	27.2	402	138	18.5	51.1	0.53	157.5	12.7	Ca-HCO3
9	Reynosa conglomerate	7.0	31.0	0.5	732	7.2	462	33	6.9	15.4	0.45	175.0	5.9	Ca-HCO3
10	Reynosa conglomerate	7.1	27.4	1.7	857	18.3	288	260	0.9	18.3	1.04	206.2	10.1	Ca-SO4
11	Mendez formation	7.0	27.8	2.0	991	43.0	270	100	15.4	24.2	0.45	145.8	5.7	Ca-HCO3
12	Alluvial deposits	6.9	27.6	2.1	949	24.8	324	103	4.6	24.2	0.66	153.4	10.4	Ca-HCO3
13	Alluvial deposits	7.1	28.9	1.7	1662	65.8	534	326	5.1	160	1.16	220.2	31.1	Ca-HCO3
14	Mendez formation	7.0	26.6	1.2	828	19.2	426	30	12.3	24.4	0.33	167.2	6.5	Ca-HCO3
15	Mendez formation	7.0	27.4	1.4	668	7.2	424	41	6.4	10.4	0.20	179.6	5.1	Ca-HCO3
16	Alluvial deposits	7.7	25.6	1.3	727	63.5	256	47	3.4	12.3	0.47	143.9	6.3	Ca-HCO3
17	Reynosa conglomerate	6.8	26.7	0.7	1214	42.2	358	90	46.7	23.1	0.47	170.0	12.2	Ca-HCO3
18	Mendez formation	8.0	27.6	1.5	831	11.2	420	61	6.6	10.6	0.49	155.6	6.7	Ca-HCO3
19	Reynosa conglomerate	7.2	27.1	1.9	785	27.3	224	235	2.1	22.3	1.13	185.3	8.7	Ca-SO4
20	Mendez formation	7.2	27.1	1.6	872	32.9	310	53	9.6	19.8	0.54	124.8	9.7	Ca-HCO3
21	Alluvial deposits	7.6	24.7	1.5	515	18.0	198	51	2.8	6.1	0.29	98.7	5.6	Ca-HCO3
22	Alluvial deposits	7.1	29.9	1.6	1666	123.0	206	350	15.5	26.4	1.34	191.0	21.5	Ca-SO4
23	Mendez formation	7.2	32.0	1.8	1644	240.0	316	111	17.9	58.2	1.98	188.3	29.9	Ca-Mixed
24	Reynosa conglomerate	7.4	31.8	2.0	1085	36.4	498	137	19.9	38.6	0.50	208.7	19.4	Ca-HCO3
25	Alluvial deposits	7.3	29.3	1.7	1055	70.6	330	175	4.3	65.7	1.04	151.3	37.1	Ca-Mixed
26	Alluvial deposits	7.5	28.1	1.6	1085	72.9	392	195	5.5	62.6	1.94	182.4	33.8	Ca-HCO3
27	Reynosa conglomerate	7.4	27.5	1.5	1234	107.0	404	152	15.4	32.6	1.39	186.9	13.2	Ca-HCO3
28	Mendez formation	7.3	25.7	1.7	650	5.5	320	15	5.0	4.7	0.46	123.6	2.7	Ca-HCO3
29	Mendez formation	7.7	30.7	1.7	763	11.3	190	119	4.5	9.7	0.27	118.3	7.3	Ca-HCO3
30	Mendez formation	7.9	28.0	1.4	826	18.1	336	81	6.8	8.6	0.15	150.0	6.7	Ca-HCO3
31	Mendez formation	8.0	28.0	1.1	762	13.5	364	31	4.8	9.4	0.29	143.6	5.3	Ca-HCO3
32	Mendez formation	8.0	30.0	1.5	751	15.5	390	36	4.5	13.1	0.46	158.0	4.7	Ca-HCO3
33	Mendez formation	7.5	30.2	1.2	2067	203.0	580	199	34.6	53.4	0.83	310.6	48.1	Ca-Mixed
34	Alluvial deposits	7.8	29.6	1.2	1107	92.4	330	164	2.2	62.7	0.68	201.7	12.6	Ca-Mixed
35	Alluvial deposits	7.8	29.1	1.2	1016	27.6	258	362	0.6	21.5	0.45	223.5	16.8	Ca-SO4
36	Alluvial deposits	7.1	28.1	1.2	2628	294.0	360	468	25.3	87.5	1.68	293.2	46.6	Ca-Mixed
37	Reynosa conglomerate	8.2	24.3	1.3	860	12.6	250	168	3.3	8.6	0.38	163.8	5.2	Ca-HCO3
38	Alluvial deposits	8.5	23.5	1.5	892	18.6	260	210	1.1	16.3	0.72	173.9	14.2	Ca-Mixed
39	Alluvial deposits	8.0	25.6	1.6	1186	80.6	420	153	9.2	74.8	1.26	207.8	16.3	Ca-HCO3

