A Preliminary Evaluation of Dissolved Carbon Concentrations and Fluxes in an Agroforestry Schist Catchment

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Abstract

Riverine carbon transport is a significant yet poorly understood component of the global carbon cycle. This study evaluates concentrations and fluxes of dissolved carbon fractions in an agroforestry schist catchment in NW Spain. Biweekly water sampling and discharge measurements were conducted at the catchment outlet over two consecutive years. Total dissolved carbon (TDC) showed a flow-weighted mean concentration of 4.94 mg L^{-1} (range: 2.77–10.19 mg L^{-1}) and was dominated by dissolved inorganic carbon (DIC). While central tendencies for TDC, DIC, and dissolved organic carbon (DOC) remained stable due to dominant baseflow conditions, the second year exhibited a much wider interquartile range across all fractions. DOC showed high variability with multiple upper outliers from episodic flushing of upper soil horizons during rainfall-runoff events. Conversely, DIC remained stable, except for a single dilution-driven lower outlier. At near-neutral pH of the studied stream, DIC existed primarily as bicarbonate. The daily mean TDC load was 93.18 kg d^{-1} (daily mean specific yield of 5.82 kg km^{-2} d^{-1}), dominated by DIC (63%). However, interannual variability was notable, with the second year reaching a daily mean TDC load of 101.32 kg d^{-1} (6.33 kg km^{-2} d^{-1}), a 17.3% increase over the first year (86.35 kg d^{-1}; 5.4 kg km^{-2} d^{-1}).

Keywords: *Stream water, headwater catchment, dissolved carbon, fluxes*

1. Introduction

Rivers and streams act as the major pathway for transporting enormous amounts of carbon (C) from terrestrial ecosystems to the ocean [1]. They are crucial in the connection between terrestrial, atmospheric and oceanic C pools with important consequences on the regulation of climate, soil and water quality and the overall ecological functioning. Terrestrial C can be exported in particulate forms and/or dissolved forms. The main sources of stream dissolved organic carbon (DOC) are soils. Soil DOC originates primarily from canopy throughfall, litter decay, and the decomposition of both natural and anthropogenic organic matter. Through leaching, surface runoff, or flooding, this soil-derived carbon is mobilized and transported into aquatic networks, serving as the main source of allochthonous riverine DOC [2, 3]. Environmental factors such as temperature, wet-dry cycles, soil saturation, and snowmelt, alongside management practices like liming and organic fertilization, significantly influence DOC production rates [4]. However, while these processes represent terrestrial inputs, DOC can also be generated within the river system itself (autochthonous) [5], as well as from other sources discharged directly into the river, such as domestic effluents and industrial wastewater. DOC play a critical role in maintaining riverine health and ecosystem functions. results.

Dissolved inorganic carbon (DIC) is present in all natural waters and is usually the most abundant form of dissolved C in rivers and contributes most carbon dioxide emissions from terrestrial aquatic ecosystems [6]. Its concentration ranges between 1.2 and 12.0 mg C L^{-1} in most systems [7]. Riverine DIC is derived from the combined effects of carbonate and/or silicate rock weathering (geogenic C) alongside biogenic carbon dioxide sources [8, 9]. This biogenic carbon dioxide is produced externally by litter decomposition, root and microbial respiration, and organic matter decomposition in soil pores, where it dissolves into infiltrating waters to form carbonic acid, thereby lowering their pH before they reach the river network. Subsurface pathways, such as interflow and leaching, alongside surface runoff, deliver soil DIC to streams and groundwater. Soils are the dominant DIC sources in headwater streams, rather than in-stream processes which include aquatic biodegradation, photodegradation, and atmospheric carbon dioxide [10]. DIC in river water exists as three main species: dissolved carbon dioxide, bicarbonate and carbonate ions, with their distribution being strictly governed by pH [11].

