

Groundwater evaluation in magdalena middle valley, Colombia: $\delta^{13}\text{C}$ evolution in dissolved inorganic carbon

Abstract

In the present study, the evaluation of groundwater is carried out with isotopic studies of $\delta^{13}\text{C}$. Isotopic fractionation studies ($\delta^{13}\text{C}$) allowed for the identification of trends in dissolved inorganic carbon (DIC) behavior in groundwater from the northern area of the Valle Medio del Magdalena basin, confirming that different sources contributing to DIC can be distinguished. By complementing the analysis with ^{14}C values, the evolution of DIC in open systems versus closed systems was discriminated. However, due to the heterogeneity of the area, it is important to conduct local characterizations, considering the water mixtures that occur due to the complexity of both the surface and underground aquifer systems. While highlighting the main sources of DIC, it is important to note that they are not the only one present. The results indicate that to the north of the study area the DIC evolution is influenced mainly by inorganic interactions, while to the south fractionations more related to organic interactions are observed.

Keywords: stable isotopes, ^{13}C , DIC, isotopic fractionation, groundwater

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Abbreviations: [...], molar concentration; *ABA*, oil industry supply well; *AE*, strategic area; *BTEX*, benzene, toluene, ethylbenzene y xylene; *C₃*, calvin cycle; *C₄*, hatch-slack cycle; *DIC*, dissolved inorganic carbon; *TOC*, total organic carbon; *DOC*, dissolved organic carbon; *HAP*, polycyclic aromatic hydrocarbons; *LIA*, environmental engineering laboratory of the universidad nacional de colombia; *MEGIA*, multiscale model for integrated water management (Project); *MO*, organic matter; *TDS*, total dissolved solids; *VMM*, middle magdalena valley

Introduction

Groundwater is a vital source of freshwater, representing up to 94% of the easily accessible freshwater.¹ Groundwater chemistry is influenced by water composition in the recharge zone and chemical interactions with geological compounds.² Chemical compounds in groundwater include dissolved inorganic species, atmospheric gases, and organic compounds, some of which can be contaminants.^{2,3} The ^{12}C and ^{13}C stable isotopes of carbon are of great significance for tracing the carbon fluxes in the carbon cycle. The isotopic fractionation of ^{13}C can help determine the origin and evolution of carbon in a process. The value of $\delta^{13}\text{C}_{\text{DIC}}$ in groundwater can indicate whether any subsequent inorganic reactions have occurred in the subsurface, as well as allow the evaluation of processes such as anaerobic oxidation, respiration of microorganisms, and biodegradation of organic contaminants in groundwater.³ Additionally, radiocarbon (^{14}C) can be used to determine the origin and evolution of dissolved CO_2 in water, using as a reference the activity of ^{14}C (percent of Modern Carbon pMC) in the living biosphere to determine the age of carbon in the samples. Unlike $\delta^{13}\text{C}$, radiocarbon is unambiguous in characterizing the conditions under which weathering of ancient carbonates occurred. Under open-system conditions, CO_2 exchange between the DIC and soil during carbonate weathering will impart ^{14}C activity from CO_2 (soil) in the DIC, maintaining a $^{14}\text{C}_{\text{DIC}}$ near 100 pMC or higher. Conversely, under closed system conditions, $^{14}\text{CO}_2$ in carbonate-dissolving groundwater will obtain a significant amount of DIC from free ^{14}C sources and thus the DIC that evolved during these weathering conditions, depending

on the exchange ratio and sources of DIC, will have a $^{14}\text{C}_{\text{DIC}}$ with values near 50 pMC.^{3,4}

Dissolved inorganic carbon (DIC) in groundwater can exhibit different isotopic fractionations, some of which serve as process indicators, such as contamination, biodegradation, and inorganic dissolution. The use of carbon isotopes in groundwater studies can provide important information regarding biogeochemical processes and water quality.⁵ Isotopic values in groundwater can indicate the presence of contaminants, hydrocarbon biodegradation, and other processes, helping to understand the origins of dissolved species and biogeochemical dynamics.³ The aim of this work is to characterize, by $\delta^{13}\text{C}$ values, the behavior of groundwater bodies in area of interest of the MEGIA project. We sought to determine the main source of inorganic carbon and its relationship with organic species such as hydrocarbons.