The NO<sub>3</sub><sup>-</sup> content was above the threshold value for anthropogenic influence (3 mg/l) in 82% of the wells and above the drinking water standard (10 mg/l, Secretaría de Salud, SSA, 1994) in 34% of the cases, with a maximum value of 46.7 mg/l. Chloride concentrations ranged from 5 to 294 mg/l with an average of 56 mg/l. The study also revealed high SO<sub>4</sub><sup>2-</sup> levels, with a maximum of 934 mg/l, an average of 240 mg/l, and 18% of the samples not complying with the 400 mg/l limit for potable

water. As shown in Fig. 3, the nitrate values in groundwater did not vary significantly between the sample campaigns in 1997, 2005 and 2006. Sample concentrations in the winter of 2009 and the summer of 2010 are, however, higher than those in previous years. Dávila-Pórcel et al. (2012) attributed the increased contamination to incidental or induced infiltration of sewage water, wastewater treatment effluent, leachate from cattle farm wastes and municipal landfills, leakage from sanitary



**Fig. 3.** Historical development of nitrate in groundwater of Zona Citricola. The left-hand side shows the nitrate values (circles) from sampling campaigns between 1995 and 2010. The right-hand side demonstrates the evolution of nitrate values from wells sampled in the last two campaigns.



sewers, septic deposits and surface contamination due to agricultural customs and practices.

A Spearman rank correlation analysis was applied to describe the association between pairs of hydrochemical parameters and to elucidate possible chemical processes. Strong correlation was found between  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  ( $r^2 = 0.8$ ,  $p = 0.00$ ),  $\text{Mg}^{2+}$  ( $r^2 = 0.9$ ,  $p = 0.00$ ),  $\text{Na}^+$  ( $r^2 = 0.7$ ,  $p = 0.00$ ),  $\text{K}^+$  ( $r^2 = 0.7$ ,  $p = 0.00$ ) cations and  $\text{Cl}^-$  ( $r^2 = 0.5$ ,  $p = 0.00$ ) anion, indicating that these species may be derived from evaporate dissolution (e.g. halite and sylvite). It is noteworthy that  $\text{SO}_4^{2-}$  is also positively correlated with DO ( $r^2 = 0.4$ ) at a p-level of 0.06, which suggests that oxidation of sulfides is not a relevant source. Nitrate is moderately associated with  $\text{Cl}^-$  ( $r^2 = 0.5$ ,  $p = 0.00$ ) and  $\text{HCO}_3^-$  ( $r^2 = 0.4$ ,  $p = 0.08$ ).

The highest  $\text{NO}_3^-$  levels were found in wells between Cadereyta Jimenez and Allende on the NW border of the study area, as well as between Hualahuises and Linares on the S portion, while the lowest levels are found in General Teran and east from Linares. A Mann-Whitney *U*-test demonstrates that livestock activities within a 1000 meter radius significantly contribute to the increased nitrate concentrations ( $p$ -value = 0.01), as shown in Fig. 4.

A factor analysis has been performed to confirm factors controlling groundwater contamination. The principle associations between variables are: gypsum dissolution represented by the association of  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  causing sulfate contamination; halite and sylvite dissolution represented by  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{K}^-$ ; organic waste or wastewater represented by  $\text{NO}_3^-$  and  $\text{HCO}_3^-$ . Silicate weathering and clay formation are represented by the association of  $\text{HCO}_3^-$  and  $\text{SiO}_2$ . While these analyses are useful and efficient, other processes may be present.

#### 4.3. Nitrate sources and transformation processes using nitrate isotopes

The isotopic composition of groundwater  $\text{NO}_3^-$  may be used for identification of major sources and behavior, since  $\text{NO}_3^-$  from different sources has characteristic  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  values. In addition isotopic signatures may further change through certain processes during subsurface transport (Clark and Fritz, 1997; Kendall, 1998; Kendall and Aravena, 2000; Kendall et al., 2007). Measured  $\delta^{15}\text{N}$  varied from +6.0‰ to +18.5‰, with an average value of  $+11.3 \pm 2.9\%$  ( $n = 54$ ) (Table 2). Values are partly within the range reported for soil organic N (+3 to +8‰; Heaton, 1986) and manure/sewage (+10 to +20‰; Kreitler, 1975), but they are generally higher than the range reported for synthetic (−4 to +4‰; Vitòria et al., 2004) and mineralized fertilizers (−7.6 to +3.6‰; Aravena and Mayer, 2010).

