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Stable carbon isotope evidence for nitrogenous fertilizer impact on carbonate weathering in a small agricultural watershed[‡]

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The isotopic signature of Dissolved Inorganic Carbon (DIC), $\delta^{13}\text{C}_{\text{DIC}}$, has been investigated in the surface waters of a small agricultural catchment on calcareous substratum, Montoussé, located at Auradé (south-west France). The Montoussé catchment is subjected to intense farming (wheat/sunflower rotation) and a moderated application of nitrogenous fertilizers. During the nitrification of the NH_4^+ , supplied by fertilization, nitrate and H^+ ions are produced in the soil. This anthropogenic acidity is combined with the natural acidity due to carbonic acid in weathering processes. From an isotopic point of view, with 'natural weathering', using carbonic acid, $\delta^{13}\text{C}_{\text{DIC}}$ is intermediate between the $\delta^{13}\text{C}$ of soil CO_2 produced by organic matter oxidation and that of the carbonate rocks, while it has the same value as the carbonates when carbonic acid is substituted by another acid like nitric acid derived from nitrogen fertilizer. The $\delta^{13}\text{C}_{\text{DIC}}$ values range from -17.1‰ to -10.7‰ in Montoussé stream waters. We also measured the $\delta^{13}\text{C}$ of calcareous molassic deposits (average -7.9‰) and of soil organic carbon (between -24.1‰ and -26‰) to identify the different sources of DIC and to estimate their contribution. The $\delta^{13}\text{C}_{\text{DIC}}$ value indicates that weathering largely follows the carbonic acid pathway at the springs (sources of the stream). At the outlet of the basin, H^+ ions, produced during the nitrification of N-fertilizer, also contribute to weathering, especially during flood events. This result is illustrated by the relationship between $\delta^{13}\text{C}_{\text{DIC}}$ and the molar ratio $\text{NO}_3^-/(\text{Ca}^{2+} + \text{Mg}^{2+})$. Consequently, when the contribution of nitrate increases, the $\delta^{13}\text{C}_{\text{DIC}}$ increases towards the calcareous end-member. This new isotopic result provides evidence for the direct influence of nitrogen fertilizer inputs on weathering, CO_2 consumption and base cation leaching and confirms previous results obtained using the chemistry of the major ions present in the field, and in soil column experiments.

Rivers play an important role in the global carbon cycle by linking terrestrial systems and oceans, transporting on average one Giga-ton of carbon per year in particulate and dissolved forms.^[1] Rivers also actively degas this carbon into the atmosphere.^[2] Dissolved Inorganic Carbon (DIC), estimated to account for 40% of the total fluvial carbon inputs to the ocean,^[1,3] originates mainly from three sources: (1) atmospheric CO_2 , (2) biogenic CO_2 produced by root respiration and organic matter decay, and (3) dissolution of carbonate minerals.

Previous studies used the isotopic composition of DIC to trace its sources and transformations by biogeochemical processes in the river itself.^[4–18] The $\delta^{13}\text{C}_{\text{DIC}}$ variations in a

river depend not only on the sources of carbon, but also on various internal biogeochemical processes, such as photosynthesis/respiration and exchange with atmospheric CO_2 . Because of their complexity, studies of carbon dynamics have focused mostly on small streams.^[19–22] More recently, carbon isotopes have been used to highlight anthropogenic impacts in a watershed.^[23–29]

In a natural carbonate system, the main source of DIC is carbonate mineral dissolution by carbonic acid, mainly derived from biogenic soil CO_2 (see Eqn. (1)). Nevertheless, other acid compounds, of natural or anthropogenic origin, can participate in carbonate dissolution. The acidity produced in soils during the nitrification of NH_4 (see Eqn. (2)) spread by fertilization^[30] was identified as one of a key influencing weathering process (see Eqn. (3)). From an isotopic point of view in a pristine watershed, the $\delta^{13}\text{C}_{\text{DIC}}$ in stream water is intermediate between the $\delta^{13}\text{C}$ of biogenic soil CO_2 and that of carbonate rocks, whereas in the case of weathering process induced by nitric acid from nitrogen fertilizer, the riverine $\delta^{13}\text{C}_{\text{DIC}}$ tends to the carbon isotopic value of carbonates.