Study area

The Middle Magdalena Valley (VMM) basin, located in the central region of the country, has been characterized as an intramontane, foreland-type basin, with an approximate extension of 34,000 km².⁶

Hydrogeological context

To the description of the hydrogeological context, the following classification is considered: A) Sediments and rocks with essentially intergranular flow. B) Sediments and rocks with essentially fracture flow. C) Sediments and rocks with limited groundwater resources.⁷ Here are the key characteristics of each unit:

Type A units:

- A1: Alluvial deposit aquifers consisting of non-consolidated sediments. They are regionally extensive with good thickness, specific capacities, and low electrical conductivity.
- A2: The Real Group Aquifer divided into U3 and U4. U3 is a regional multi-layered aquifer, while U4 is an incised alluvial fan. Both have specific capacities and bicarbonate-calcium to sodium hydrochemistry.

- A3: Includes San Rafael Plateau, Alluvial Terraces, Terrace and Alluvial Fan, and Floodplain Deposits. They are locally to regionally limited aquifers with varying hydrochemistry and thicknesses.

- A4: Consists of Alluvial Fan Deposits and Fluvial-Lacustrine Deposits. These are Quaternary aquifers with variable productivity.

Type B units:

- B1: Comprises a regional confined aquifer with intercalations of shales and limestones. It has high specific capacity and possibly brackish water.

- B2: Regional confined aquifers, they have medium specific capacity and possibly brackish water.

Type C units:

- C1: These are continuous regional aquitards and aquicludes with low productivity and variable water quality.

- C2: Includes Jurassic igneous-metamorphic and sedimentary rocks with very low or no productivity but good water quality.

Material and methods

The methodology used consisted of sampling water from the surface and subway sources over a period of 10 days. The physicochemical analyses were performed at the Environmental Engineering Laboratory (LIA for its Spanish abbreviation) of the Universidad Nacional de Colombia and the isotopic analyses were carried out at the Environmental Isotope Laboratory (EIL) of the University of Waterloo; the total number of samples analyzed for each characterization parameter is detailed in Table 1. The analyzed samples were distributed in the study area according to the map shown in Figure 1. The precise location of each sampling point, along with the depth and characterization, is detailed in [Annex A. Geographic location and description of the sampled points](#). For the analysis of the results, the study area was divided into six groups based on their geographic location. The division is as follows:

- I. North of Aguachica: As the name suggests, it corresponds to the samples collected north of the town of Aguachica. These are deep wells ranging from 80 m to 105 m, with surface geological units consisting of floodplain deposits, alluvial fan deposits, and Quaternary terraces.⁷ The hydrogeological units are A3 and A4, with good to regular recharge.
- II. South of Aguachica: South of the town of Aguachica, extending towards the town of San Martín. The wells in this area are located superficially in the Quaternary, over floodplain deposits (M104, W202, W210), alluvial fan and terrace deposits (W204), and alluvial fan deposits (W216). The hydrogeological units are A3, A4, and A1, with good to regular recharge. With depths ranging from 75 m to 168 m, they are situated in Quaternary units, except for well M104, which reaches the third unit of the Real Group (N1r (U3)).⁷
- III. North of the Lebrija River: This zone corresponds to the region that extends from the south of San Martín to the vicinity of the Lebrija River to the north. Generally, the wells in this area have depths ranging from 54 m to 100 m and are located on the Quaternary. The hydrogeological units of these wells are A3 and A4, with good to regular recharge, except for the supply well ABA 4, which reaches the fourth unit of the Real Group (N1r (U4)) with regular recharge.⁷

IV. Between Rivers: It is bounded to the north by the Lebrija River, to the south by the Sogamoso River, to the west by the Magdalena River, and to the east by the Eastern Cordillera. This region has the highest number of sampling points. The artisanal wells and supply wells Chiquita and Santos 6, located on the San Rafael Plateau, reach depths that extend to units U3 and U4 of the Real Group, while the supply wells ECP-2, PCM-1, and PCM-2 reach unit U2 of the Real Group.⁷