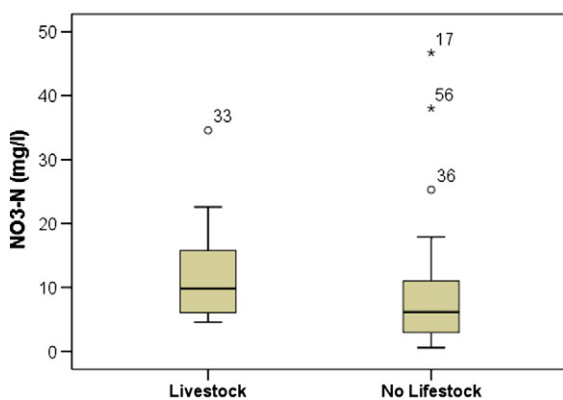


Fig. 4. Boxplot of the sampled groups with and without livestock activities within a 1000 meter radius. The central dark line across each box indicates the median nitrate concentrations, the bottom and top of the box indicate the 25th and 75th percentile, the whiskers indicate approximately 95th percentile, while points indicate outliers and the asterisks indicate extreme outliers.

Natural soil N is a plausible source only for a few samples inside this pool which have low  $\text{NO}_3^-$  concentrations. For higher concentrations, ammonia fertilizers may have become a plausible enriched in  $^{15}\text{N}$  due to ammonia volatilization and explain part of the higher  $\delta^{15}\text{N}$  values. Kreitler (1979) observed that this process may cause an enrichment of up to +6‰ in calcareous terrains.

The hypothesis is that most of elevated nitrate values are derived from animal and domestic waste as well as ammonia fertilizers. This is in principle congruent with the predominant use of urea, ammonium sulfate and manure in agriculture. Grouping land uses/land covers shows that shrubland from recharge area and grassland from the plain have the lowest  $\text{NO}_3^-$  concentration (4.9 and 2.7 mg/l, respectively) with lowest  $\delta^{15}\text{N}$  values (9.4 and 10.4‰, respectively), while vegetable agriculture and orchards consistently show higher and highly variable  $\text{NO}_3^-$  contents (11.0 and 11.9 mg/l, respectively), and the highest  $\delta^{15}\text{N}$  values (12.4 and 11.4‰, respectively). Residential plots are in-between these two groups (10.3 mg/l and 10.4‰, respectively).

The  $\delta^{18}\text{O}_{\text{NO}_3}$  values in the study area varied from +2.6‰ to +12.0‰, with an average value of  $+6.8\% \pm 2.3\%$  ( $n = 52$ ) (Table 2). The conversion of ammonium and manure to nitrate includes the incorporation of two oxygen molecules coming from water and one coming from dissolved oxygen (Anderson and Hooper, 1983). Our calculations show that values of  $\delta^{18}\text{O}_{\text{NO}_3}$  derived from nitrification of  $\text{NH}_4$  of fertilizers and manure ranged between +3.0 and +5.7‰, using groundwater  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  minimum (−7.0‰) and maximum (−3.2‰) values and +23.5‰ for atmospheric oxygen  $\delta^{18}\text{O}_{\text{O}_2}$  (Aravena and Mayer, 2010). Values below +5.7‰ are consistent with nitrification of  $\text{NH}_4$  from manure, fertilizer or septic systems and mineralization of organic N. This range is consistent with groundwater samples collected from shrubland (+2.6 to +6.5‰) and residential areas (+0.4 to +6.6‰) (Table 2). The expected  $\delta^{18}\text{O}_{\text{NO}_3}$  value for commercial fertilizers other than ammonium sulfate was estimated to be in the order of +19.5‰. Values above +5.7‰ were observed mostly in samples from vegetable agriculture, orchards, where these values likely represent a commercial fertilizer source, and in grassland, where the high  $\delta^{18}\text{O}_{\text{NO}_3}$  likely represents rainwater (atmospheric source).

