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Investigation of the geochemical evolution of groundwater under agricultural land: A case study in northeastern Mexico

Rogelio Ledesma-Ruiz [a], Ernesto Pastén-Zapata [a], Roberto Parra [a], Thomas Harter [b], Jürgen Mahlknecht [a,*]

[a] Centro del Agua para América Latina y el Caribe, Tecnológico de Monterrey, Av. Eugenio Garza Sada Sur No. 2501, CP 64849 Monterrey, Nuevo León, Mexico
[b] Department of Land, Air and Water Resources, University of California, CP 95616 Davis, CA, USA

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SUMMARY

Zona Citrícola is an important area for Mexico due to its citriculture activity. Situated in a sub-humid to humid climate adjacent to the Sierra Madre Oriental, this valley hosts an aquifer system that represents sequences of shales, marls, conglomerates, and alluvial deposits. Groundwater flows from mountainous recharge areas to the basin-fill deposits and provides base flows to supply drinking water to the adjacent metropolitan area of Monterrey. Recent studies examining the groundwater quality of the study area urge the mitigation of groundwater pollution. The objective of this study was to characterize the physical and chemical properties of the groundwater and to assess the processes controlling the groundwater's chemistry. Correlation was used to identify associations among various geochemical constituents. Factor analysis was applied to identify the water's chemical characteristics that were responsible for generating most of the variability within the dataset. Hierarchical cluster analysis was employed in combination with a post-hoc analysis of variance to partition the water samples into hydrochemical water groups: recharge waters ($Ca–HCO_3$), transition zone waters ($Ca–HCO_3–SO_4$ to $Ca–SO_4–HCO_3$) and discharge waters ($Ca–SO_4$). Inverse geochemical models of these groups were developed and constrained using PHREEQC to elucidate the chemical reactions controlling the water's chemistry between an initial (recharge) and final water. The primary reactions contributing to salinity were the following: (1) water–rock interactions, including the weathering of evaporitic rocks and dedolomitization; (2) dissolution of soil gas carbon dioxide; and (3) input from animal/human wastewater and manure in combination with by denitrification processes. Contributions from silicate weathering to salinity ranged from less important to insignificant. The findings suggest that it may not be cost-effective to regulate manure application to mitigate groundwater pollution.

1. Introduction

The Zona Citrícola aquifer system in northeastern Mexico constitutes the major source of local drinking water and provides base flows to surface water used to supply drinking water to Monterrey (~4.2 million inhabitants), the third largest metropolitan area in Mexico. Attention to groundwater abstraction has increased during the last decade due to the rising water demands from a growing population and economy and an apparently increasing concentration of some constituents such as total dissolved solids (TDS), nitrate, chloride and sulfate (CONAGUA, 2002a,b; IANL, 2007). In addition, climate change is projected to exacerbate the pressure on the hydrologic system (PACC, 2010).

Historically, Monterrey's water demand has been satisfied by the combined extraction of surface and groundwater resources. Water use restrictions are expected due to limited water availability in the San Juan River basin beyond 2015. Thus, local and federal water authorities are planning to convey surface water from a distant river basin for Monterrey's water supply. However, there is an urgent need to improve the understanding of existing groundwater and surface water resources for an effective strategy to reduce the pressure on the hydrologic system. For instance, a comprehensive understanding of the groundwater's physical and chemical processes by water managers, decision makers and users enhances the consciousness and opens a dialogue among the different actors. This understanding strengthens the consensus regarding important groundwater managerial decisions and in the long run benefits not only local communities but also Monterrey's metropolitan area.

Some previous work has been performed recently regarding groundwater quality issues in the study area. Dávila-Porcél et al. (2012) estimated that the potential sources of contamination are the infiltration of sewage water, wastewater treatment effluents,

* Corresponding author. Tel.: +52 81 8155 2573.
E-mail address: jurgen@itesm.mx (J. Mahlknecht).

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leachates from cattle farm wastes and municipal landfills, leakage from sanitary sewers, septic deposits, surface contamination due to agricultural practices, and concentrations of calcium and bicarbonate from natural mineralization processes. Using stable isotopes and halides, Pastén-Zapata et al. (2014) indicated that the main nitrate sources were animals (manure application, cattle ranches) and human sewage (leakage from urban sewers, septic tanks).

The main objectives of this study were to characterize the physical and chemical properties of the groundwater and assess the processes controlling the groundwater's chemistry and its relevance for salinity. Spatial and temporal variability evaluation of major ions in groundwater is a widely accepted tool to provide insight not only regarding the aquifer's heterogeneity and connectivity but also for the processes controlling the water's chemistry (Hem, 1989; Güler et al., 2002; Chenini and Khmiri, 2009; Kamtchueng et al., 2014). Graphical representations of the water samples' chemistry help define the spatial change patterns among different geologic units or along a section line or pathway. A useful classification technique is cluster analysis, which involves sorting a set of individual samples into smaller groups that can be correlated by location (e.g., Güler et al., 2002; Mahlknecht et al., 2004; Helstrup et al., 2007). Another approach for developing an evolution model is making predictions about the direction of the processes using thermodynamic calculations (Merkel et al., 2007; Andrade and Stigter, 2011; Belkhiri et al., 2012). The primary issue addressed by this study is the contributions of natural and anthropogenic salinity sources by evaluating the general groundwater chemistry and developing geochemical evolution models.