In this paper, we present the results of water chemistry and carbon isotopes (soil organic carbon, molassic deposit and DIC) in the small agricultural watershed of the Montoussé during a hydrological cycle. The main objectives are:

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- (1) to trace the sources of DIC in the watershed and its variation in the stream at the outlet.
- (2) to provide evidence using carbon isotopes for the impact of N-fertilizers on carbonate dissolution, as already suggested by Perrin *et al.*,^[31] using major elements in stream water and by Gandois *et al.*^[30] using soil column experiments.

EXPERIMENTAL

Study area

The Montoussé catchment at Auradé is located in the Midi-Pyrénées province (south west of France), 35 km west of Toulouse (see Perrin *et al.*^[30] for details). The study area is a hillside of the 'Coteaux de Gascogne' with an average altitude of approximately 300 m. The geological substratum is a Miocene molassic deposit (called molasse) resulting from the erosion of the Pyrénées Mountains and the subsequent sediment deposition in the Gascogne fan at the end of the Tertiary Period. This molasse consists of a mixture of sands, clays, limestones and calcareous sediments. The study area is characterized by a fairly impermeable substratum due to its widely extended clay content. As the result of this geological substratum, the river discharge is mostly supplied by surface and sub-surface run-offs. Groundwater reservoirs are very limited and, during the summer dry period, the stream discharge is very low and sometimes the stream dries up. The hill slopes are very steep and the slopes can reach up to 20%.

The Montoussé catchment area (328 hectares) is mainly used for agriculture (90% of the drainage area) and sustainable agricultural practices have been carried out for many years, notably in limiting the spreading of nitrogen fertilizer, such as ammonium nitrate (NH_4NO_3) and, to a lesser extent, urea [$\text{CO}(\text{NH}_2)_2$] and ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$]. Winter wheat (20%) and durum wheat (31%) are cultivated in rotation with sunflower (47%). All these cultivated plants have a C3 photosynthetic pathway type.

The climate is of an oceanic type because the nearby Atlantic Ocean plays an important role in regulating the temperature and precipitation regimes. The average annual precipitation is about 700 to 800 mm, which is the main hydrological source of water supply for surface and sub-surface runoffs in this area. The highest discharges occur in February, and major flood events occur in May, while the low water flow period is from June to September. The bulk of the annual rainfall comes from thunderstorms occurring from November to December and from April to May. The average water evapotranspiration from the soil-vegetation system is very high and ranges between 500 and 600 mm. This leads to an annual mean discharge rate of 80–120 mm,^[31,32] which corresponds to semi-arid climate conditions.

Sampling and analytical procedures

Water samples were collected weekly at the outlet of the catchment from March to December 2010. Flood samples were collected according to discharge variations with an automatic sampler. The discharge is continuously measured at the outlet gauging station. In April 2007, spatial sampling of springs and headwaters was performed (Fig. 1). The water samples were filtered in the laboratory through $0.22\text{ }\mu\text{m}$ nitrocellulose filters, kept in the dark at $4\text{ }^\circ\text{C}$ and analyzed rapidly. The first filtrate was used for the analysis of the samples for major elements: anions with high-performance liquid ion chromatography (DX-120; Dionex, Sunnyvale, CA, USA) and cations with a inductively coupled plasma-optical emission spectroscopy (ICP-OES) system (Iris Intrepid II XLD; Thermo Electron. Madison, WI, USA), and the second one for the measurement of dissolved organic carbon (DOC) and the $\delta^{13}\text{C}$ of the dissolved inorganic carbon (DIC). The DOC was measured using a total organic carbon analyzer (TOC 5000; Shimadzu, Champs sur Marne, France). For analysis of carbon isotopes, the filtrate was treated with HgCl_2 to prevent microbiological activity, and was stored in 10 mL vials taking care that no trapped air remained in contact with the sample before analysis.