V. South of the Sogamoso River: All sampling points located in the area bounded to the north by the Sogamoso River and to the west by the Magdalena River. Most of the wells are situated on the Real Group, except for M601 located where the Colorado Formation crops out and M614 on the San Rafael Plateau. The artisanal wells have depths ranging from 92 m to 165 m, while LLA1 reaches a depth of 300 m and LIZAMA reaches a depth of 303 m. The hydrogeological unit is C1 with regular to poor recharge, except for M614, which has good recharge over hydrogeological unit A3.⁷

VI. West of the Magdalena River: The samples in this group are in various locations from south to north but are delimited to the east by the Magdalena River. It consists of samples taken from supply wells near Yondó and aqueduct wells on the western bank of the Magdalena River. With good to regular recharge over fluvial canal deposits and outcrops of the Real Group, the depths range from 100 m to 125 m for aqueduct wells, while supply wells are in the range of 300 m to 335 m. In the southern part, the supply wells and well 489 reach unit U1 of the Real Group, while moving north, well 506 reaches unit U2 of the Real Group, well 505 continues the Quaternary, and well 504 reaches unit U3 of the Real Group.⁷

Table 1 Standardized methods^{8,9}

S. No	Parameter	Method
1	Alkalinity Bicarbonates	SM 2320 (Indicator)
2	BTEX (Benzene, Toluene, Ethylbenzene and Xylene)	Own method
3	Total Organic Carbon (TOC)	SM 5310 C
4	Chemical Oxygen Demand (COD)	SM 5220 C
5	Fats and Oils	SM 5520 B
6	Polycyclic Aromatic hydrocarbon (PAH)	Own method
7	Total Petrogenic Hydrocarbon (TPH)	Own method
8	pH	SM 4500 H+B
9	Temperature	SM 2550 B

Field measure parameters

Multiparametric equipment was used to measure the pH, conductivity, and water temperature. This equipment was provided by LIA.

Physicochemical analysis

The test methods used for the physicochemical parameters evaluated were mostly standardized from the Standard Methods manual,⁸ as detailed in Table 2. The tests performed using their own methods were based on standardized test methods from the American Public Health Association (APHA), American Water

Works Association (AWWA) and Water Pollution Control Federation (WPCF) manuals.⁸ The total alkalinity, hardness, and sulfides were analyzed by volumetry. Chloride, sulfate, and fluoride anions were analyzed by liquid chromatography, while metals were quantified by atomic absorption spectroscopy.^{7,8} In the case of organic species, fats and oils were prepared by the liquid-liquid extraction method, in which the analytes were passed by the solubility difference between water and hexane, and then distilled and quantified by gravimetry, that is, the difference between the initial and final weights of the balloon used. For PAHs, a liquid-liquid extraction was performed, similar to the previous one, but this time the organic solvent was dichloromethane, which was concentrated to a volume of 2 mL and analyzed by gas chromatography with mass spectrometry (GC/MS) to quantify and identify the compounds.^{8,9} In the case of BTEX, the same analytical method was used, but the analyte extraction and concentration steps were omitted because the detection limits were parts per billion ($\mu\text{g/L}$), making direct reading possible. This is done using the headspace technique, in which a sample volume is heated to 85°C for 50 min so that there is a thermodynamic equilibrium in the liquid and vapor phases, of which one mL is taken, injected, and analyzed.^{7,8}

