

Hydrogeochemical and isotopic assessment of the origin of NO_3^- and N-NH_3 contents in the aquifer located in a closed lacustrine volcano-sedimentary basin in the metropolitan area of Mexico City

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Abstract To explain the presence and spatial distribution of NO_3^- and N-NH_3 in the Aquifer of the Metropolitan Area of Mexico City (AMAMC), a hydrogeochemical and isotopic analysis using $^{13}\text{C}_{\text{DIC}}$ (as well as the stable isotopes ^{18}O and ^2H) in groundwater was conducted. This aquifer is located in an old closed lacustrine volcano-sedimentary basin; some wells hosted in the semi-confined zone contain high N-NH_3 concentrations, while others present NO_3^- contents in the recharge zones (hosted in an oxidizing environment). In this study, a change in the isotopic signature (primarily in ^{18}O and ^2H) was observed from the recharge zones to the basin center in some of the wells with high NO_3^- concentrations, this behavior can be attributed to evaporation during the incorporation of recently infiltrated water. In addition, the results for ^{13}C (along with ^2H) in wells with the highest N-NH_3 concentrations exhibited an atypically broad range of values. Results indicated the occurrence of hydrogeochemical and/or biochemical processes in the aquifer (in an oxidizing or reducing environment), such as organic degradation, bacterial decomposition (primarily in

the ancient Lake Texcoco and which acts as a natural sink for carbon, nitrogen, sulfur, and phosphorus), besides rock weathering and dissolution, which may be responsible for a very marked isotopic modification of the ^{13}C (and, to a lesser extent, ^2H). Methanotrophic bacterial activity and methanogenic activity may be related to N-NH_3 removal processes by oxidation and residual water incorporation respectively, whereas the increase in the NO_3^- content in some wells is due to the recent contribution of poor-quality water due to contamination.

Keywords ^{18}O and ^{13}C isotopes · Iron · Hydrogeochemical processes · Nitrate · Nitrogen species

1 Introduction

Global environmental degradation has been caused by the presence of reactive nitrogen species in surface and groundwater bodies (Lord and Anthony 2002). The incorporation of wastewater, leaching from landfills, or intense agricultural (nitrogen fertilization) or livestock activities are the main sources of environmental contamination that leach nitrogen compounds from the upper horizons of soil profiles, contaminating aquifers and increasing the concentration of nitrates (NO_3^-), nitrites (NO_2^-) or ammonium (NH_4^+) (Liu et al. 2006; Chen et al. 2009; Schroeder et al. 2004; Wick et al. 2012).

In Mexico, the high content of nitrogen compounds in groundwater is an environmental problem, which has been increasing over time; the main causes are anthropogenic activities in rural areas, such as agriculture and livestock, or in urban areas, such as discharges of water used for industrial

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activities, leachates from landfills, septic tanks or the incorporation of wastewater into aquifers (Brito-Castillo et al. 2010; Montiel et al. 2014). Various studies have been conducted to determine the quality of the Aquifer in the Metropolitan Area of Mexico City (AMAMC) (Ryan 2012; Lesser et al. 1993; Edmunds et al. 2002; Montiel et al. 2014). Some of these investigations detected nitrates, indicating the input of reactive nitrogen species from anthropogenic sources in the recharge zones (Armienta and Rodríguez 2013). In addition, the hydrogeochemical behavior of nitrates in the southern zone of Mexico City has been determined (Montiel et al. 2020). Some authors have attributed the isotopic behavior of $\delta^{18}\text{O}$ in the AMAMC to the incorporation of pore water of the lacustrine material, others to high salinity at some sites due to intense ancient evaporation processes, or to the interaction of water with volcanic rocks; and others to the discharge of regional groundwater flow (Ryan 1988; Ortega-Guerrero et al. 1997; IMTA 2019). Ortega-Guerrero et al. (1997) postulated that ammonia results from ion exchange with K⁺ in the clays present in high-salinity water. Agriculture has been identified as a potential source of groundwater contamination in the region (Galán 2018). Despite the fact that agriculture is limited to a specific area of the city, the intensive use of nitrogen compounds and their transformations may be involved in contamination processes. Several studies have observed that the organic matter present in the unsaturated zone and saturated zones can participate by the interaction with bacteria and microorganisms in the transformation of the ammonium ions (NH_4^+) into nitrites (NO_2^-), and, finally, into nitrates (NO_3^-). Montiel et al. (2014) reported this process in the study area. However, little is known about the transformations that occur with these reactive nitrogen species and their relationship to the behavior of $\delta^{13}\text{C}$, $\delta^2\text{H}$, and $\delta^{18}\text{O}$ in the confined aquifer region of the AMAMC.

The behavior of nitrogen species is reflected in biodegradation processes that can be traced using $\delta^{13}\text{C}$ isotopic analysis (Mohammadzadeh et al. 2005). Understanding the dynamics of reactive nitrogen species requires knowledge of both the water and the pollutant's oxygen isotopic composition (Peters et al. 2015). The application of $\delta^{13}\text{C}$ determination is most beneficial in biochemical environments where bacteria preferentially degrade ^{12}C of the substrates (fulvic acid, fatty acid, and acetate) and discriminate the ^{13}C fraction during oxidation reactions of organic matter in soil or shallow groundwater (Ruess et al. 2005). This behavior, in conjunction with the hydrogeochemical information of an aquifer, helps to determine the geochemical evolution, incorporation of CO_2 from the recharging area, dissolution processes (Clark and Fitz 1997), or the occurrence of a deep contribution of CO_2 by a geological source (Berner 2004; Macpherson et al. 2008). In addition to the influence of seismic and volcanic activity (Barbieri et al. 2021a,

2021b). Likewise, the $\delta^{13}\text{C}$ isotopic signature helps to define the evolution of groundwater throughout the hydrological cycle since mineralization affects the $\delta^{13}\text{C}$ value (Ruess et al. 2005; Bottrell et al. 2017; Sabagh et al. 2021; Akbar et al. 2020).

In Mexico, the interpretation of the behavior of $\delta^{13}\text{C}$ has recently been applied to complement hydrogeological and hydrogeochemical evaluations with different approaches. In the north and central parts of Mexico, specific isotopic studies were carried out to estimate the age of groundwater flows and determine the origin of the water (Edmunds et al. 2002; Mahlnecht et al. 2004, 2008; Horst et al. 2008; Armienta et al. 2014; Montiel 2020) and to define geochemical evolution of groundwater, natural baseline conditions and hydrogeochemical processes (Edmunds et al. 2002). Likewise, In the Mexican Bajío area, the application of $\delta^{13}\text{C}$ signature allowed to deduce the possible participation of carbon dioxide in different hydrogeochemical reactions in groundwater (Morales et al. 2020 a and b; Mahlnecht et al. 2004, 2006; Horst et al. 2008; Morales-Arredondo et al. 2018; Morales-Arredondo et al. 2022).

Under this scenario, an environmental assessment focused on quantifying the presence of reactive nitrogen species was conducted, in addition, this work evaluated the relationship between the transformations of reactive nitrogen species, the behavior of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$, and the release of elements (e.g., iron, manganese), that are sensitive to the change of redox conditions. The AMAMC is exposed to both natural and anthropogenic sources of contamination due to the incorporation of water from urban activities or due to the release of N from Lake Texcoco and its historical dynamics as a source-sink. In this work, the source of this pollution was identified using isotopic and hydrogeochemical studies.

1.1 Background

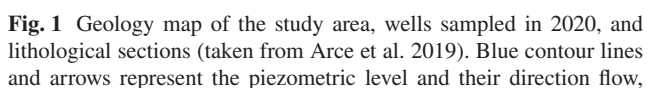
1.1.1 Study area

The Study zone is situated in an endorheic basin in which 8.92 million people inhabit an area of 1 485 km² and obtain the majority of their water requirements from the Aquifer of the Metropolitan Area (IMTA 2019). Mexico City is located between 2940 and 3930 m above sea level in a closed basin affected by tectonic processes. The rivers that once flowed through the city have been piped, and the water is sent out of the city; only in the south and southeast remain remnants of what was Lake Texcoco (e.g., Xochimilco, Milpa Alta, Tláhuac). The City is mainly supplied by groundwater (about 62 %), which comes from more than 2 000 extraction wells, in addition to surface water systems, including those from the Lerma, Cutzamala, and Magdalena rivers. The volume of water extracted from the aquifer system (45 m³/s) is greater than that which enters naturally through precipitation

Physiographically, Mexico City is comprised of a volcanic mountain range of stratovolcanoes (to the center and east with 41.8 %), a volcanic mountain range of steep slopes (to the west and south with 9.93 %), a volcanic shield

1.1.2 Geology and hydrogeology of the study area

Figure 1 depicts the lateral boundaries of the aquifer: Chichinautzin mountain range to the south, Las Cruces mountain range to the west, Sierra Nevada to the east, Guadalupe mountain range, and Chiconautla hill to the north. The lower boundary was conceptually designated as the lowest aquitard with minimal hydraulic interactions with the principal aquifer above. The groundwater recharge zone is primarily located in the southern half of the Mexico Basin and consists of around 250 m of alluvial-lacustrine deposits, 250 m of the Tarango formation (Las Cruces mountain range), and approximately 300 m of Quaternary volcanic rocks (Chichinautzin and Santa Catarina mountain ranges). In addition, there is evidence that the strata of the Middle Tertiary constitute a fractured aquifer (Edmunds et al. 2002). In Consideration of the region's stratigraphy, a subdivision based on