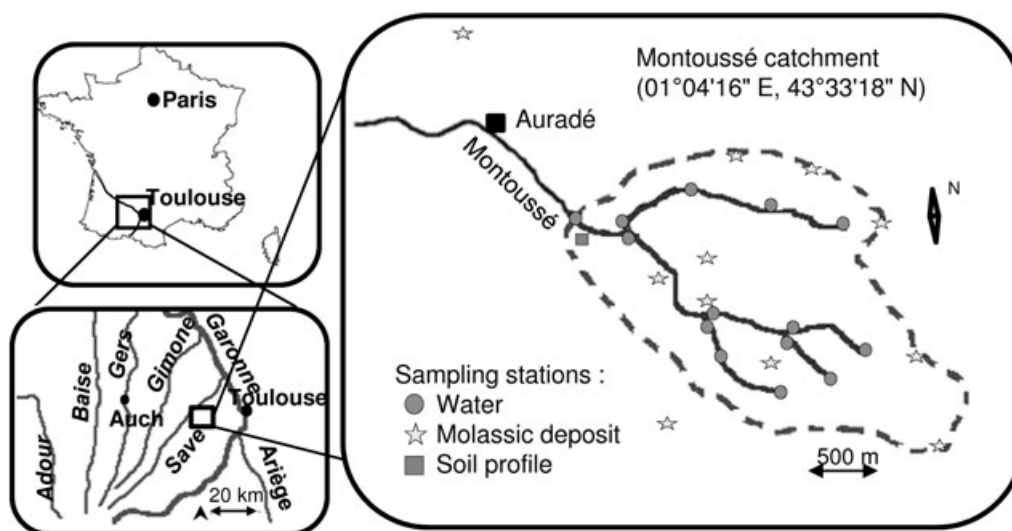


Figure 1. Location maps of the Montoussé catchment and sampling points for soil, molassic deposits and surface waters.

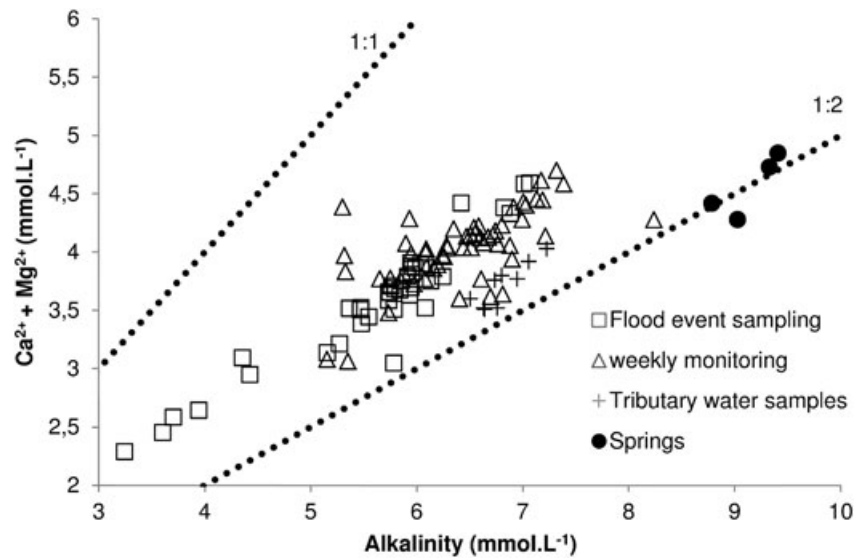


Figure 2. Relationship between $\text{Ca}^{2+} + \text{Mg}^{2+}$ (mmol.L^{-1}) and alkalinity (mmol.L^{-1}) in surface waters of the Montoussé catchment during the period March to December 2010. Dotted lines 1:2 and 1:1 represent the carbonate dissolution equilibrium, respectively, with carbonic acid (Eqn. (1), NWP) and nitric acid (Eqns. (2) and (3), AWP).