$\delta^{13}\text{C}_{\text{DIC}}$, $^{14}\text{C}_{\text{DIC}}$, and $\delta^{13}\text{C}_{\text{DOC}}$ in the corresponding dissolved species.¹¹ For carbon species, different preparation techniques were followed depending on their nature (organic or inorganic, stable, or radioactive). Thus, in the case of $\delta^{13}\text{C}_{\text{DIC}}$, a sample aliquot equivalent to 0.2 mg of carbonate was extracted according to the concentration supplied in the chain of custody and injected into a 12 mL borosilicate vial filled with helium. Then, a small volume of 85% phosphoric acid (H_3PO_4) was injected, and the vials were shaken to achieve a complete reaction, in which the inorganic carbon passed into CO_2 in the headspace. The vials were then placed in an automatic sampler and analyzed using a mass spectrometer. In the case of $\delta^{13}\text{C}_{\text{DOC}}$, the water sample was placed in a 12 mL vial and treated with phosphoric acid and bubbled with a helium stream to remove carbonates (DIC) generated by CO_2 dissolution. Potassium persulfate was then added, and the sample was sealed in a vial and heated to 100°C . During heating, the DOC in the sample was oxidized to CO_2 , and then CO_2 is analyzed in the same way as for $\delta^{13}\text{C}_{\text{DIC}}$. The variation in the results is $\leq 0.2\%$. In the case of $^{14}\text{C}_{\text{DIC}}$, 3 mg of carbon is required for joint $^{14}\text{C}/\delta^{13}\text{C}_{\text{DIC}}$ analysis, passed to CO_2 in the same manner as for $\delta^{13}\text{C}_{\text{DIC}}$, then reduced to graphite and measured in a Pelletron 1.5SDH-1 accelerator (AMS). The accelerator produces measurements with an accuracy of 0.3% (10).

Table 2 Samples analyzed in area of study

	Physicochemical analysis	$\delta^{13}\text{C}_{\text{DIC}}$	$\delta^{13}\text{C}_{\text{DOC}}$	$^{14}\text{C}_{\text{DIC}}$
N. of samples	179	44	34	42

Results

Results of experimental analysis is detailed in **Annex B. Physicochemical and isotopic analysis of water in the Middle Magdalena Valley**

$\delta^{13}\text{C}_{\text{DIC}}$ vs $1/[\text{DIC}]$

In Figure 2, the different evolutions of $\delta^{13}\text{C}_{\text{DIC}}$ and $[\text{DIC}]$ are depicted for the six sampled zones, highlighting the potential carbon sources. Near Aguachica, there was an exception in sample W216 (a 90-meter deep well in Barranca de Lebrija) with a $\delta^{13}\text{C}$ value of -7.68% , suggesting contributions from atmospheric or geogenic CO_2 . Other samples exhibited more negative fractionation, which correlates with nearby soil-derived CO_2 and the presence of C_4 plant crops. However, some samples (M113 and M111 aqueduct wells) suggest organic CO_2 contributions, although not directly linked to hydrocarbon species, because their degradation products would display more negative $\delta^{13}\text{C}$ values. Groundwater displays complex interconnections and potential mixing of different water sources in certain samples. In southern Aguachica, well M104 exhibits a distinct pH and reaches a different geological unit compared to the other samples. Similarly, wells M119 and M121, located in the same zone at the same depth (80 m) and reaching the Quaternary layer, displayed similar pH and $[\text{DIC}]$ values but differed in $\delta^{13}\text{C}$ values (-17.44% and -14.90% , respectively), indicating intricate groundwater interconnections and suggesting mixed water sources. These results indicate that the variation in fractionation is independent of pH, suggesting that water provenance may result from various processes. North of the Lebrija River, an increase in dissolved inorganic carbon (DIC) concentration was observed with increasing pH, indicating an evolution toward closed systems with limited CO_2 input during flow pathways. At point ABA 4, despite the low pH, there was a high concentration of DIC, suggesting contributions from carbonate mineral dissolution and biodegradation of organic species.