Interacting drivers govern DOC and DIC fluxes, introducing complexities that challenge our understanding of their transport and behavior. Beyond river-floodplain interactions, human activities—such as damming, land use change, and management—alongside natural geological and topographic features, hydrology, and extreme climatic events, heavily influence the export of dissolved carbon [12, 13, 14]. For example, the application of limestone to agricultural lands within the basin has been linked to rising bicarbonate concentrations in the Mississippi River [15, 16]. Therefore, a thorough understanding of riverine C fluxes and their underlying controls is essential, particularly for assessing how they respond to anthropogenic activities and ongoing climatic changes. Global fluxes of riverine dissolved carbon typically surpass those of particulate carbon, highlighting the need for accurate total flux estimations [17]. Yet, while DOC represents a standard parameter in routine water quality assessments, DIC has received less attention despite the substantial contribution of riverine DIC to global carbon emissions [18, 19]. This monitoring asymmetry

results in a scarcity of data regarding the exact role of DIC in aquatic carbon fluxes and modern cycling processes. The lack of knowledge regarding the dynamics of DOC and DIC concentrations and loads within watersheds is particularly critical for headwater rivers and streams recharging drinking water reservoirs, where temporal variations of carbon impact water quality and treatment processes. In these systems, DIC fluctuations alter the aquatic carbonate balance and drive baseline primary production, while DOC compromises drinking water safety by degrading color, taste, and odor, acting as a carrier for toxic pollutants like pesticides and radionuclides, and altering dissolved oxygen and nutrient dynamics (N, P, S). Furthermore, its biodegradable fraction reduces biological stability, promoting bacterial regrowth in distribution systems. Most critically, DOC acts as a primary precursor to the formation of carcinogenic disinfection by-products during water treatment [20].

This study provides an exploratory assessment of the total and interannual variation in dissolved carbon concentrations, loads, and fluxes in the Corbeira stream draining an Atlantic headwater catchment located in the NW Spain. Prior data on dissolved carbon in the Corbeira stream have been limited exclusively to DOC [21-23]. To address this gap, this study conducts the first simultaneous evaluation of both DOC and DIC in this stream. Such an approach is especially pertinent because, beyond being a headwater stream, it is a tributary of the Mero River, which discharges into the Abegondo-Cecebre reservoir—the primary drinking water source for over 450,000 inhabitants in the city of A Coruña and its surrounding areas. Consequently, dissolved carbon fluxes must be taken into account to improve catchment management, mitigating dissolved carbon loads that could degrade water quality in these river-reservoir systems.

2. Materials and methods

2.1. Description of the Study Area

The Corbeira stream headwater catchment (NW Spain; 16 km^2; UTM: 562658 N 4785332 W; European 1950 datum zone 29 N) flows into the Mero River, the primary source for the Abegondo-Cecebre drinking water reservoir, located approximately 30 km away, to the southeast of A Coruña city. Altitudes range from 65 m to 470 m a.s.l., with a mean slope of 19%, and 27% of the area exceeding 25%. Geologically, it belongs to the Ordenes Complex [24], whose lithology is dominated by schists of basic composition featuring a sharp fissure system throughout the catchment, which creates hydrological pathways and areas of water storage, promoting spring and seep emergence at specific near-stream slopes where the topography intersects the saturated fractures [25]. These rocks are rich in weatherable minerals, including biotite/chlorite, plagioclase, and amphiboles, whose alteration promotes the development of deep soils. The dominant soils are moderately acidic, silty and silty loam Umbrisols and Cambisols [26]. High topsoil organic matter content across all land uses (ranging from 4.4% in croplands to 10.5% in forest soils) underscores the critical role of land management in carbon sequestration.