Isotopic values of dissolved  $\text{NO}_3^-$  in groundwater are plotted in Fig. 5a together with those of the main  $\text{NO}_3^-$  sources in the study area. The  $\delta^{15}\text{N}$  values of elevated nitrate values fit well in the manure/sewage range. Samples with elevated  $\text{NO}_3^-$  values show also increased  $\text{Cl}^-$  concentration as expected from manure application and sewage from septic tanks. In the case of samples with  $\delta^{15}\text{N}$  in the range of manure/sewage, and with  $\delta^{18}\text{O}_{\text{NO}_3}$  values greater than +5.7‰, nitrate isotopic values displayed an upward trend between winter 2009 and summer 2010. The isotopic composition of nitrogen and oxygen appears to increase at a ratio of about 2:1 (Fig. 5a,b), which is indicative of denitrification processes. It therefore appears that these samples may have undergone denitrification between winter and summer.

However, chemical data indicate that denitrification is not a significant process due to the presence of dissolved oxygen > 1 mg/l in 53 out of 56 samples and the practical absence of Mn (<4 μg/l) in all water samples, indicating oxidized conditions overall. Nitrification can occur rapidly, even down to the concentration of about 0.3 mg/l dissolved  $\text{O}_2$  (Aravena and Mayer, 2010). Furthermore, the samples with the highest (>20 mg/l) and lowest (<1.0 mg/l)  $\text{NO}_3^-$  contents have similar  $\delta^{15}\text{N}$  ( $\sim +11.0 \pm 1.8\%$ ) and  $\delta^{18}\text{O}_{\text{NO}_3}$  values ( $\sim +8.8 \pm 0.9\%$ ) which is another indication that denitrification is not a major process. However, it is possible that partial denitrification takes place or that denitrification occurs under locally anoxic conditions in orchards as reported in previous studies (e.g. Kaown et al., 2009).

Between December 2009 and June 2010, nitrate concentration ranges were from 1.1 to 38.0 mg/l (mean =  $11.3 \pm 8.9$  mg/l) and 0.9 to 49.7 mg/l (mean =  $10.1 \pm 10.7$  mg/l), respectively. Nitrogen isotope values ranged from +6.0 to +17.6‰ (mean =  $+11.1 \pm 3.3\%$ ) in the winter and from +7.2 to +18.5‰ (mean =  $+12.3 \pm 3.5\%$ ) in the summer. The more enriched isotope values in the summer may be

**Table 2**

Land use and other activities in radius &lt;100 and 1000 m, halide and isotopic results, and main sources from interpretation in the text. Note: n.d. stands for "not determined".