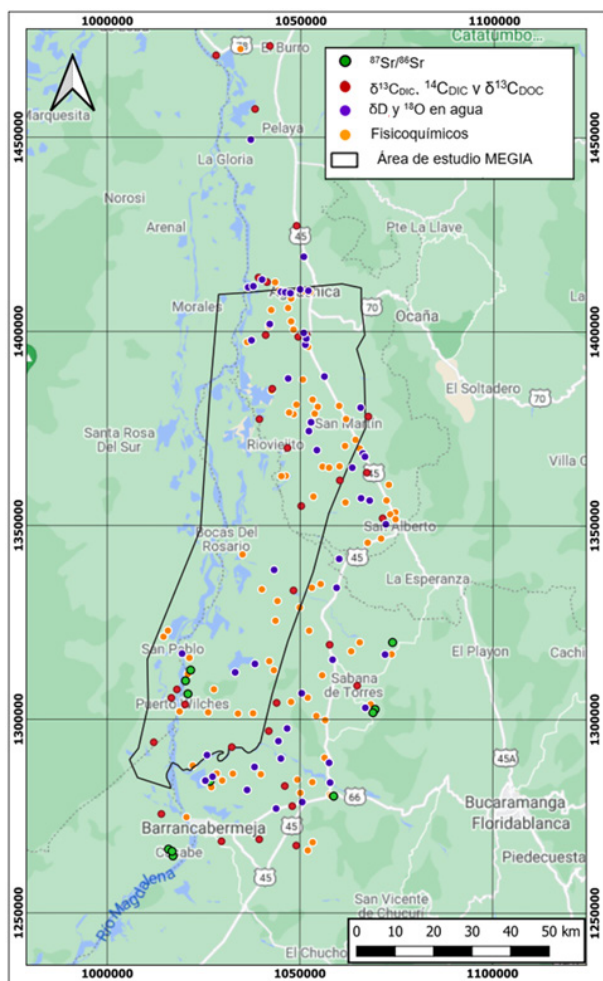


Figure 1 Sampling points for isotopic analysis and physicochemical characterization.

Isotopic analysis

The EIL laboratory follows rigorous technical procedures, complying with Quality Control according to the ISO 17025 technical standard.¹⁰ The tests performed were aqueous analyses for the species

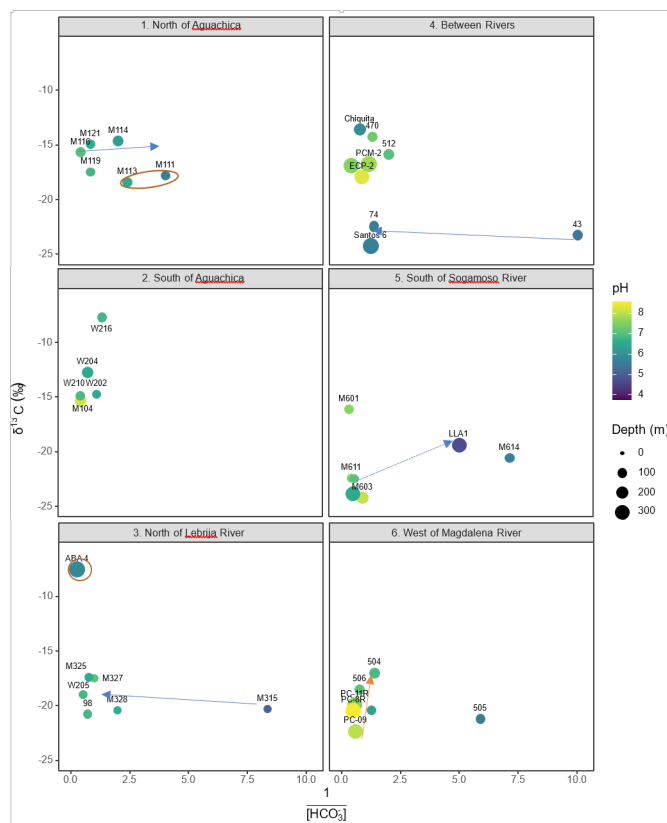


Figure 2 $\delta^{13}\text{C}_{\text{DIC}}$ vs $1/[\text{DIC}]$.

In the southern zones (Entre Ríos and south of the Sogamoso River), the lowest $\delta^{13}\text{C}$ values are observed, indicating increased DIC input from the biodegradation of organic matter. In the area west of the Magdalena River, although the values are not as negative as those in the northern areas, they remain more negative than those in the southern areas. Different behaviors were observed in Entre Ríos; some samples showed highly negative fractionation and low DIC concentration, while others exhibited similar fractionation but higher DIC concentration, suggesting different processes governing DIC evolution, potentially involving organic species biodegradation (Figure 3). Some samples displayed a decrease in $\delta^{13}\text{C}$ fractionation with increasing pH and DIC concentration, indicating carbonate dissolution, which can occur when DIC originates from inorganic sources. In these samples, limited interaction with the soil occurred because of the predominant local cultivation practices. Wells near the eastern margin of the Magdalena River (PCM-1, PCM-2, and ECP-2) exhibit mixtures of various sources and processes, likely because of their proximity to the river. The increase in DIC from points 43 to 74 is primarily associated with subsurface organic matter degradation or hydrocarbon products, as reflected by the high fractionation and increased DIC concentration, irrespective of pH variation. South of the Sogamoso River, a relationship was observed between pH and DIC concentration, but due to the variation in $\delta^{13}\text{C}_{\text{DIC}}$, pH, and DIC values, an open evolving system with different sources and processes was suggested.