2. Description of the study area

2.1. General settings

The Zona Citrícola area (8000 km^2), located in the State of Nuevo Leon, northeastern Mexico, provides approximately 10% of Mexico's citrus production along with other crops. Fertilizers, namely, manure, urea and ammonium sulfate, are applied to 90% of the Zona Citricola area to improve plant growth (Agronuevoleón, 2008). The region also houses urban areas such as the cities of Linares, Montemorelos, Santiago, Hualahuises and Allende (Fig. 1) and a significant amount of rural population spread throughout the region, totaling ~200,000 inhabitants (INEGI, 2010).

The hilly landscape of the region is part of the Coastal Plain of the Gulf of Mexico physiographic province and slopes to the NE with elevations decreasing from 430 to 300 m above sea level (masl). It is bordered to the W by several ranges from the Sierra Madre Oriental (SMOr), including California, Santa Maria and La Muralla, which reach a maximum altitude of 2200 masl. The SMOr is a 2–3 km-thick Mesozoic–Cenozoic sedimentary belt stretching along NE and central Mexico that is composed of carbonate, siliciclastic and evaporative rocks and deposited over a basement-complex of metamorphic rocks and schists (Goldhammer, 1999; Chávez-Cabello et al., 2004).

The region comprises a warm, sub-humid to humid climate with an annual mean temperature of 22 °C and extreme minimum and maximum values of −10 °C in winter (December to February) and 45 °C in summer (June to August). Rainwater is produced by warm air masses originating from the Gulf of Mexico, which move across the SMOr and generate higher elevated rainfall along its flanks (1100 mm/year) and between 350 and 750 mm/year in the plain, with the highest values observed SW of Allende and Montemorelos and the lowest values near the town of General Terán (Fig. 1). Most rainfall occurs between May and October (77%). On the other hand, the driest months are between November and March (~3% each) (García, 1998; CONAGUA, 2002a,b).

Surface waters from the region are perennial and flow in the SW–NE to W–E direction toward the Gulf of Mexico (Fig. 1). In the northern and central part, the main waterway is the San Juan River, which originates in the La Boca dam and ends at the El Cuchillo dam and ultimately in the Grande River/Bravo River (~150 km NE of the study zone). The Santa Catarina, Garrapatas and Pilon Rivers are tributary streams (CONAGUA, 2002a). On the southern portion of the study area, the El Pablillo, Cabezones and Hualahuises Rivers merge and flow into the Cerro Prieto dam, finally ending in the San Fernando River (CONAGUA, 2002b). The Cerro Prieto, El Cuchillo and La Boca dams are the main surface water reservoirs used for local agriculture and the drinking water supply for Monterrey's metropolitan area (~20 km NW of Cadereyta Jimenez).

2.2. Geology and hydrogeology

The rock types outcropping in the valley are predominantly of marine sedimentary origin, representing a geological interval from the Upper Jurassic to Recent (Fig. 2a). The units in the SMOr are from the Upper Cretaceous to Upper Jurassic, and in the plain from the Upper Cretaceous to Recent. In the study area, the oldest unit corresponds to the Mendez formation, a sequence of shale, calcareous shale and stratified calcareous marl with a thickness of 1500–2800 m (Padilla y Sánchez, 1982; Dávila-Pórcel, 2011) and low permeability, except in zones of fractures and faults. From a hydrogeological point of view, it is considered a semi-confined aquifer. On the other hand, the Reynosa conglomerate comprises calcareous fragments packed in a sandy Tertiary matrix with a maximum thickness of 60 m and a moderate permeability, forming isolated plateaus and hills (CONAGUA, 2002a). Finally, more recent materials from the Tertiary to Quaternary correspond to alluvial deposits consisting of gravel, sand, silt and clay mixed in different proportions and degrees of compaction, with a variable thickness of up to 25 m (Padilla y Sánchez, 1982). This unit with medium to high permeability is considered an unconfined aquifer (CONAGUA, 2002a). The main recharge area is located in the California, Santa Maria and La Muralla ranges adjacent to the study area (Fig. 2b). Infiltration over the surface of the aquifer, especially at the mountain-front, is another important recharge mechanism besides infiltration from irrigation. The depth to the groundwater in the study area varies from 5 to 25 m, with the shallowest levels located in the surroundings of the Cerro Prieto dam SE of the study area and the deepest levels in isolated areas to the SE of Allende, E of General Terán and NW of Hualahuises. The water table elevation varies between 550 and 200 masl with the highest values in the SW portion of the study area near the foothills of SMOr, showing a SW–NE groundwater direction in the central and northern portions and a W–E direction in the southern portion of the study area.

2.3. Lithology and mineralogy

The mineralogical composition in the SMOr mountain ranges and basin-fill represents a constraint on the phases that participate in the water–rock interactions of the study area. Shales and carbonates dominate the mineralogy of the region. Mineralogical analyses of the Mendez formation suggest a marly lithology with an average composition of 47% calcite, 30% phyllosilicates, 15% quartz and 8% plagioclase (Keller et al., 1997). This formation is overlain disconformably by clastic Cretaceous–Tertiary (KT) boundary deposits, which can be divided into three units according to Adatte et al. (1994) from bottom to top: (i) a poorly cemented, spherule-rich layer characterized by high calcite (50–70%) and low phyllosilicate (smectite and chlorite) contents (<20%), quartz, and plagioclase (albite, 5%); (ii) a massive sandstone with quartz (up to 40%), calcite (20–40%), plagioclase (albite, 15–25%) and low phyllosilicate content (chlorite and mica); and (iii) the