The climate is temperate humid-oceanic, characterized by mesic temperature and udic moisture soil regimes, with a long-term mean annual rainfall of 1,075 mm and a temperature of 13 ºC (historical series 1983-2019; Meteorological Service of the Galician Government, station 10045). Rainfall occurs throughout the year, although the wettest months are October–March (fall-winter), driving a pluvial oceanic hydrological regime with high discharge in fall–winter. Conversely, the driest and hottest months occur in June–September, resulting in a low-flow period during late spring and summer. Mean daily stream discharge is 0.18 m^3 s^{-1}, with the baseflow primarily sustained by groundwater [27].

Forestry is the dominant land use (65% of the catchment area), consisting primarily of commercial eucalyptus and pine plantations, with dense riparian corridors of *Alnus*, *Betula*, and *Salix* spp. Agricultural land covers 30%, divided into pastures and wet meadows (26%) and croplands (4%). The remaining 5% consists of impervious surfaces, mainly roads and forest tracks distributed throughout the basin. The area features low population and livestock densities, along with low-intensity agriculture characterized by minimal inorganic fertilizer inputs. Additional information on the environmental and hydrological setting of this catchment is provided by [28-31].

2.2. Water sampling and analysis

Biweekly manual water sampling and instantaneous discharge measurements were conducted at the catchment outlet over two consecutive years (January 2005 to December 2006). Stream data were mostly acquired on days without rainfall events (under baseflow conditions) and only occasionally on days with rainfall events (during high flow, mainly in the fall and winter). During hydrological events, sampling occurred either before or after the peak discharge.

Each water sample was stored in a polyethylene bottle. The bottles were washed with ultrapure water and thoroughly rinsed with stream water before sample collection. The samples were stored at 4 °C to prevent any chemical changes between sampling and analysis. Unfiltered samples were used to determine pH using a Crison 2000 pH meter. Aliquots of the water samples were filtered through 0.45 µm Millipore polycarbonate filters, and the filtrates were collected for analysis. Concentrations of TDC and DOC (commonly defined as the organic carbon fraction passing through a 0.45 µm filter [32]) were measured using a Shimadzu TOC-VCSN analyzer, while DIC was calculated as the difference between them. All dissolved carbon fraction concentrations are reported in milligrams per liter as carbon.

Instantaneous discharge was measured at the catchment outlet at the time of sampling using the velocity–area method. Precipitation data were obtained from the Mabegondo meteorological station (43º14'50" N, 8º15'47" W), located 4 km from the study area.

2.3. Hydrochemical calculations and statistical analysis

2.3.1. Baseline Statistical Analysis. Descriptive statistics—including the mean, median, range, IQR, and coefficient of variation (CV)—were calculated for all analyzed parameters. Additionally, to integrate the hydrological regime, the flow-weighted mean concentration (FWMC) was determined for the dissolved carbon fractions.

2.3.2. Calculation of FWMCs, Loads, and Specific Yields. Flow-weighted mean concentration (FWMC) values for DIC, DOC, and TDC were determined independently for each year (referred to as Period 1 and Period 2) and for the entire study period according to the following equation:

$$FWMC = \frac{\sum_{i=1}^{n}(Qi\ x\ Ci)}{\sum_{i=1}^{n} Qi}$$

where Qi is the instantaneous discharge ($m^3\ s^{-1}$) and Ci is the solute concentration ($mg\ L^{-1}$) measured at each sampling time, and n is the total number of samples collected during the respective study period.

The observed mean daily loads (L_d, $kg\ d^{-1}$) for each respective carbon fraction and study period were then computed as the arithmetic mean of the instantaneous loads obtained on each sampling date:

$$\text{Observed Mean Daily Load (kg d}^{-1}) = \frac{\sum_{i=1}^{n}(Qi\ x\ Ci\ x\ 86.4)}{n}$$

where 86.4 is the unit conversion factor used to express the final load in $kg\ d^{-1}$, and n is the number of samples as defined above.

The mean daily specific yield (Y_d, $kg\ km^{-2}\ d^{-1}$) and its associated standard deviation (SD) were obtained by dividing the observed mean daily load and its SD by the total catchment area (A, km^{-2}), according to the following equation:

$$Y_d = \frac{L_d}{A}$$

where L_d is the observed mean daily load ($kg\ d^{-1}$) and A is de catchment area.