Along the western margin of the Magdalena River, a correlation was observed between the DIC concentration and pH, with predominantly high values. However, point 505 deviated from this trend, indicating a better hydraulic connection with the Magdalena River or another nearby surface source. In conclusion, significant variations in $\delta^{13}\text{C}$,

pH, and DIC concentration across different zones indicate the influence of diverse sources and processes in the evolution of DIC in the studied region.

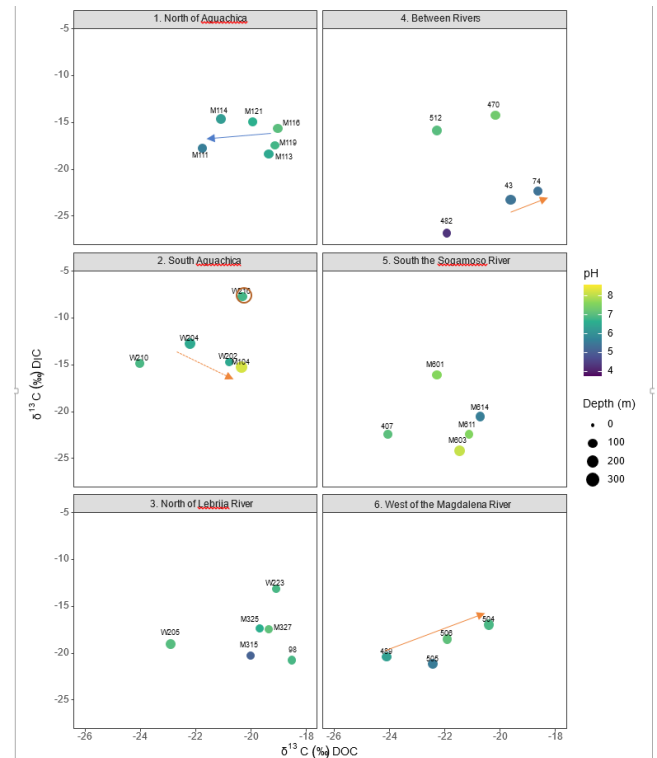


Figure 3 $\delta^{13}\text{C}_{\text{DOC}}$ vs $\delta^{13}\text{C}_{\text{DIC}}$.

$\delta^{13}\text{C}_{\text{DOC}}$ vs $\delta^{13}\text{C}_{\text{DIC}}$

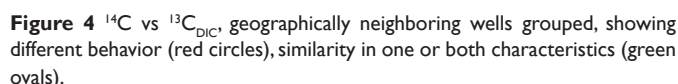
The fractionation of dissolved organic carbon (DOC) exhibits greater homogeneity than that of dissolved inorganic carbon (DIC). This suggests that the current organic source in the aquifer did not predominantly control the evolution of inorganic carbon. To the north of Aguachica, $\delta^{13}\text{C}_{\text{DOC}}$ values hover approximately -20‰ , while the fractionation for DIC was slightly more positive. Conversely, in the southern region of Aguachica, the fractionation of DOC became more negative, whereas that of DIC decreased. These contrasting trends imply that different processes influence the evolution of inorganic carbon in this area, questioning the significance of current DOC as a major source. In the analysis conducted north of the Lebrija River, no distinct trend was observed in $\delta^{13}\text{C}_{\text{DOC}}$ concerning local flows, unlike observations made with $\delta^{13}\text{C}_{\text{DIC}}$ and $[\text{DIC}]$. This confirms that dissolved organic carbon species (DOC) do not play a crucial role in the evolution of inorganic carbon in this zone. Entre Ríos presents an absence of correlation between the fractionations of DOC and DIC, except for wells 43 and 74, which exhibit similar trends. However, owing to the wide variation in DIC concentration, it appears that different carbon sources contributed to the evolution of DIC. No significant correlations were observed between DOC fractionation and DIC in the southern region of the Sogamoso River.