inputs. This process was also recently shown by a soil experiment where N-fertilizer added to soil was found to significantly increase base cation fluxes relative to pure carbonate dissolution.^[30]

Stable carbon isotopes

The isotopic composition of dissolved inorganic carbon in a river, $\delta^{13}\text{C}_{\text{DIC}}$, reflects the sources of inorganic carbon: biogenic/soil CO_2 , atmospheric CO_2 and carbonate dissolution.^[32] Atmospheric CO_2 has a $\delta^{13}\text{C}$ value of about -8‰ relative to VPDB. Dissolution and gas transfer into water are both isotopically fractionating processes, yielding $\delta^{13}\text{C}$ values near -1‰ for dissolved inorganic carbon originating from atmospheric CO_2 .^[37] Soil organic matter has an isotopic composition of between -24 and -34‰ ^[38] and its biologically mediated breakdown produces CO_2 with a similar isotopic composition. Dissolution of carbonates produces DIC, without fractionation and with an average isotopic composition about 0‰ .^[39] Once carbon from these sources is transported into the river, biogeochemical processes may further alter its isotopic composition. Aquatic photosynthesis preferentially consumes ^{12}C , leaving the residual CO_2 pool enriched in ^{13}C .^[40] As a result, the organic matter produced by aquatic photosynthesis is isotopically depleted, with a $\delta^{13}\text{C}$ value approximately 20‰ lighter than the isotopic composition of the dissolved CO_2 .^[41] The competing process, *in situ* respiration, consumes this depleted organic matter and produces CO_2 with a similarly depleted isotopic composition.^[42] When an aquatic system is oversaturated in CO_2 , degassing under non-equilibrium conditions can lead to isotope enrichment of the remaining CO_2 pool.^[22]

We first measured the isotopic composition of these different sources of carbon in the Montoussé catchment. Twelve samples of Miocene molassic deposits (called molasse), collected in the Montoussé catchment or very close to the

catchment, give an indication of the isotopic composition of the bedrock. The average $\delta^{13}\text{C}$ value of the molasse is -7.9‰ (Table 1). This value is lower than the average values for carbonate rocks that generally range around 0‰ .^[39] This isotopic difference can be explained by the molassic sediment deposition processes. We have also measured the concentration and the isotopic composition of the organic carbon in a soil profile, at the outlet of the basin. The weighted average $\delta^{13}\text{C}$ value of organic carbon is -25.7‰ (Table 1). This value is representative of C3 plants (wheat and sunflower) cultivated in this catchment.

In the case of the Montoussé catchment, the source of DIC is mainly carbonate of molassic deposits. As mentioned in the previous section, one can consider at least two weathering pathways:

- (1) NWP, using carbonic acid derived from the CO_2 produced by root respiration and organic matter decay in the soil.
- (2) AWP, using nitric acid produced by the nitrification process of N-fertilizers.

The soil CO_2 inherits the isotopic signature of soil organic matter. However, due to the difference in diffusion coefficients between the two carbon isotopes (^{12}C and ^{13}C), the soil CO_2 becomes enriched in ^{13}C by at least $+4.4\text{‰}$.^[43] As a result, with the $\delta^{13}\text{C}$ value of organic carbon being -25.7‰ , the soil CO_2 $\delta^{13}\text{C}$ value can be estimated as -21.3‰ . With an average isotopic composition of -7.9‰ for the calcareous molasse, the DIC produced by carbonate dissolution with carbonic acid in equilibrium with soil CO_2 (NWP) should have a $\delta^{13}\text{C}$ value close to -14.6‰ , with one carbon originating from the carbonates and the other from the soil CO_2 (Eqn. (1)). The other potential source of DIC is carbonate weathering with hydrogen ions (H^+) released by the N-fertilizer nitrification processes (AWP). In this case, the DIC originates only from the carbonate mineral