Sample no.	Land use	Activities r < 100 m	Other activities r < 1000 m	NO <sub>3</sub> <sup>-</sup> (mg/l)	Mn (mg/l)	Br (μg/l)	I (μg/l)	δ <sup>18</sup> O (‰ VSMOW)	δ <sup>2</sup> H (‰ VSMOW)	<sup>3</sup> H (T.U.)	δ <sup>15</sup> N-NO <sub>3</sub> (‰ AIR)	δ <sup>18</sup> O-NO <sub>3</sub> (‰ VSMOW)	Main N source
1	Agriculture		Cattle confinement	7.6	3.1	170	6	-4.02	-28.01	1.7	17.20	8.75	Manure
2	Orchard	Residences		9.1	10.4	255	26	-3.62	-26.62	1.7	7.12	8.32	Manure
3	Agriculture			6.2	0.4	403	20	-3.95	-27.49	1.9	14.81	8.74	Manure
4	Orchard	Residences		11.9	2.5	849	23	-4.31	-27.43	2.3	16.69	7.76	Sewage
5	Orchard		Stagnant water body	3.2	1.4	185	9	-4.48	-30.00	2.3	9.03	4.82	Not applied
6	Agriculture		Stagnant water body	2.4	0.3	139	8	-4.46	-27.33	1.9	12.26	5.98	Not applied
7	Agriculture			11.0	1.0	169	5	-3.98	-28.93	1.9	12.36	3.91	Manure
8	Agriculture	Residences	Cattle confinement	18.5	2.4	395	6	-3.66	-28.46	1.8	11.81	n.d.	Sewage
9	Grassland	Residences		6.9	0.3	158	4	-5.95	-42.40	1.5	8.18	6.39	Sewage
10	Grassland			0.9	0.9	43	3	-4.41	-30.16	1.4	8.81	6.81	Not applied
11	Orchard		Poultry confinement	15.4	0.3	177	2	-4.44	-28.15	2.4	10.09	3.34	Manure
12	Orchard	Residences	Cattle confinement	4.6	0.4	153	5	-6.35	-44.90	2.1	10.42	4.85	Sewage and/or manure
13	Agriculture	Residences	Cattle confinement	5.1	0.7	574	24	-7.01	-48.81	1.7	n.d.	n.d.	Sewage
14	Orchard		Cattle confinement	12.3	0.2	104	4	-4.69	-35.54	2.0	11.32	4.85	Unknown
15	Agriculture	Residences	Farm and water body	6.4	0.2	74	2	-3.80	-26.87	2.5	18.54	10.96	Sewage and/or manure
16	Orchard			3.4	0.2	104	4	-5.38	-31.68	2.2	11.32	4.85	Not applied
17	Orchard	Residences	Cattle confinement	46.7	0.7	304	7	-6.17	-43.82	1.9	n.d.	n.d.	Sewage and/or manure
18	Residential			6.6	0.3	68	1	-3.57	-27.17	1.8	7.31	4.97	Synthetic fertilizers or soil nitrogen
19	Grassland	Residences	Oxidation lagoons	2.1	1.4	310	10	-6.59	-43.99	1.5	11.34	7.08	Not applied
20	Agriculture	Residences	Cattle confinement	9.6	0.6	310	10	-6.11	-45.41	2.2	11.34	7.08	Manure
21	Grassland		Natural water body	2.8	<0.1	491	23	-5.58	-39.57	2.3	10.92	6.44	Not applied
22	Orchard	Residences		15.5	15.8	491	23	-5.74	-41.75	1.9	10.92	6.44	Manure
23	Agriculture		Stagnant water body	17.9	0.8	801	14	-6.57	-41.39	1.9	12.55	9.44	Sewage and/or landfill
24	Residential		Cattle confinement	19.9	0.8	235	6	-6.33	-42.75	1.6	8.97	9.67	Sewage
25	Agriculture	Residences		4.3	0.2	363	10	-4.90	-31.52	2.1	10.03	n.d.	Sewage
26	Orchard			5.5	0.3	258	8	-3.64	-27.62	1.7	10.25	3.49	Sewage and/or manure
27	Agriculture			15.4	0.3	390	9	-4.65	-31.44	2.6	10.33	4.74	Manure
28	Shrubland		Poultry confinement	5.0	0.3	34	1	-4.23	-27.90	1.5	13.09	n.d.	Soil nitrogen
29	Residential	Residences		4.5	0.4	43	<1	-5.26	-33.05	1.6	11.64	4.17	Unknown
30	Shrubland	Residences		6.8	1.5	36	<1	-4.03	-29.00	2.2	8.67	6.64	Synthetic fertilizers or soil nitrogen
31	Shrubland	Residences	Cattle confinement	4.8	1.7	84	2	-4.48	-28.47	2.3	10.95	6.54	Soil nitrogen
32	Shrubland	Residences		4.5	<0.1	55	2	-5.26	-34.67	1.9	10.67	2.64	Soil nitrogen
33	Agriculture	Residences	Cattle confinement	34.6	0.3	363	40	-6.48	-41.91	1.5	9.94	4.83	Manure
34	Agriculture	Residences		2.2	0.2	225	14	-3.96	-27.27	1.7	9.79	5.26	Not applied
35	Agriculture	Residences		0.6	0.5	66	8	-4.38	-28.55	1.1	11.00	5.89	Not applied
36	Agriculture	Waste dump		25.3	3.0	1170	83	-4.10	-28.05	1.8	11.26	7.02	Landfill
37	Shrubland			3.3	0.5	41	4	-4.76	-33.81	2.3	6.26	5.00	Synthetic fertilizers or soil nitrogen
38	Grassland	Residences		1.1	0.4	54	4	-4.91	-34.13	2.2	13.32	7.77	Not applied
39	Agriculture	Residences		9.2	0.4	248	6	-3.20	-24.54	2.4	14.89	8.75	Sewage