AA', BB', CC' sections and MM' profile show the geological characteristics of the study area

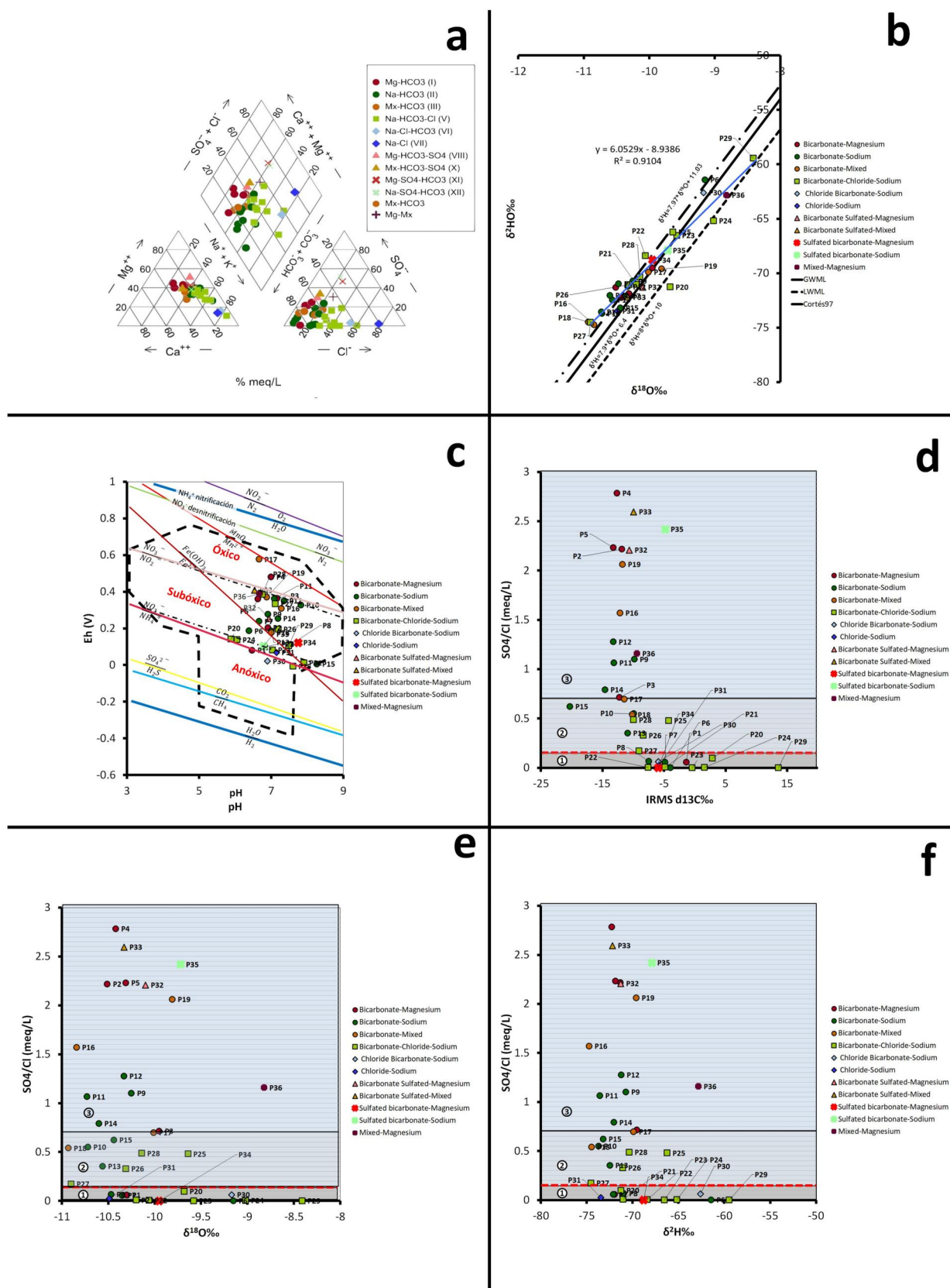


Fig. 2 Piper diagrams from AMAMC for the year 2020 sampled in August **a** Isotopic composition of water from wells in the study area; **b** Mexico groundwater line (dotted line, LWML), isotopic hydrology of the Basin of Mexico City proposed by Cortés et al. (1997) and global meteoric water line (straight line, GWML) (Wassenaar et al. 2009; Craig 1961) are also shown. Eh–pH diagram for some redox buffer pairs in water (oxygen, hydrogen, nitrogen, manganese, iron, sulfur, and carbon), location of samples in oxic, suboxic, and anoxic zones are indicated for **c** August 2020; **d** SO_4/Cl ratio (meq/L) vs $\delta^{13}\text{C}$; **e** SO_4/Cl ratio (meq/L) vs $\delta^{18}\text{O}$; **f** SO_4/Cl ratio (meq/L) vs $\delta^2\text{H}$ where SO_4/Cl ratios values meaning: (1) Samples with ratios < 0.15 are subject to S removal due to sulfates precipitation or bacterial metabolism; (2) common ratio for rainfall varies between 0.15 and 0.7; (3) Samples with ratio > 0.7 have additional S derived from geochemical sources

the hydraulic features of the strata is proposed and conceptualized as follows: (1) upper aquitard; (2) major aquifer; (3) lower aquitard; and (4) independent units. Due to the deposition of clayey lacustrine sediments and the fact that the aquitard extends across the entire lake plain, it is categorized as a regional aquitard.

The principal aquifer is underlain by an alluvial-type aquitard, with lava flows toward the foothills of the basin; There are two other hydraulic units: a middle aquifer and a deep aquifer, separated by a very low permeable element (the Balsas formation and the Upper Cretaceous marls and shales); the Miocene and Oligocene volcanites must be largely impermeable. Recently, demonstration or production wells have been drilled to the sea-level limestone base of the carbonate sequence of the deep aquifer.

2 Methodology

2.1 Sampling and chemical analysis of groundwater samples

Groundwater sampling studies were conducted from urban groundwater wells in the study area in March (end of the dry season) and August 2020 (end of the rainy season) (36 wells), following the standard methods of APHA-AWWA (2005) and Mexican standards (NOM-127-SSA1 and NOM-230-SSA1).

Following APHA-AWWA protocols (APHA-AWWA 2005), chemical analyses of major ions were performed in the Analytical Chemistry Laboratory of the Institute of Geophysics, UNAM, Mexico, the main ions were analyzed following standard methods. Bicarbonate was determined by volumetry (HCl titration), Cl^- was analyzed by potentiometry with selective electrodes (4500- Cl^-), and SO_4^{2-} was determined by turbidimetry (method 4500- SO_4^{2-}). Ca^{2+} and Mg^{2+} were analyzed by volumetry (titration with EDTA); whereas Na^+ and K^+ were determined by atomic emission spectrophotometry (3500- Na^+ and K^+).

Mn and Fe were determined by atomic absorption spectrometry, SiO_2 was determined using atomic absorption spectrophotometry with flame and UV–visible spectroscopy (molybdosilicic acid method). The analytical quality was evaluated using ionic balance (less than 10 %) and the use of certified (NIST traceable) reference solutions. The laboratory participates in international calibration exercises (Verma et al. 2015, 2022; Stewart et al. 2020).

Using UV spectrophotometry with a Thermo Evolution 300 equipment, nitrate concentration was determined. For this analysis, H_2SO_4 was added to the samples as a preservative during the process. In the case of the samples where the highest nitrate values were obtained, results were corroborated using the methodology proposed by EPA 353.2 for the Determination of ammonia-nitrate-nitrite, nitrogen by Automated Colorimetry; the method may be applied from 0.05 to 10.0 mg/L ammonia-nitrate-nitrite nitrogen that can be expanded with sample dilution.

Samples were collected directly from the discharge of the well in operation. The isotopes of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$ were determined in Beta Analytic Testing Laboratory by Isotope Ratio Mass Spectrometry (IRMS); the laboratory has ISO/IEC 17025:2017 accreditation for determining stable isotope ratios of carbon, deuterium, and oxygen in water via IRMS and CRDS (Cavity Ring-Down Spectroscopy). The isotopic ^{13}C measured here corresponds to Dissolved Inorganic Carbon (DIC), the $\delta^{13}\text{C}$ value is relative to VPDB-1, and the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope ratios were determined concerning the VSMOW and SLAP scale, respectively (Coplen 1988).

The results of stable water isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$) and concentrations of major ions (Cl^- , HCO_3^- and SO_4^{2-}) were used as a clue to identify nitrogen processes related to nitrification and to evaluate hydrogeochemical reactions that affect the behavior of the superficial and the deep aquifer. Additionally, a hydrogeochemical characterization was performed using Piper, Eh–pH, $\delta^{18}\text{O}$ vs $\delta^2\text{H}$, $\text{SO}_4^{2-}/\text{Cl}$ vs $\delta^{13}\text{C}$, $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$, $\text{HCO}_3^-/\text{SiO}_2$ ratio vs $\delta^{13}\text{C}$, $\delta^{13}\text{C}$, NO_3^- vs $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, N-NH_3 , and Fe vs $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ diagrams.

3 Results

Table 1, included in the supplementary material (Table 1 SM) shows the results of the pH and Eh measurements, nitrogen species (nitrate, nitrite, and ammonia), iron, bicarbonate, and silica concentrations and isotopic values of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$ in the sampled wells, the maximum, minimum and average values of the standard deviation of the measured isotopes were min = 0.02, max = 0.08, average = 0.045 for $\delta^{13}\text{C}$; min = 0.01, max = 0.05, average = 0.016 for $\delta^{18}\text{O}$ and min = 0.01, max = 0.65, average = 0.136 for $\delta^2\text{H}$.