Along the western margin of the Magdalena River, a general trend of increasing fractionation was observed for both DOC and DIC, except for well 505, which deviated from this pattern. This suggests a potential connection between wells on the eastern margin of the Magdalena River and the behavior of well 505. This indicates that the substantial degradation of organic species contributes significantly to the evolution of dissolved inorganic carbon (DIC) in this specific area.

such as extracted hydrocarbons. The supplying wells in the western Magdalena region show similarities in terms of dissolved inorganic carbon concentration ([DIC]), isotopic fractionation ($\delta^{13}\text{C}_{\text{DIC}}$), and the percentage of modern carbon (pMC). These similarities suggest a strong relationship between dissolved inorganic carbon in the aquifer and the biodegradation of hydrocarbon species. Furthermore, the similarity in [DIC] values implies that these wells receive a comparable contribution of dissolved inorganic carbon, potentially linked to the presence of hydrocarbons within the aquifer. Isotopic fractionation ($\delta^{13}\text{C}_{\text{DIC}}$) analysis indicated that the predominant origin of inorganic carbon in these wells is organic in nature. The observed $\delta^{13}\text{C}_{\text{DIC}}$ values deviated significantly from the expected fractionation associated with atmospheric CO_2 , soil CO_2 , or geogenic CO_2 inputs.

Analysis of $^{14}\text{C}_{\text{DIC}}$ revealed a wide differentiation in the percentage of modern carbon (pMC) within the study area, indicating the contributions of dissolved inorganic carbon (DIC) ranging from recent to very old sources.

It is important to note that the Chiquita and Santos 6 wells exhibit a distinct evolution of dissolved inorganic carbon compared to other wells in the region. The differences in depth between these wells may explain the variations in the composition of dissolved inorganic carbon. Specifically, Chiquita receives inputs from water sources with lower fractionation and higher pMC values, which is likely attributed to atmospheric and soil contributions. In contrast, Santos 6 may be influenced by the contamination and subsequent biodegradation of organic compounds with low or no carbon-14 content. In summary, the supply wells in the western Magdalena River region display a strong relationship with the biodegradation of hydrocarbon species. The similarities observed in [DIC], isotopic fractionation, and pMC among these wells indicate that the dissolved inorganic carbon within the aquifer primarily originates from this source. These findings have significant implications for water quality and resource management within this region.



Discussion

The southern region of the Sogamoso River displays a wide variation in pMC values, indicating distinct evolution of DIC within this zone. The sources contributing to dissolved inorganic carbon in this area varied considerably. Two identifiable trends were observed in the western region of the Magdalena River. One trend is associated with carbonate dissolution and atmospheric CO₂ inputs, whereas the other is linked to the biodegradation of young organic species.

Moving westward of the Magdalena River, the evolution of DIC was influenced by the presence of organic matter during sampling, establishing a correlation between DIC and hydrocarbon biodegradation. This connection suggests the involvement of hydrocarbons in DIC dynamics, despite their absence in most wells when analyzing $\delta^{13}\text{C}_{\text{DIC}}$.

Conclusion

Isotopic analysis of groundwater wells in the middle Magdalena Valley revealed different predominant processes in the evolution of dissolved inorganic carbon (DIC) in the study area. Inorganic inputs from the soil were the main drivers of DIC evolution towards the north and south of Aguachica. As one moves southward, local processes become more difficult to relate, possibly because of interactions with organic matter. However, towards the west of the Magdalena River, DIC evolution was influenced by the organic matter present at the sampling time. The analysis of modern carbon percentage (^{14}C pMC) allowed differentiation of the age of carbon sources and geochemical processes affecting DIC evolution. There was evidence of organic species derived from hydrocarbons in some supply wells and in the southern part of the study area. In summary, isotopic analysis of groundwater wells is valuable in elucidating carbon processes and sources, complementing physicochemical characterization, and providing additional insights into the presence of hydrocarbons and organic matter in the study area. These combined findings enhance our understanding of hydrocarbon distribution and organic matter dynamics in groundwater systems.

Acknowledgments

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Conflicts of interest

The authors declare that they have no conflicts of interest.

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