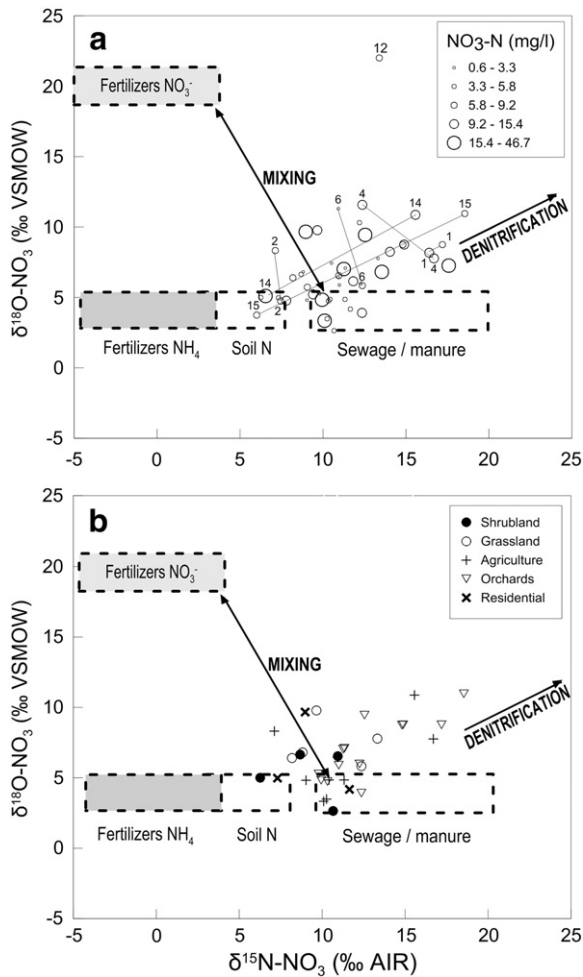
due to a more intensive use and/or a more enhanced volatilization of manure and ammonia-based fertilizers during spring and summer months compared to autumn and winter season. Nitrate concentrations, however, do not significantly change between the two sampling dates, possibly due to a better assimilation by plants and due to partial denitrification during these months. Some pairs of winter and summer samples (well no. 3, 14 and 15) show an increase of δ<sup>15</sup>N vs. δ<sup>18</sup>O<sub>NO<sub>3</sub></sub> with a ratio 2:1, suggesting that these samples underwent denitrification between winter and summer. Other sample pairs (no. 2, 4 and 6) indicate mixing processes (Fig. 5a).

#### 4.4. Differentiation between sources using halides as proxies

Some halides (Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>) are conservative anions because they have minimal interactions with the surrounding substrate in most situations as they migrate with ground water. Cl/Br ratios have

been used in previous studies as a proxy to trace wastewater contamination (Nissenbaum and Magaritz, 1991; Davis et al., 2004; Panno et al., 2006; Alcalá and Custodio, 2008; among others). Katz et al. (2011) developed the systematics of Cl/Br versus Cl concentration based on these studies. Therein, several end-member fields and mixing lines were developed considering dilute groundwater, septic tank leachates, treated sewage effluents, seawater, table salt and urine. Leachates from human sewage may be differentiated from leachates from animal manure. The Cl/Br ratio may however be influenced by different factors which differ from region to region (Davis et al., 2004).

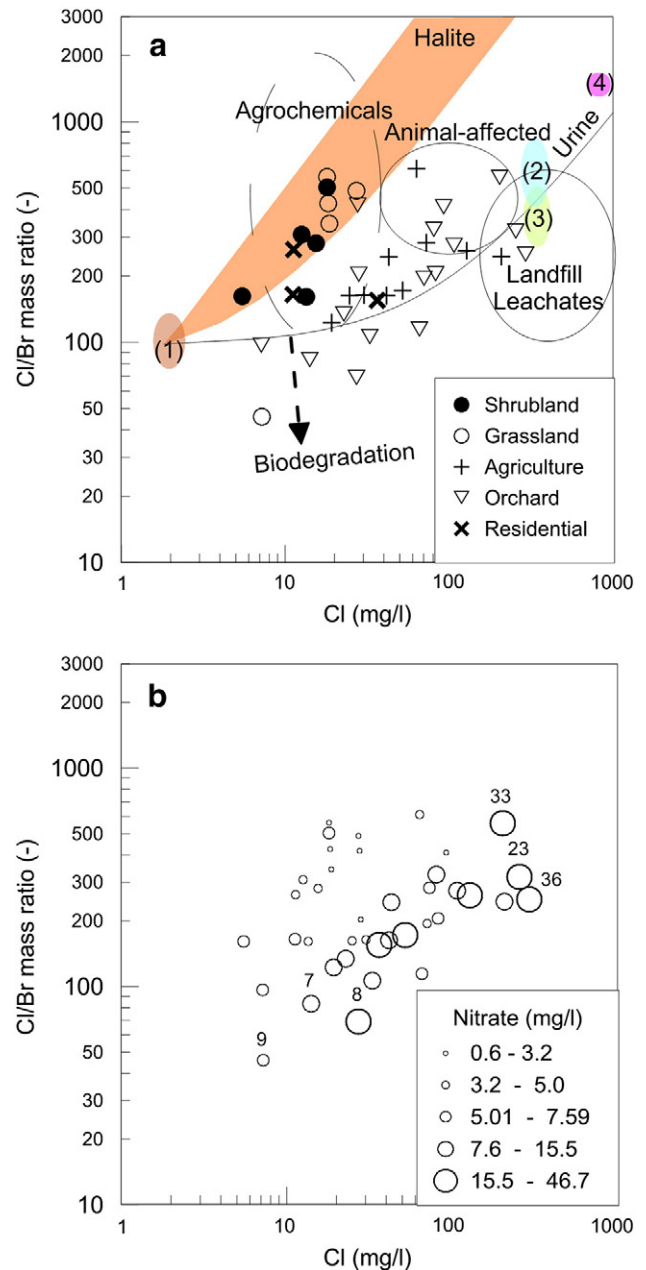
Mixing lines between precipitation and different end members selected from the literature are shown in Fig. 6a. Davis et al. (2006) found out that inland rainwater has Cl/Br ratios between 75 and 120, and domestic wastewater between 300 and 600 for Arizona, although Vangosh and Pankratov (1998) reported values between 410 and 870 for Israel. Ratios for halite vary between 1000 and 10,000 (Davis et al.,