3.1 Hydrogeochemical evaluation of water samples

The classification of water types for the Piper diagram (Apelo and Postma 2005), as depicted in Fig. 2a, shows that calcium and/or magnesium bicarbonate and sodium bicarbonate are the main groundwater family types. However, water family types hosted in the lacustrine zone exhibit an increase in SO_4^{2-} and Cl^- , which exceeds or is equal to the bicarbonate content resulting in bicarbonate sulfate, chloride, or mixed families. The hydrogeochemical processes observed in the Piper diagram primarily indicate water–rock interaction and the occurrence of mixing processes associated with the transition between volcanic and sedimentary lithological change (Figs. 1 and 2a). The Na-Cl water type, which may be representative of the upper aquitard is a special case; however, the temperature measured *in-situ* (Table 1 SM), the EC, and the isotopic composition imply that it may be a regional flow discharge.

The isotopic composition of the local wells was depicted in Fig. 2b to verify the water's sources and the physical processes occurring in the study area. The isotopic composition of the samples was compared with the meteoric water line of Mexico City reported by Cortés et al. (1997) and the meteoric water line for Mexico postulated by Wassenaar et al. (2009). Craig (1961) found that in regions where evaporation occurs at average temperatures, the meteoric waters present an increase in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ consistently with a slope of about 5. Clark (2015) states that in arid regions, phreatic groundwater may also exhibit evaporation, which is typically characterized by a local evaporation line with a slope of about 5.6. No evidence of a geothermal footprint as an increase of $\delta^{18}\text{O}$ typical of geothermal waters (Wassenaar 1995; Wassenaar et al. 2009) due to water–rock interactions was observed ($\delta^{18}\text{O}$ value more positive than meteoric water, deuterium isotopic composition like the local meteoric water).

As a result of the migration of subhumid to semiarid conditions in a semiconfined aquifer, water samples from the study area had an isotopic composition similar to that of meteoric waters. Figure 2b depicts the equation derived from the isotopic results of the groundwater samples collected in March ($\delta^2\text{H} = 6.0529 * \delta^{18}\text{O} - 8.9386$).

The d-excess data were evaluated in consideration of the local topographic, climatological, and physiological conditions, and this value was used to calculate the difference between the local conditions in the CDMX and the global line of meteoric water $\delta^2\text{H} = 8 * \delta^{18}\text{O} + 10$ (Craig 1961). The d-excess values range from 6.17 ‰ to 12.97 ‰, with an average of 10.7 ‰ (Table 1 SM) and $\text{st dv} = 1.62$; the highest d-excess value was recorded in well P-18, the lowest value was in well P-20, indicating the greatest separation with respect to the LMWL (primarily the lowest values), as 28 wells present a value greater than 10 ‰ while 8 wells

present a value less than 10 ‰. In an evaluation using isotopic data and the calculation of d-excess, Barshaw (2018) determined that d-excess values >10 ‰ are associated with the addition of other moisture sources, both oceanic and recycled continental, whereas d-excess values <10 ‰ are associated with subcloud evaporation of raindrops throughout the relatively arid basin located in Asia. In Mexico City, the behavior is caused by an abrupt enrichment in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ at altitudes greater than 1000 and 1400 m, which may be due to local topographic conditions and/or an isotopic shift caused by specific climatological conditions (torrential storms or area with frequent fogs or by plant evapotranspiration leading to isotopically depleted fogs and clouds), rainfall is progressively depleted by the loss of heavy isotopes as rainfall events progress in an upward topographic gradient direction where the temperature is lower and the condensate is isotopically enriched, however, the heavily forested region surrounding Mexico City in the highlands, can influence the stable isotope signature of precipitation (Pérez-Quezadas et al. 2015).

The Eh–pH values of groundwater transition from an oxic to a suboxic environment and then to an anoxic environment. This change may influence the behavior of elements such as NO_3^- or N-NH_3 or certain metals in the aquifer, as higher concentrations of nitrates were found in an oxic environment, whereas in an anoxic environment, the ammonia nitrogen, Fe_{Tot} , and Mn contents are very high (Fig. 2, Table 1 SM).

In the study area, it was observed that the wells with the highest values in $\delta^{13}\text{C}$ have a very low SO_4/Cl ratio (<0.15) (e.g., P29, P24, P20, P23, and P1; this behavior can be associated with S removal due to sulfate precipitation or bacterial metabolism), in addition, these wells also present an increase in $\delta^{18}\text{O}$ and in some cases in $\delta^2\text{H}$ (Fig. 2d, e and f) (Dogramaci et al. 2017).

In contrast, the majority of wells exhibit a typical rainfall behavior (SO_4/Cl between 0.15 and 0.7 value), as well as additional S derived from geochemical sources ($\text{SO}_4/\text{Cl} > 0.7$). Wells with a SO_4/Cl value greater than 0.15 also show an increase in $\delta^2\text{H}$ and $\delta^{18}\text{O}$, suggesting that evaporation is associated with their isotopic signature (Fig. 2e and f).

3.2 Evaluation of the concentration of nitrogen species regarding the isotopic behavior of $\delta^{13}\text{C}$, $\delta^2\text{H}$, $\delta^{18}\text{O}$, and d-excess

The comparative evaluation of $\delta^{13}\text{C}$ vs NO_3^- in the study area reveals that the samples with low values of $\delta^{13}\text{C}$ are those that present the highest value of NO_3^- ; the majority of the samples exhibiting this behavior are of bicarbonate-sodium, bicarbonate-magnesium, bicarbonate-mixed, bicarbonate-sulphate-magnesium, bicarbonate-sulphate-mixed

water types, and bicarbonate-chloride-sodium type (Figs. 1 and 2a, c and d, Table 1 SM), the highest concentrations of NO_3^- presented an isotopic signature of $\delta^{18}\text{O}$ between -10.93‰ and -9.81‰ (except for the P36 well that presents a value of -8.82‰). These samples are hosted in an oxic-suboxic system with the possible incorporation of recently infiltrated water (e.g., P15, P13, P11, P14, P18, P10, P27, P12, P16, P2, P4, P3, P9, P19, P17, P28, P33, P32, P5, and P36) (Figs. 2c and 3a), considering the lateral connectivity of the aquifer observed in the study zone (Medina-Ortega et al. 2019), which is a factor that can contribute to lateral migration of nitrate. In addition, some of these wells are situated at high altitudes and where the volcanic rocks are beginning to be covered by the lake deposits of the sedimentary basin (Fig. 1). This characteristic is reflected in the behavior of the d-excess, as the majority of the samples with a high NO_3^- content, present d-excess values $>10\text{‰}$, that is, they reflect the influence of moisture sources as oceanic and recycled continental, whereas the samples that present the highest NO_3^- values have a d-excess value $<10\text{‰}$ (P16, P32, P36), which is indicative of sub-cloud evaporation of

raindrops throughout the relatively arid basin. This behavior may be attributable to the assimilation of recycled water with high NO_3^- contents in high-altitude regions that migrate towards the lower basin regions and increase the NO_3^- contents during their migration (Fig. 3d).

3.3 Reducing environment and isotopic behavior of ^{13}C , ^{18}O , ^2H , and d-excess vs N-NH_3

The comparison of $\delta^{13}\text{C}$ vs N-NH_3 in the study area shows that the samples with the highest $\delta^{13}\text{C}$ values also contain the greatest concentrations of N-NH_3 (Fig. 4a). This behavior is also observed when comparing NO_3^- with the isotopic value of $\delta^{18}\text{O}$ and $\delta^2\text{H}$, however, in this case, a higher evaporation rate can occur concurrently, modifying the isotopic value of both isotopes (Fig. 4b, y, c). This behavior is very evident in 3 wells (P20, P24, P29), located in low areas of the basin with a sub-humid to semi-dry temperate climate and that have a d-excess value $<10\text{‰}$. However, the evaluation of the d-excess for other wells that present a high N-NH_3 content presents values $>10\text{‰}$, suggesting that there could be an