dissolution in soils and bedrock and it should have an isotopic composition similar to that of the calcareous molassic deposits. Diffusion of atmospheric CO_2 , with a $\delta^{13}\text{C}$ of -8.6‰ , in the Massif Central (central area of France),^[44] into the soil, particularly when the biological activity is low,^[45] or CO_2 degassing across the stream water/atmosphere interface, can significantly increase the $\delta^{13}\text{C}_{\text{DIC}}$. The residence time of water within the catchment is not sufficient to generate an isotopic equilibrium between the DIC in stream water and atmospheric CO_2 , as already observed for larger watersheds such as the St. Lawrence.^[8] In river water, photosynthesis and respiration can further modify the DIC pool and its isotopic signature. The former will increase the $\delta^{13}\text{C}$ and diminish the DIC pool, while respiration will cause opposite effects. In our catchment, however, we considered that these processes are secondary and that they do not significantly affect the isotopic composition of DIC because the biological activity in the stream water remains low.

At the outlet of the catchment, the $\delta^{13}\text{C}_{\text{DIC}}$ values range from -15.2‰ to -12.7‰ , with an average value of $-13.7 \pm 0.6\text{‰}$ (Table 1 and Fig. 3). Within this range, we can distinguish two different periods: the first from March to the end of September, with an average value of $-13.5 \pm 0.5\text{‰}$, and a second period, from October to December, with lower values (average $-14.5 \pm 0.5\text{‰}$). During the flood events (May, end of June and end of November), we observed generally a significant increase in the $\delta^{13}\text{C}_{\text{DIC}}$, except at the beginning of the June event. As can be seen in Fig. 4 for the flood event of May 2010, the $\delta^{13}\text{C}_{\text{DIC}}$ measured at the outlet of the Montoussé catchment rapidly increases with increasing stream discharge. In the upper stream waters, the $\delta^{13}\text{C}_{\text{DIC}}$ is slightly lower (-13.9‰ on average) than at the stream outlet. This low isotopic difference is mainly due to the homogeneity of the bedrock and of the agricultural activities within the watershed. However, we observed a significant difference in $\delta^{13}\text{C}_{\text{DIC}}$ values between the spring waters (-17.1 to -15.8‰ , Table 1) and the other water samples (flood event

and baseflow at the outlet, upper streams). This difference can be attributed to CO_2 degassing into the atmosphere going from the spring to the lower part of the catchment.^[19,21,22]

Relationship with the CO_2 partial pressure

The partial pressure of CO_2 ($p\text{CO}_2$) in the river was calculated using the DIC concentration, pH and temperature.^[46] The riverine $p\text{CO}_2$ values in the Montoussé varied from $10^{-3.07}$ to $10^{-1.51}$ atm (Fig. 4) and were intermediate between the atmospheric ($10^{-3.5}$ atm or 360 ppmv) and soil $p\text{CO}_2$ ($10^{-1.5}$ atm) average values. With the presence of carbonate rocks, the DIC could have originated from these rocks as well as from the two CO_2 sources as in the case of silicate weathering,^[16,21] the biogenic/soil CO_2 end-member with a $\delta^{13}\text{C}$ of about -21‰ to -26‰ for C3-plant ecosystems or agrosystems and atmospheric CO_2 at -8.6‰ . However, we can observe a relationship (Fig. 5) between $p\text{CO}_2$ and $\delta^{13}\text{C}_{\text{DIC}}$. The spring water samples are close to the biogenic end-member, while the lower $p\text{CO}_2$ values observed at the outlet tend to the isotopic composition of the atmospheric CO_2 . The stream waters collected in the different tributaries exhibit intermediate values. The general trend shows degassing of CO_2 during downstream transport, coupled with exchange and equilibration with atmospheric CO_2 . This is similar to trends already observed in other rivers, such as the Danube,^[4] the Great Lakes-St. Lawrence system,^[8] or the Nyong.^[16] Nevertheless, if we focus on samples from the outlet of the watershed (weekly monitoring and flood events sampling), the cluster of points is more scattered and this may be due to the relative contribution of the two main sources of DIC: carbonate dissolution and soil CO_2 , depending on the hydrological conditions.