**Fig. 5.** Observed  $^{18}\text{O}$  and  $^{15}\text{N}$  nitrate values in groundwater and pool ranges according to: (a) nitrate concentrations considering field campaign 2010, and (b) land uses and considering samples from 2009 and 2010. The pools are based on Heaton (1986) for soil organic C, Vitória et al. (2004) for synthetic fertilizers; and mineralized fertilizers (Aravena and Mayer, 2010).

1998), while agrochemicals produce values between 100 and 1200 (Panno et al., 2006). The graph in Fig. 6a shows also ranges of landfill leachates, animal-affected and agrochemicals, according to Panno et al. (2006). It can be observed that groundwater below grassland and shrubland is influenced by halite dissolution which is congruent with the local geology (Mahlknecht et al., 2013). In theory these samples are also compatible with agrochemical-affected groundwater, however this assumption is unrealistic or not relevant under the given land use and field observations. Most samples from vegetable agriculture and orchards are plotting along the mixing line between precipitation and domestic wastewater/animal waste. The values for residential land use fall between halite and wastewater mixing lines. Several samples (No. 7, 8, and 9) plot below the wastewater mixing line indicating organic biodegradation. As evidenced in Fig. 6b, values that fall into the domestic wastewater/animal waste-affected region are higher in nitrate concentration. These samples represent organic fertilizers, leachates from cattle confinement, septic tanks effluents and/or leakages in the sanitary system. These results are generally compatible with nitrate isotopes.

Iodine is also a conservative ion with minimal interactions with the environment. It only tends to concentrate in marine vegetation and may be concentrated in some brines (Hem, 1985). Seawater has a mean iodine content of  $58 \mu\text{g/L}$ , while non-saline surface waters have lower and very variable levels (Fuge et al., 1986). With some exceptions (Turin et al., 2002), it's use as tracer for groundwater contamination



**Fig. 6.** Relationship between Cl/Br ratio and Cl concentrations for evaluating of sources. The evolution trend is from precipitation/pristine water to endmembers. Fields are indicated with numbers: (1) inland rainwater (Davis et al., 2004); (2) and (3) septic tank effluents (Vangosh and Pankratov, 1998; Davis et al., 1998); (4) animal waste (Panno et al., 2006). Other fields are dilution of halite dissolution (Davis et al., 1998); urine (McArthur et al., 2012), agrochemicals and landfill leachates (Katz et al., 2011).

sources is uncommon. Panno et al. (2006) developed a system for I/Na against  $\text{Br}^-$  with ranges of sources affecting groundwater for tracing  $\text{Na}^+$  and  $\text{Cl}^-$ . Fig. 7 illustrates separation of precipitation, unaffected, animal-affected, human-affected and landfill-affected groundwater samples. It shows that samples taken from grassland and shrubland plot in the pristine groundwater field, while those from vegetable, agriculture and orchards are distributed between the animal-affected and human-affected fields. It indicates that one sample (No. 36) is affected by landfill leachate which is congruent with Cl/Br against Cl plot in Fig. 6a and field observations.