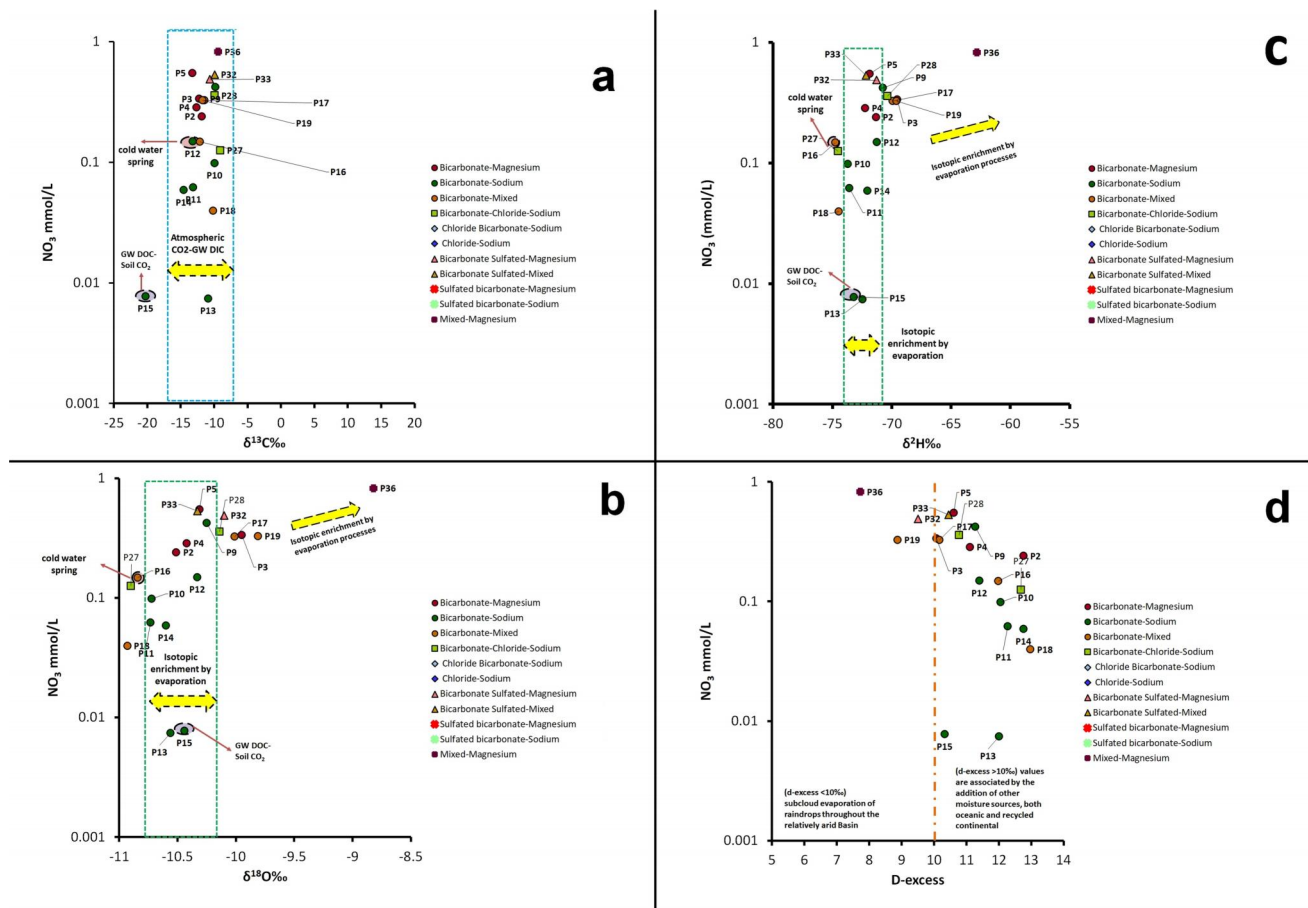


Fig. 3 a $\delta^{13}\text{C}$ vs NO_3^- , b $\delta^{18}\text{O}$ vs NO_3^- , c $\delta^2\text{H}$ vs NO_3^- and d d-excess vs NO_3^- in sampled wells and corresponding hydrogeochemical classification

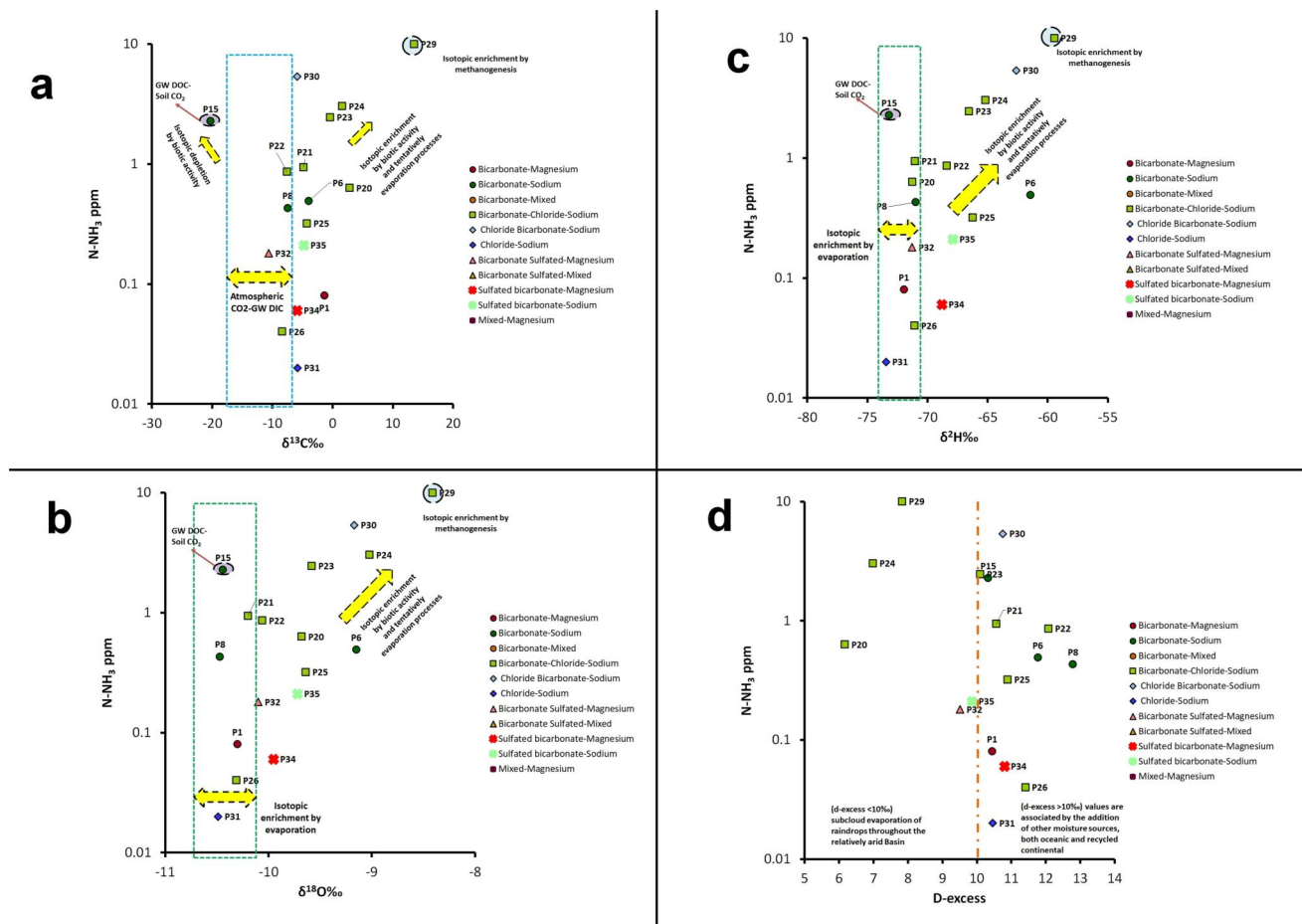


Fig. 4 **a** Evaluation of the behavior of $\delta^{13}\text{C}$ vs N-NH_3 , **b** evaluation of the behavior of $\delta^{18}\text{O}$ vs N-NH_3 , **c** evaluation of the behavior of $\delta^{13}\text{C}$ vs N-NH_3 and **d** evaluation of the behavior of d-excess vs N-NH_3 in sampled wells and corresponding hydrogeochemical classification

incorporation of poor-quality water in these wells during their migration from the upper parts of the basin to the low areas (Fig. 4d). The samples that exhibit this behavior are hosted in a closed suboxic-anoxic system (e.g., P31, P34, P35, P25, P6, P21, P30, P20, P23, P24, P29) (Figs. 1, 2c and 3a). In the current case, the increases in N-NH_3 concentration and simultaneous change in the isotopic values of $\delta^{13}\text{C}$, $\delta^2\text{H}$, d-excess, and $\delta^{18}\text{O}$, especially the increase in heavy ^{18}O isotopes, may be attributed to the increase in the heavier isotopic characteristics of residual oxygen due to oxygen diffusion and water evaporation. However, it is crucial to identify whether this modification results from nitrification–denitrification processes, surface water incorporation, or the application of nitrogen fertilizers. Certain water samples exhibit a significant N-NH_3 concentration, yet their $\delta^{13}\text{C}$ isotopic value falls within the range of atmospheric CO_2 and groundwater DIC. This discrepancy could potentially be attributed to the release of effluent into the aquifer, which occurs under oxic-suboxic conditions (e.g., P22, P8, P32 and P26) (Fig. 4a).

When comparing samples with high values of N-NH_3 vs $\delta^{18}\text{O}$ and $\delta^2\text{H}$ the isotopic signatures do not change significantly (Fig. 4b and c). At sites containing both NO_3^- and N-NH_3 (e.g., P15, P32), evidence of transformation of reactive nitrogen species was identified. Lastly, sites with a high SO_4^{2-} and N-NH_3 content simultaneously may be the result of agricultural practices involving the use of ammonium sulfate-based fertilizers $[(\text{NH}_4)_2\text{SO}_4]$ (Galán 2018) that provide nitrogen in the form of ammonium, which is transformed into nitrates and could also increase the SO_4^{2-} content in groundwater. This mechanism would account for the overall increase of both elements in certain wells (Fig. 4). The increase in SO_4^{2-} content in particular Mg-HCO_3 , Na-HCO_3 , and Mx-HCO_3 water types may have this origin, although the incorporation of wastewater may also occur (Kolpin et al. 1994; Morales-Arredondo et al. 2020).

