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

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HIGHLIGHTS

- A new multiple tracer approach for improved evaluation of nitrate sources and transformation processes was developed.
- Nitrate $\delta^{15}N$ and $\delta^{18}O$ 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^2 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.

1. Introduction

Nitrate (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 N_2O (Haag and Kaupenjohann, 2001).

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

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(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^2) is an example of an agricultural area which is characterized by an increase in concentrations of NO_3^- in a local flow system caused by multiple sources. The area produces 10% of the national citrus production (Agronuevoleón, 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_3-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 (δ^{15}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 δ^{15}N and δ^{18}O of nitrate has allowed evaluating nitrate transformation processes in a groundwater system with microbial denitrification, since not only δ^{15}N but also δ^{18}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 (^{11}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_3^- 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^2 within the State of Nuevo Leon, 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, siliciclastic 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

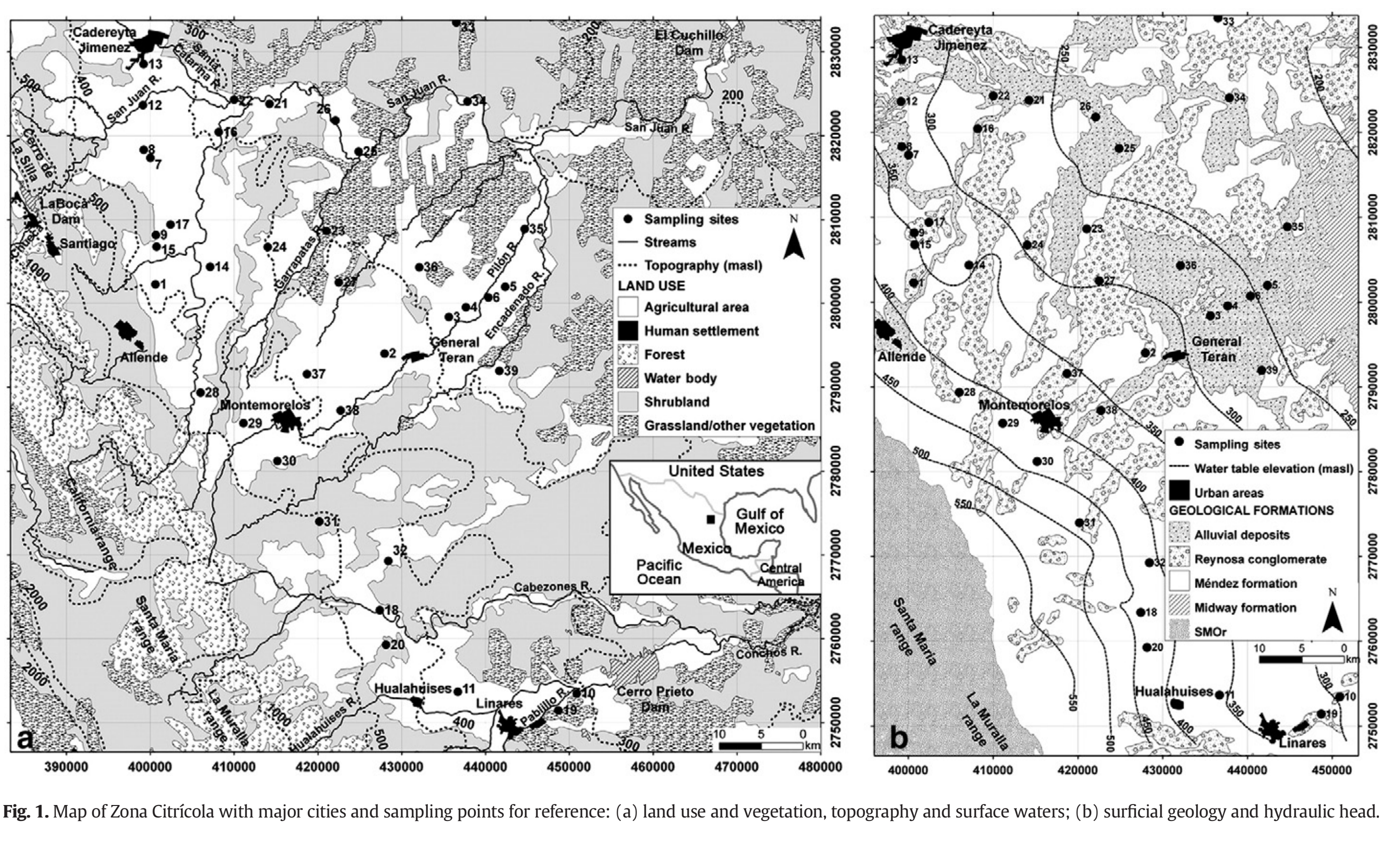

Fig. 1. Map of Zona Citrícola with major cities and sampling points for reference: (a) land use and vegetation, topography and surface waters; (b) surficial geology and hydraulic head.