Relationship with nitrate contents

Ammonium (NH_4^+) is spread, usually in the form of NH_4NO_3 , on cultivated soil. Subsequently, N-fertilizer nitrification releases nitrates (NO_3^-) and hydrogen ions

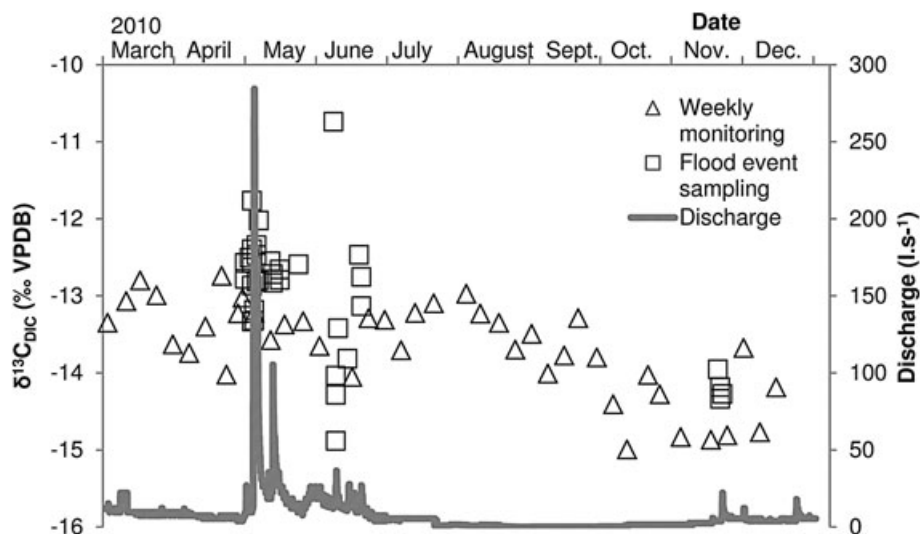


Figure 3. Temporal variations of stream water discharge and isotopic composition ($\delta^{13}\text{C}$) of riverine DIC at the outlet of the Montoussé watershed during the period March to December 2010.

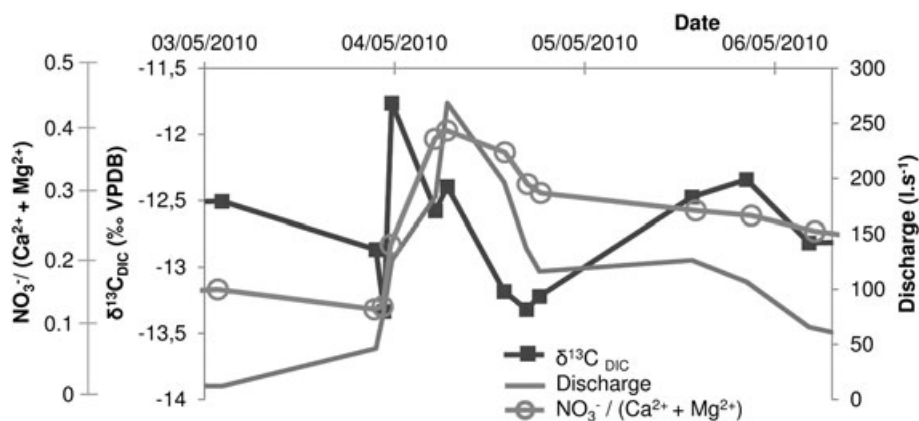


Figure 4. Temporal variations of stream water discharge, isotopic composition ($\delta^{13}\text{C}$) of riverine DIC and molar ratio ($\text{NO}_3^-/(\text{Ca}^{2+} + \text{Mg}^{2+})$) at the outlet of the Montoussé watershed during the flood event of May 2010.