3.4 Reducing environment and isotopic behavior of ^{13}C , ^{18}O , and ^2H vs Fe contents

The hydrogeochemical and isotopic behavior of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$ were evaluated to trace the origin of Fe^{2+} in an aquifer zone owing to the complexity of the processes involved with their presence. In the study area, suboxic (and in some instances anoxic) conditions govern iron behavior (Fig. 5). Wells with the greatest iron content (e.g., P24, P6, P1, P35, P30) (Fig. 5a, b and c), presented the highest ammonia nitrogen and manganese concentrations (Table 1 SM)). In addition, these wells exhibited an isotopic modification of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$ (high values) that has previously been attributed to processes such as bacterial participation or an increase in evaporation rates. In contrast, those with the lowest iron concentrations also have the greatest nitrate concentrations (Table 1 SM).

The volcanic medium (e.g., basalt) that dominates the entire region is the raw material for mineral alteration (ferromagnesian minerals), which can release iron into the water; however, in oxidizing environments, the element precipitates as oxide or hydroxide, whereas in reducing environments, these compounds are not formed, and iron remains free (Apelo and Postma 2005).

4 Discussion

Results show that the presence of nitrogen compounds in certain groundwater wells hosted in the recharge zone (e.g., P9, P32, P39) and in sites located in the center of the basin (e.g., P23, P24, P29, P30) is due to the incorporation of water from anthropogenic activities such as fertilizer application, wastewater, or leaching from landfills. This incorporation may generate reactions in the aquifer matrix

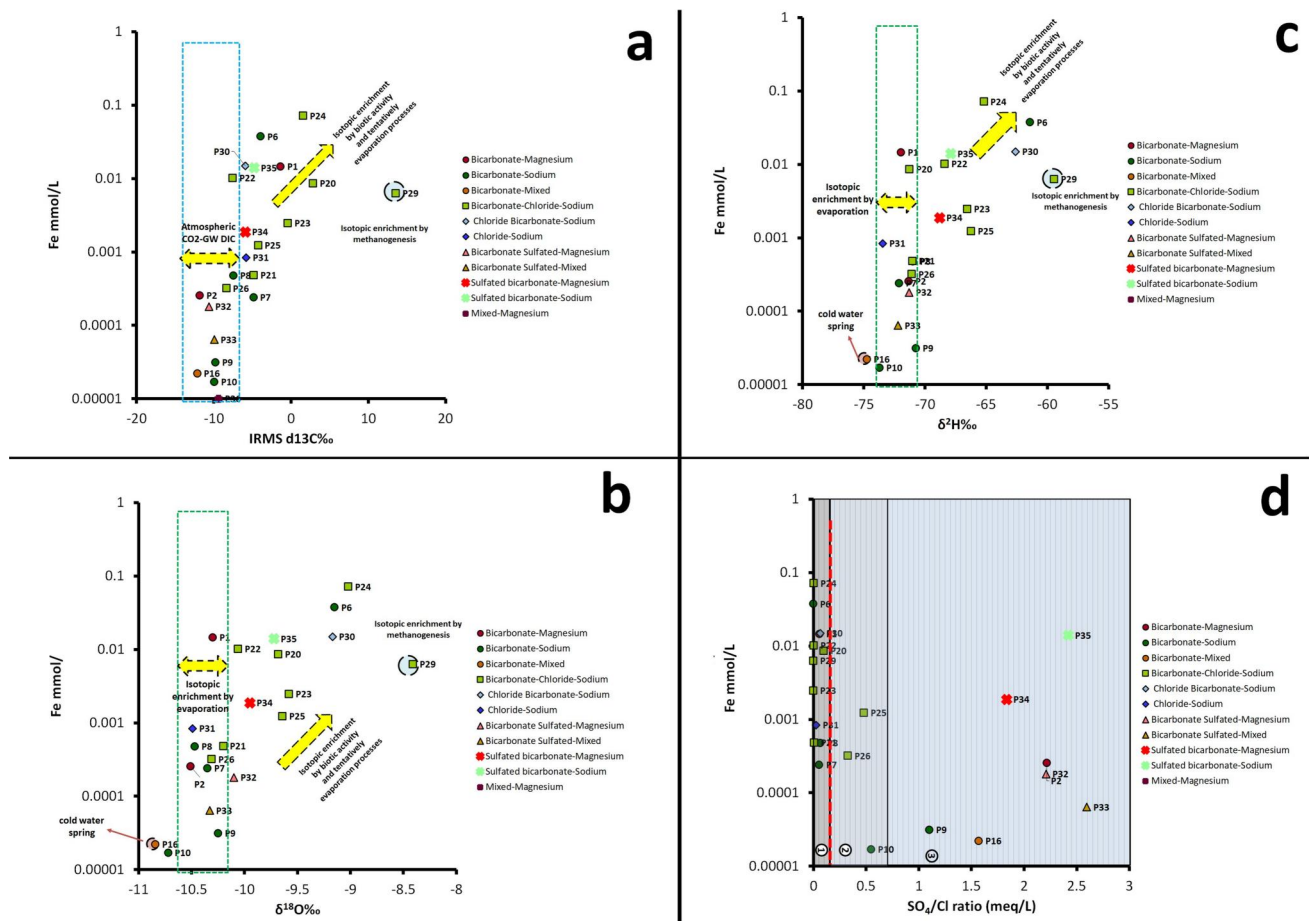


Fig. 5 **a** Evaluation of the behavior of $\delta^{13}\text{C}$ vs Fe^{2+} in sampled wells and corresponding hydrogeochemical classification **b** Evaluation of the behavior of $\delta^{18}\text{O}$ vs Fe^{2+} in sampled wells and corresponding hydrogeochemical classification **c** Evaluation of the behavior of $\delta^2\text{H}$ vs Fe^{2+} in sampled wells and corresponding hydrogeochemi-

cal classification **d** SO_4/Cl ratio (meq/L) vs Fe mmol/L where SO_4/Cl ratio values meaning: (1) samples with ratios < 0.15 are subject to S removal due to sulphates precipitation or bacterial metabolism, (2) common ratio for rainfall varies between 0.15 and 0.7, (3) samples with ratio > 0.7 have additional S derived from geochemical sources,

or catalyze biodegradation processes such as the simple mobilization of salts, humification of organic matter, silicate, and carbonate weathering, and the mineralization of N_{org} , cellulose fermentation, acetogenesis, iron reduction, sulfate reduction, methanogenesis and CO_2 reduction (Hounslow 1995).

The hydrogeochemical and isotopic behavior of the sampled wells (Figs. 2, 3, and 6), indicated processes related to the nitrogen incorporation into the aquifer as a result of anthropogenic pollution such as sulfate reduction and methanogenesis (e.g., P22, P8, P34, P30, P31, P7, P21, P6, P1, P23, P20, P24, P29), these wells had an isotopic signature of $\delta^{13}C$ between -20 ‰ and -9 ‰. Wells with a high value of $\delta^{13}C$ (between -9 ‰ and $+1$ ‰) indicate that CO_2 may be linked to the possible participation of marine limestones (regional flow) such as those located east-northeast of the study area (e.g., P23), although, this process is unlikely because the limestones are located at considerable depth and it is difficult to affect the entire aquifer. Described below are the processes that could provide evidence of the variables governing the hydrogeochemical and isotopic behavior of the aquifer.

4.1 NO_3^-

During the transition from oxic to anoxic conditions in the aquifer, we identified the wells with the greatest nitrate concentrations in the first environment and the wells with the highest ammonia nitrogen concentrations in the second environment (Fig. 2c). The wells located in the recharge zone of the study area (e.g., Tlalpan and Xochimilco) have the lowest $\delta^{18}O$ and δ^2H values in conjunction with high NO_3^- contents, whereas the wells located in the agricultural zone (e.g., Milpa Alta, Tlahuac) have the highest $\delta^{18}O$ values in conjunction with higher NO_3^- contents; in both cases, the source of NO_3^- may be due to the incorporation of wastewater or recently infiltrated water in agricultural areas (Figs. 1, 3, 6a, b, and c, 7a); however, additional studies (particularly with nitrogen isotopes) are required to identify the specific sources. This is primarily because of the complexity of evaluating the isotopic behavior of $\delta^{18}O$ and δ^2H in conjunction with the behavior of NO_3^- in water, as the migration of water from recharge to confined areas decreases oxygen in the aquifer (Paces et al. 2001; Paces and Šmejkal 2004; Burns and Kendall 2002; Kendall et al. 2007). On the other hand, it has been observed in other studies that the intensive use of nitrogen