Based on the field campaign observation, isotopic and geochemical data, the samples have been classified into most likely sources of  $\text{NO}_3$  (Table 2). It showed that I/Na against Br fields facilitated an easier



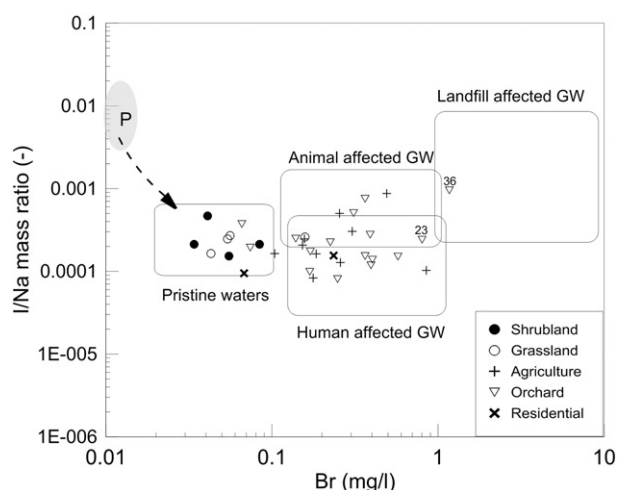


Fig. 7. Relationship between I/Na ratios and  $\text{Br}^-$  concentrations showing separation of sources according to Panno et al. (2006). Note: P means precipitation.

differentiation between manure, sewage and landfill sources. Roughly 43% of samples with  $\text{NO}_3^- > 3 \text{ mg/l}$  are affected by manure, 40% by sewage (mostly from septic tanks), 6% by soil nitrogen, and only 3% by synthetic fertilizers. Samples not complying with drinking water standard have as likely main source manure (55% of these samples) and sewage (45% of these samples).

## 5. Conclusions

Groundwater from a rural region in NE Mexico was analyzed along multiple geochemical dimensions to identify main sources and transformation processes of  $\text{NO}_3^-$  in groundwater and the relationship with land use. The methodology included the integration of geochemical and isotopic techniques as well as physical and hydrogeological information.

Stable water isotopes showed a direct relationship to local meteoric water, as well as seasonal and evaporation effects. The main recharge in the local system is through alluvial deposits and conglomerates outcropping in the valleys and plateaus, infiltration along rivers and streams, and infiltration of excess irrigation in agricultural plots. Tritium analysis revealed the presence of modern groundwater and a relatively homogeneous recharge process. Groundwater recharge estimates range from 200 to 360 mm/year. These results confirm the hypothesis that active recharge carries solutes into the subsurface under present conditions.

Groundwater chemistry is dominated by hydrochemical facies ranging from  $\text{Ca-HCO}_3$  to  $\text{Mg-SO}_4$  chemistry. Historical data reveal that there may be an increasing trend of nitrate contamination. One third of groundwater samples do not comply with the drinking water standard. Recharge area land use associated with the most contamination was agriculture while the least pollution was associated with shrubland. It was demonstrated that dairy activities within a 1000 meter radius of sampled water significantly increased nitrate levels.

Based on geochemical evidence, N sources below vegetable and orchard lands are animals (manure application, confined cattle ranches), human sewage (leakage from urban sewers, septic tanks), and urban solid waste landfills. These waters are subject to partial, local denitrification and to mixing processes. The assimilation of nitrate through plants and denitrification during summer months reduced nitrate concentrations. Sources of nitrate in groundwater from shrubland and grassland are soil N and animal waste. Partial denitrification is observed locally in grassland. Sources of nitrate in groundwater underneath residential areas appear to be dominated by human waste from infiltration of septic tanks.

Our work demonstrates that a multi-tracer approach using geochemical and isotopic techniques, together with field observations of land use and hydrogeology provides a solid basis for an integrated approach to differentiate between various  $\text{NO}_3^-$  sources and processes. Nitrate isotopes identified sources and processes such as mixing, volatilization and attenuation through denitrification, while halide ratios served as proxies for sources. Plots of I/Na ratios against  $\text{Br}^-$  were a very effective tool that allowed for a complete separation between different sources. This technique should be given more attention in tracing  $\text{NO}_3^-$  sources. The approach in general is applicable to address a wide field of question in hydrogeology. The parameters mentioned should be measured routinely in groundwater studies. It is however necessary to make local measurements of any sources to constrain the conceptual model on contamination, because halide ratios may show local variations.

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