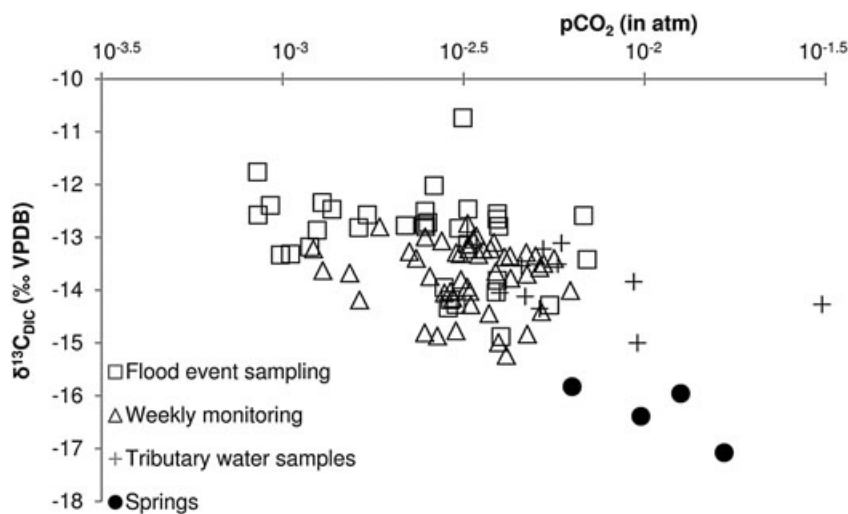


Figure 5. Relationship between $\delta^{13}\text{C}_{\text{DIC}}$ and pCO_2 in surface waters of the Montoussé catchment during the period March to December 2010.

(H^+) (Eqn. (2)).^[47,48] As shown in a previous section (Major ion chemistry), these ions associated with strong acid anions can replace carbonic acid in the carbonate weathering process (Eqn. (3)). To highlight this process, we used the molar ratio $\text{NO}_3^-/(\text{Ca}^{2+} + \text{Mg}^{2+})$. When the nitrate concentration is very low, this ratio tends towards zero and we can assume that carbonate dissolution is mainly due to carbonic acid (NWP). Conversely, when the nitrate concentration increases, this ratio increases and indicates that the nitric acid contribution to carbonate dissolution increases. The Montoussé watershed is characterized by relatively high nitrate contents in surface waters, due to the use of N-fertilizers on more than 90% of its area. The NO_3^- concentrations vary between 0.3 and 1.3 mmol.L^{-1} (Table 1), except in spring waters (below 0.3 mmol.L^{-1}). We observed a general positive trend between $\delta^{13}\text{C}_{\text{DIC}}$ and the molar ratio $\text{NO}_3^-/(\text{Ca}^{2+} + \text{Mg}^{2+})$ (Fig. 6). Even if the cluster of points is relatively scattered, it still lies between two poles, one with high molar ratio and high $\delta^{13}\text{C}_{\text{DIC}}$ corresponding

to AWP and the other with low ratio and more negative $\delta^{13}\text{C}_{\text{DIC}}$ values corresponding to NWP. The spring waters are close to NWP because they are supplied by ground waters less concentrated in nitrates. The chemical composition of these ground waters is in equilibrium with carbonate dissolution by carbonic acid in molassic deposits. Consequently, water samples collected during low flow conditions tend to this end-member. Conversely, water samples collected during flood flows tend to AWP because they are supplied by subsurface waters with high nitrate contents resulting from soil leaching.^[49] The chemical composition of subsurface waters is mainly due to soil carbonate dissolution with nitric acids.

The cluster of points lies between the two end-members (NWP and AWP) depending on the weathering pathway, the hydrological conditions and the contribution of the different streamflow components (surface runoff, subsurface flow and groundwater flow) to the total streamflow, and to the N-fertilizer spreading period.