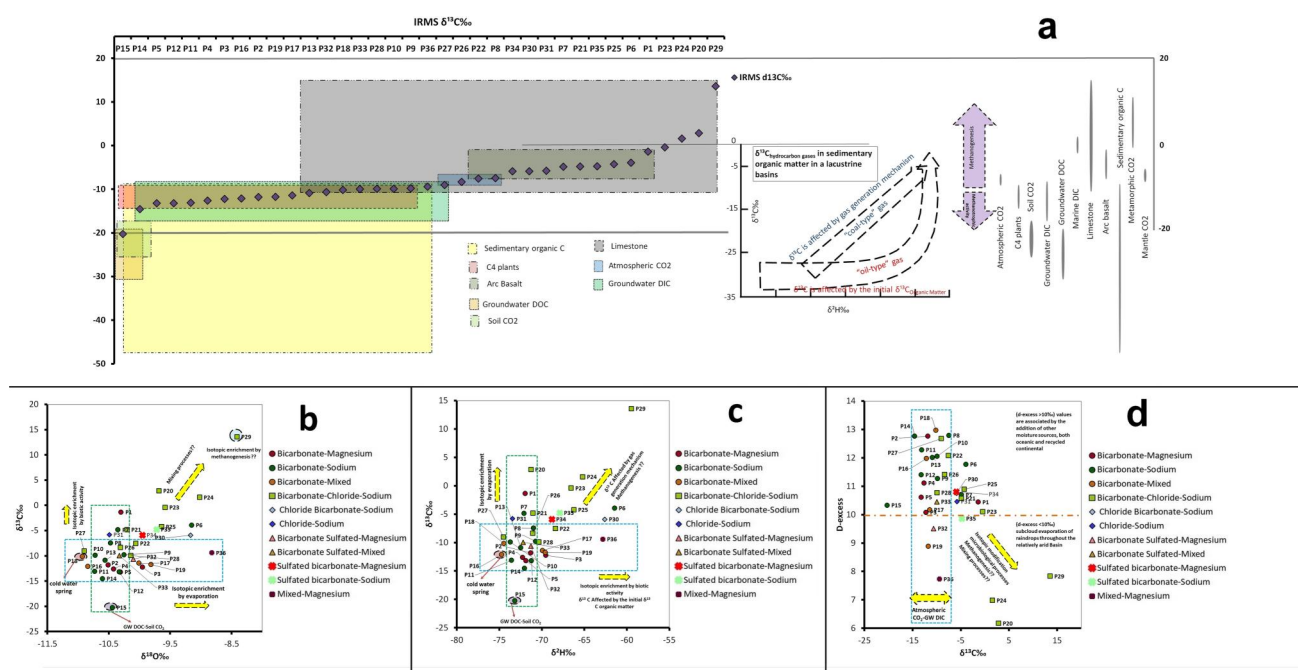


Fig. 6 **a** $\delta^{13}C$ values of water samples collected in the study area, where colored squares represent the $\delta^{13}C$ values in groundwater in different environments and from different geological materials (Clark, 2015; Rollinson and Paese 2021). Arrows indicate tentative ranges of microbial methane, where schematic trends of methanogenesis and methanotrophic activities are divided. The $\delta^{13}C$ vs δ^2H plot represents the isotopic behavior of ^{13}C in a sedimentary basin where gas is

produced proposed by Chen et al. (2022). The estimated initial $\delta^{13}C$ value is -10 ‰ which is a typical value in carbonate aquifers (Avrahamov et al. 2015) **b** Evaluation of $\delta^{13}C$ and $\delta^{18}O$ in water samples from the study area, **c** Evaluation of $\delta^{13}C$ and δ^2H in water samples from the study area, **d** Evaluation of $\delta^{13}C$ and d-excess in water samples from the study area

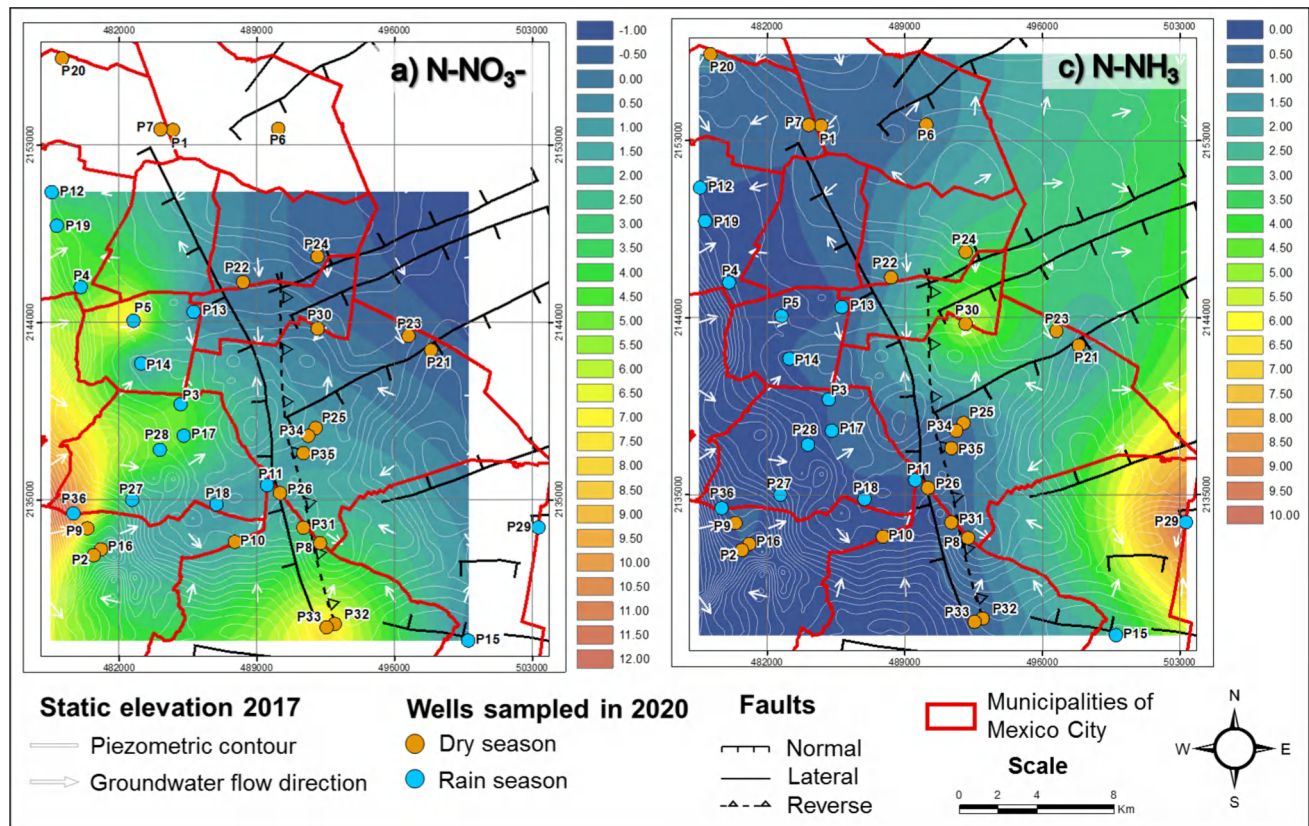


Fig. 7 Distribution of the iso-concentrations of **a** NO_3^- and **b** NH_3

compounds, particularly in the transformation of nitrogen species, can lead to an increase in the isotopic values of $\delta^{18}\text{O}$ in the nitrogen species (Clark 2015). Several of the wells with the highest concentration of NO_3^- and the lowest values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Figs. 1, 2b, 3b and c) may be the result of isotopic fractionation caused by intensive evaporation in the basin plain or condensation in elevated zones (Fig. 2b). Ortega-Guerrero et al. (1997) observed that the infiltration of rainwater causes significant evaporation, which modifies the isotopic values of $\delta^{18}\text{O}$ prior to the water reaching the aquifer in the study area. Before rainwater reaches the aquifer, significant evaporation can occur due to the sluggish infiltration rate (Burns and Kendall 2002).

According to the results obtained when comparing d-excess vs NO_3^- , the water samples with a value $>10\%$ of d-excess have significant NO_3^- concentrations (mainly P5, P33, P28, P3, P17, P9, and P4 wells); these samples are preferentially located in these areas (Fig. 3d), indicating that the incorporation of NO_3^- occurs in elevated areas, whereas the water samples with the highest NO_3^- and a value $<10\%$ of d-excess are found in the transition boundary zone between the beginning of the sedimentary basin and the end of the volcanic zone.

The results of this study indicate that anthropogenic activities impact water quality, which in turn can affect the characteristics of groundwater. This process is more evident by the analysis of d-excess and the comparison with NO_3^- and NH_3 above, as there is a significant variation in the value of d-excess among water samples that are relatively close geographically and have a similar geological environment. In this study, the incorporation of nitrogen compounds from wastewater infiltration into the recharge zone that migrates from oxidizing to reducing zones in the deep aquifer is one of the most important sources of -poor-quality water; however, the presence of cemeteries and surface bodies with evidence of eutrophication, which is close to faults, also could be an environmental implication (e.g., P2, P29 and P16 near to a local cemetery and P8 near to San Lorenzo civil pantheon, or P29 next to Chalco Lake, P32 P33 and P15 next to Amecameca river or P8, 31 and P26 near to Chalco channel, and P13, P22, and P24 next to the intubated Gran Desagüe channel and Piedad river). Robertson et al. (2012) showed that the infiltration of septic waste in groundwater from Long Point, Ontario, increased the concentration of NO_3^- in the groundwater. They also observed that a contamination plume was formed, mainly at the top of the plume where the nitrification of the $\text{NH}_4^+ - \text{NO}_3^-$ begins; in the core

of the plume, anammox oxidation of NH_4^+ using NO_3^- and N_2 is produced, and the denitrification of NO_3^- – N_2 occurs below the plume, these processes may occur in P15 and P32 wells, which show NO_3^- and NH_3 concentrations at the same time (Table 1 SM). Regularly, in a reaction that converts both species to elemental nitrogen, N_2 , anammox bacteria use NH_4^+ as an electron donor and NO_2^- is produced by partial reduction of NO_3^- as an electron acceptor (Reimann et al. 2015).

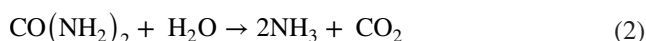
Due to the complexity of the processes involved in the poor-quality water by the presence of different species and elements (e.g., N– NH_3 by the possible incorporation of wastewater or the application of N fertilizers), it was necessary to evaluate the transformation of reactive nitrogen species in the water in conjunction with the isotopic behavior of $\delta^{13}\text{C}$, $\delta^2\text{H}$, and $\delta^{18}\text{O}$ to identify the possible sources (Hounslow 1995), mainly because these reactions can modify isotopic values of $\delta^{13}\text{C}$ (as well as in some cases $\delta^2\text{H}$). It is important to note that during certain other processes (aerobic bacterial processes that use oxygen to carry out their metabolic processes), large amounts of oxygen are required.

Considering that some sequences and reactions are related to the transformation of nitrogen species (e.g., reactions 1 to 6 and 9 to 11), the oxide-reducing conditions of the study site were considered from the following reactions:

Organic degradation of N where NH_2 reacts with H^+ and an oxidation reaction occurs (in a reducing medium) that generates NH_3 (1)

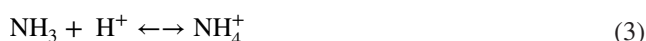


Decomposition of urea with the participation of microorganisms that generate NH_3 and CO_2 in the medium (Reaction 2)



Bacterial decomposition in an oxidizing medium releases CO_2 and produces NH_3 and RCOOH (carboxylic acid groups).

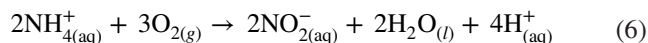
RCHNH_2COH Ammonia ionization where NH_3 reacts with H^+ (in a reducing medium) that generates NH_4^+ (and OH^-) (Reactions 3 and 4)



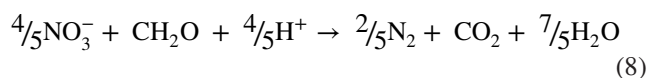
Volatilization of ammonia from aqueous to gaseous form (reaction 5)



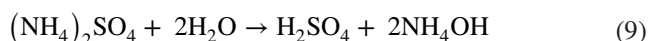
The ammonium ion in an oxidizing medium reacts with oxygen, producing NO_2^- which immediately transforms into NO_3^- (Reactions 6 and 7).



Transformation of nitrates to nitrogen and release of CO_2 (Reaction 8).



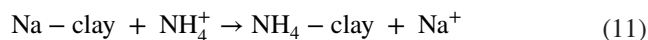
Transformation of manure (Reaction 9).



Transformation of ammonium hydroxide to ammonia (Reaction 10)



Sorption of ammonium in clays by ion exchange processes (Reaction 11)



4.2 NH_3

The possible source of natural nitrogen in reaction 11, was postulated by Ortega-Guerrero et al. (1997) in the study area, according to modeling, the mobilization of NH_4^+ is significantly delayed by the presence of clays, due to the reversible sorption of ammonia by ion exchange processes with a selectivity coefficient close to that of K^+ (Hounslow 1995; Clark 2015).

As NH_3 concentrations increase in the samples analyzed, the deuterium isotope also increases, as observed in wells P29, P30, P24, P23 (Fig. 4c and 7b). This behavior is related to the reactions previously proposed as microbacterial metabolic processes (in which methanogenesis is included as a process that occurs in anaerobic conditions; reactions 2, 4, and 8), as evidenced by the isotopic grouping in the ^{13}C vs NH_3 concentrations (Figs. 3, 4 and 6), in which this group of samples is separated from the others and exhibits an increase in the concentration of NH_3 and the value of ^{13}C . This phenomenon is associated with the production of CO_2 gas, which modifies the isotopic signature of ^{13}C (Fig. 6a and c); a specific instance occurs with sample P15, which has the maximum concentration of NH_3 depleted in $\delta^{13}\text{C}$ without a change in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values. Similarly, this behavior responds to the previously mentioned reactions (e.g., reactions 6, 8 and 10), although in this case, an isotopic

modification of ^2H does not occur during the increase of NH_3 and the generation of ^{13}C (Figs. 3, 4, and 6). This phenomenon is related to an initial concentration of nitrogen in the sediment deposit of lacustrine origin, and an initial value of ^{13}C associated with the presence of organic matter in this sediment (Fig. 6a and c) or may be related to methanotrophic process (due to organisms capable of oxidizing methane, common in biotechnological bioremediation techniques).

The previously obtained results (Fig. 2b, c, and d), could provide evidence of redox and biogeochemical processes occurring in wells hosted in the semiconfined aquifer since the wells with the highest values in $\delta^{13}\text{C}$ have a very low SO_4/Cl ratio (<0.15), high NH_3 contents and Eh–pH conditions corresponding to an anoxic system (e.g., P20, P23, P24, P29, P30, and P35; Figs. 2c, 4 and 6). In these wells, a low presence of SO_4^{2-} is probably due to sulphate precipitation or bacterial metabolism (mainly in samples hosted in suboxic-anoxic environments), as has been observed in other studies (Dogramaci et al. 2017).

The wells with simultaneous NO_3^- and NH_3 presence (P15 and P32) and an average $\delta^2\text{H}$ isotopic value between -75‰ and -70‰ and an average $\delta^{18}\text{O}$ isotopic value between -11‰ and -10‰ (Table 1 SM), coincide with those whose $\delta^{13}\text{C}$ values are more negative (for P32 $<10\text{‰}$, for P15 $<20\text{‰}$); the presence of both nitrogen species suggests that reactive nitrogen is transformed (where the value of $\delta^{13}\text{C}$ depletes), this behavior may be a consequence of the incorporation of wastewater.

The behavior samples that show an isotopic increase of $\delta^{18}\text{O}$ as the N– NH_3 content may result from a common process related to biotic activity (in which methanogenesis may even be occurring) (Fig. 4a, b, and c) (e.g., P31, P34, P35, P25, P6, P21, P30, P20, P23, P24, P29). The wells with the highest N– NH_3 concentrations have $\delta^{18}\text{O}$ values between -9.5‰ and 8.5‰ , which differs from the isotopic range of meteoric water in the study area (between -11‰ and -10‰), (Table 1 SM). Isotopic nitrogen analysis (either ^{14}N or ^{15}N) would be required to confirm the occurrence of this process.

4.3 $\delta^{13}\text{C}$

As depicted in Fig. 6a there are both organic and inorganic potential sources of $\delta^{13}\text{C}$ in the water samples of the study area, based on the references proposed by Clark (2015) and Rollinson and Paese (2021), with the influence of sedimentary organic carbon and limestone being this one the most prominent (Fig. 6a). However, other sources of C may be influencing wells as P15, showing the incorporation of CO_2 from the soil in conjunction with dissolved organic carbon (DOC) typical of groundwater interacting with an organic environment. Atmospheric CO_2 may be incorporated in wells P27, P26, P22, and P8; although these wells present

an isotopic signature similar to carbonate rocks, this type of rock is uncommon in the study area; therefore, its significance due to carbonate dissolution is not likely, although secondary carbonate alteration in the volcanic rocks is possible. Samples P22, P8, P34, P30, P31, P7, P21, P35, P25, P26, and P1 have an isotopic $\delta^{13}\text{C}$ value comparable to that of basaltic arc rocks. However, it should be noted that even though the $\delta^{13}\text{C}$ isotopic signature coincides with basaltic arc rocks, the basalts in this region result from the lower crust partial melting (Márquez 1999). Therefore, various questions arise about this group of samples: (a) Does the isotopic signature of ^{13}C reflect atmospheric CO_2 from recently infiltrated water? (b) Does the isotopic signature of ^{13}C reflect the dissolution or alteration of the lithological environment in which the water is hosted? (c) Does the isotopic signature reflect a process related to a microbial activity that enriched the value of ^{13}C ? Almost all wells that have an isotopic value of $\delta^{13}\text{C}$ related to organic C sedimentation have a $\delta^{13}\text{C}$ value similar to groundwater DIC and C4 type plants. A special case is the P29 well (and relatively P30 and P24 wells that are adjacent to the “Gran Desagüe” –meaning great wastewater channel–, with a high $\delta^{13}\text{C}$ value), this behavior could be related to microbial metabolic processes involved in methanogenesis (Birgel et al. 2015). Evidences of these processes are its high isotopic modification of the ^{18}O and ^2H values (more positive than all the samples), a very low SO_4/Cl ratio, and a low Eh value, in addition to its location very close to Lake Chalco; all these characteristics evidence that biotic processes, in a reducing environment, could be occurring, although further studies would be necessary to confirm this process. Since in the study area volcanic rocks predominate, the water is extracted from fractured basalts, and carbonate rocks serve as a deep basement that does not outcrop in the region, the $\delta^{13}\text{C}$ isotopic signature of some wells could be affected by processes such as bacterial activity (which can even result in methanogenesis in specific locations), particularly in P29 well as discussed above (Fig. 6a).