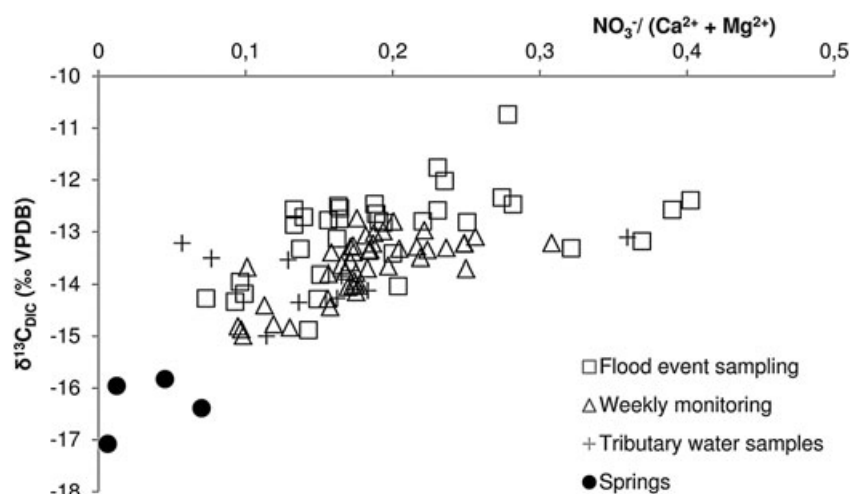


Figure 6. Relationship between riverine $\delta^{13}\text{C}_{\text{DIC}}$ (‰) and the molar ratio $\text{NO}_3^-/(\text{Ca}^{2+} + \text{Mg}^{2+})$ in the different surface waters of the Montoussé catchment during the period March to December 2010.

CONCLUSIONS

The isotopic signatures of dissolved inorganic carbon (DIC), measured in surface waters draining the Montoussé catchment at Auradé, are between -17.1 and -10.7‰ , with more negative values for spring waters (from -17.1 to -15.8‰), which increase in the stream from upstream to downstream by CO_2 degassing processes, reaching at the outlet an average value of -13.7‰ . These $\delta^{13}\text{C}_{\text{DIC}}$ values are very negative compared with the values previously published for the watershed draining calcareous substratum. This is partly due to the $\delta^{13}\text{C}$ of Miocene calcareous molassic deposits (on average -7.9‰) that constitutes a comparatively negative end-member with most carbonate rocks having values around 0‰ .

The molar ratio $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ (on average 0.63) is greater than the value of 0.5 , which corresponds to the stoichiometric coefficient ratio of carbonate mineral dissolution by carbonic acid. These results indicated that carbonic acid is not the only weathering agent. As already observed by Perrin *et al.*,^[31] in this region, hydrogen ions released by nitrification of nitrogenous fertilizers can participate in rock weathering. A significant relationship between the isotopic signature of dissolved inorganic carbon (DIC) and the ratio $\text{NO}_3^-/(\text{Ca}^{2+} + \text{Mg}^{2+})$ in surface waters confirms this hypothesis. We observed a general trend going from spring waters corresponding to a 'natural weathering' end-member with negative $\delta^{13}\text{C}_{\text{DIC}}$ values and a low $\text{NO}_3^-/(\text{Ca}^{2+} + \text{Mg}^{2+})$ ratio towards stream waters, particularly during flood events, corresponding to an 'anthropogenic weathering' end-member, with less negative $\delta^{13}\text{C}_{\text{DIC}}$ values and a higher $\text{NO}_3^-/(\text{Ca}^{2+} + \text{Mg}^{2+})$ ratio. This new isotopic result using stable carbon isotopes provides evidence for the first time of the impact of nitrogenous fertilizers on carbonate dissolution and confirms results that we obtained recently using major ion chemistry in the field^[31] and in soil experiments.^[30]

This new result must be now extended to other agricultural catchments draining calcareous substratum where N-fertilisers are intensively used in order to confirm this first result.

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