The evaluation of $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ vs $\delta^2\text{H}$ behavior revealed a gradual and dispersed modification in the isotopic signatures in various proportions as the water evolves from bicarbonate-magnesium, bicarbonate-mixed, and bicarbonate-sodium, towards sodium bicarbonate chloride water type (Fig. 6b and c). The isotopic behavior may be attributable to several processes that are not necessarily mutually exclusive, such as oxygen and hydrogen depletion caused by evaporation during infiltration (e.g., P16, and possibly P18, and P27 wells) and migration toward the center of the Basin (e.g., P11, P10, P14, P13, P2, P4, P12, P5, P9, P26, P33, and P8), as reported in other works (Herrera et al. 2006). In addition, at specific sites (e.g., P28, P32, P22, P17, P3, P19) there is a possibility of wastewater infiltration. Another group of water samples, which are located in

a suboxic-anoxic environment, present an increase in $\delta^{13}\text{C}$, higher than -7.55 ; in this group, bacterial metabolic processes affect the $\delta^{13}\text{C}$ isotopic signature (making it more positive), possibly due to the incorporation of wastewater in a reducing (e.g., P1, P21, P7, P31) or extremely reducing environment (e.g., P24, P23, P20, P25, P6, P35, P34) even up to methanogenesis (e.g., P29). This behavior was also observed when comparing $\delta^{13}\text{C}$ vs. d-excess values, particularly for those with d-excess <10 ‰ (Fig. 6d). These samples may be affected by a higher evaporation rate, which caused the increase in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic signature. The samples with a higher value of $\delta^{13}\text{C}$ show a $\text{SO}_4/\text{Cl} < 0.15$ ratio and values of d-excess <10 ‰ (besides samples with a value close to 10 ‰ of d-excess) (Figs. 2, 5, and 6); such conditions are suitable for redox reactions that require consuming S or N releasing C (S removal due to sulfates precipitation or bacterial metabolism). In other studies, it was found that anaerobic respiration during microbial metabolic processes could be involved in the isotopic modification of $\delta^{13}\text{C}$ (e.g., denitrification, although it must be clarified that it does not occur in water with low nitrate concentrations) via carbon fixation processes as an energy source since organic carbon is required for these reactions to occur (Van Stempvoort et al. 2015; Vandekerckhove et al. 2019; Han and Plummer 2016). This phenomenon does not typically occur in oxygenated water where aerobic bacteria outperform denitrifiers for available carbon substrates (Clark 2015); according to Morales-Arredondo et al. (2022), S removal due to sulfate precipitation occurs in specific zones in the aquifer. All these wells show high values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Fig. 6b and c). This work considers that this behavior could be due to the residual oxygen becoming heavier because of water evaporation processes and the simultaneous diffusion of oxygen to the water caused by hydrodynamic dispersion, but a slight increase could also occur in both isotopes by redox processes, in which bacterial metabolism may be involved.

4.4 Methanogenesis conditions

Agriculture with intensive use of nitrogen compounds and their transformations may be involved in modifying the isotopic signature of $\delta^{18}\text{O}\text{--NO}_3^-$, this should be confirmed by this specific analysis in future studies, even though nitrate does not readily exchange $\delta^{18}\text{O}$ with water and it can only modify its signature through denitrification or anammox reactions (Clark 2015).

Although evaluated wells in this study showed no evidence of methanogenesis (only P29 has a very high $\delta^{13}\text{C}$ value) this does not rule out this possibility, we must emphasize that the P15 well (next to Amecameca River) has the most significant decrease in $\delta^{13}\text{C}$, one of the most reducing conditions, and the highest pH of all samples (Fig. 2a, b, c,

d, e, and f). In this case, it is possible that a methanotrophic process (associated with organisms capable of oxidizing methane, common in biotechnological bioremediation) is taking place. However, further studies are required to confirm this process since, as other works have observed, the decrease only in $\delta^{13}\text{C}$ may be due to microbacterial activity (Clark 2015). Besides, in environments with a very intense redox evolution, there is evidence that methane-generating archaea (by archaeal reduction of CO_2 with H_2) tend to decrease $\delta^{13}\text{C}$, but high $\delta^2\text{H}$ (in water) because of the incorporation of hydrogen from water (a situation that can occur in P15). Acetoclastic archaea are less discriminating and produce methane higher $\delta^{13}\text{C}$ values but more decreased deuterium because the hydrogen comes from the methyl group in acetate. The organic matter (and the reactive nitrogen species) present in the unsaturated zone and later in the saturated zone can be transformed (NH_4^+ to NO_3^-) by interacting with bacteria and microorganisms. This process has been previously reported in the study area by Montiel et al. (2014), and in this work it is conceivable that this process occurs in wells P32 and P15, which have NO_3^- and NH_3 content and a modification of the ^{13}C isotopic signature.

As previously mentioned, wells located southeast of the City, with high $\delta^{13}\text{C}$ values (greater than $+1$ ‰) or low $\delta^{13}\text{C}$ values (lower than -20 ‰) could be involved with methanogenic or methanotrophic processes by reducing conditions measured in wells (range between 0.00508 and 0.1378 (V) Eh values) or by the incorporation of poor quality water and the participation of microorganisms (e.g., P15, P30, P29, and P32), processes that are not exclusive. Some southeast-located wells may also have ^{13}C isotopic values associated with incorporating biogenic CO_2 and/or atmospheric CO_2 (P22, P27, P26). We also observe that additional CO_2 incorporation may accelerate mineral alteration processes, such as those in the recharge zone (such as P16), or in the central and southern portion of the CDMX, just at the transition boundary between the fractured basalts and the sedimentary Basin (such as P15, P32).

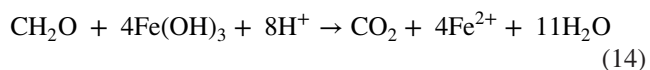
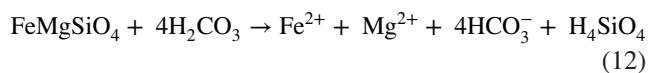
4.5 Silicate weathering

The interaction of surface water with groundwater can result in a series of reactions (e.g., silicates and carbonates weathering) and acceleration of biodegradation processes (e.g., cellulose fermentation, acetogenesis, methanogenesis, CO_2 reduction), as well as an increase in the concentration of ions in groundwater (iron or manganese release by silicate weathering) and the transformation of others (oxidation of metallic iron and reduction of sulfates) (Hounslow 1995; Clark 2015).

In this study, we showed that the heavy isotopes $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$ are more enriched in wells with a higher concentration of Fe^{2+} and more reducing conditions (Figs. 5a,

b, and c), Fe^{2+} concentrations are low in the recharge zone but rise in the central Basin (Table 1 SM). More profound isotopic studies are required to confirm this process, but there is concern about whether this behavior may be related to very reducing environments with the incorporation of residual water rich in organic matter and the presence of bacteria that also produce the release of Fe^{2+} from the aquifer matrix. Another possibility is that as nitrate does not readily exchange oxygen with water, the $\delta^{18}\text{O}$ isotopic value can only be altered by denitrification or anammox reactions (anaerobic ammonium oxidation) (Clark 2015; Kendall and Aravena 2000). To confirm if denitrification or anammox reactions modified the $\delta^{18}\text{O}$ value in the wells with high values of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$, as well as higher contents of reactive nitrogen species (Fig. 1, Table 1 SM), it is necessary to conduct extensive research in the study area (particularly with nitrogen isotopes).

As has been observed in other complicated geological settings (Zhang et al. 2015; Vandekerckhove et al. 2019; Hartland et al. 2011), reducing conditions may regulate the behavior of iron. In the wells with the highest iron content, the highest concentrations of ammonia nitrogen (Table 1 SM) or manganese were found, and vice versa (Table 1 SM). In contrast, those with the lowest iron concentrations also have the greatest nitrate concentrations (Table 1 SM). The volcanic medium (basalt) that dominates the entire region, serves as raw material for mineral alteration (ferromagnesian minerals), which can release iron into the water; however, in oxidizing environments, the element precipitates as oxide or hydroxide, whereas in reducing environments, these compounds are not formed, and iron remains free (reactions 12, 13, and 14) (Hounslow 1995; Apelo and Postma 2005; Clark 2015).



5 Conclusions

Some wells in the high altitude zones have high NO_3^- contents, while wells in the lower zones have high NH_3 concentrations. The higher zones function as an oxidizing medium and the lower part becomes reductive due to the semi-confined conditions of the aquifer. Wells with high NH_3 and NO_3^- concentrations indicate the existence of

transformation processes of nitrogen species, which suggests the occurrence of bacterial processes in the aquifer that regulate their transformation. The wells with the highest nitrate concentration show the greatest decrease in $\delta^{13}\text{C}$, and, as the presence of NH_3 in the water increases, the $\delta^{13}\text{C}$ also increases; this phenomenon suggests the transformation of nitrogen species along with the release of CO_2 . The behavior of $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ shows an incipient and scattered common isotopic increase related to various processes, such as oxygen decrease that occurs as water migrates from the upper parts to the confined areas of the aquifer. The wells that show the most oxidizing characteristics are those that present the highest NO_3^- values and the lowest $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$ (and absence of ammonia), but when the ammonia content increases (and the nitrate content is zero), most of the wells in this condition generally show an increase in $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$ (even with a positive value of $\delta^{13}\text{C}$).

The wells hosted in suboxic environments (with tendencies to be anoxic) present an increase in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, and increases in the concentrations of ammonia, iron, and manganese. Which implies that elements sensitive to oxidizing or reducing conditions, such as Fe^{2+} and Mn^{2+} , will remain dissolved in this part of the aquifer. However, one well exhibits the highest decrease of $\delta^{13}\text{C}$, the most reducing conditions, and the most basic pH of all samples but very low concentrations of Fe and Mn, probably due to the particular lithology of the well with the absence of Fe and Mn containing minerals. The wells presenting NO_3^- and NH_3 show a decrease of $\delta^{13}\text{C}$ concerning all the samples, mainly the P15 well (methanotrophic process may occur in this well related to the presence of organisms capable of oxidizing methane). More detailed studies are required in all the study area (especially with nitrogen isotopes) to confirm or discard if denitrification or anammox reactions modified the $\delta^{18}\text{O}$.

The information obtained in this study unravels complex hydrogeochemical processes resulting from the application of isotopes and hydrogeochemistry that could be used at other locations and gives valuable information to decision-makers to manage water quality in the study area.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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