3. Results and discussion

3.1. Hydrochemical characteristics

The general hydrochemical characteristics for the entire study period are summarized in table 1, whereas the concentration distributions of TDC, DIC, and DOC between Period 1 (P1) and Period 2 (P2) are displayed in box plots (Fig. 1).

Stream discharge was highly variable throughout the study period (table1) with instantaneous flows averaging 0.22 $m^3\ s^{-1}$ (range: 0.01-1.17 $m^3\ s^{-1}$; CV 81.82%). Under this fluctuating hydrological framework, stream pH remained predominantly neutral to slightly acidic, averaging 6.9 (range: 6.4–7.2). For the entire study period, TDC exhibited an FWMC of 4.94 mg L^{-1}, with a wide range from 2.77 to 10.19 mg L^{-1}. DIC was the predominant fraction, with an FWMC of 3.12 mg L^{-1}, a moderate range (1.90–4.47 mg L^{-1}), and a coefficient of variation (CV) of 17%. In contrast, DOC concentrations ranged between 0.87 and 6.77 mg L^{-1}, with a CV of 50% and an FWMC of 1.82 mg L^{-1}. Consequently, DIC constituted the major component of the TDC pool, accounting for 63.2% of the total dissolved carbon. Notably, for all carbon fractions, the arithmetic means, medians, and FWMC values were similar (table 1), reflecting the predominance of baseflow conditions during the monitoring period. Although the DOC concentration range falls within [1] typical values for pristine temperate rivers (1-20 mg L^{-1}), the dominance of DIC suggests a lithological control over dissolved carbon.

Tab. 1. Statistical summary of the hydrochemical characteristics for the entire study period.

	Min-Max	Range	Mean ± SD	CV (%)	FWMC	Median	IQR
pH	6.40 - 7.20	0.80	6.90 ± 0.16	2.3	-	-	-
Q ($m^3\ s^{-1}$)	0.01 - 1.17	1.16	0.22 ± 0.18	81.8	-	-	-
TDC (mg L^{-1})	2.77 - 10.19	7.42	5.45 ± 1.19	21.8	4.94	5.34	0.92
DIC (mg L^{-1})	1.90 - 4.47	2.57	3.47 ± 0.59	17.0	3.12	3.60	0.57
DOC (mg L^{-1})	0.87 - 6.77	5.90	1.98 ± 0.99	50.0	1.82	1.71	0.72

When analyzing the concentration distribution by periods (Fig. 1), both the medians and FWMC values of TDC, DIC, and DOC were similar between both years. Since the median represents the central tendency and the FWMC reflects the flow-weighted concentration, this similarity confirms that baseline carbon levels remained stable due to dominant baseflow conditions. Although the FWMC and median remained within the IQR in both periods, a notable shift in IQR amplitude was observed. Period 2 exhibited a larger IQR—doubling the box height of Period 1—indicating greater variability in baseflow concentrations across all carbon fractions. Conversely, the narrower IQR in Period 1 demonstrates highly stable baseflow concentrations for all three fractions. Despite this baseline stability, DOC exhibited higher extreme variability, characterized by multiple scattered upper outliers that suggest episodic flushing events or heterogeneous sources. Conversely, DIC remained more structurally stable, showing only a single lower outlier during Period 1. This contrast stems from their distinct origins within the catchment; while DOC generally comes from the shallow, organic-rich mineral horizons of the catchment's acid soils [33, 34], DIC—as expected for a catchment dominated by schists—is presumed to derive from the steady weathering of silicates driven by soil CO_2 [8]. At a mean stream pH of 6.9 (6.4–7.2), DIC exists primarily as bicarbonate ion, ensuring a highly stable and uniform supply [35].

A detailed evaluation of these anomalous concentrations is provided in the subsequent section.

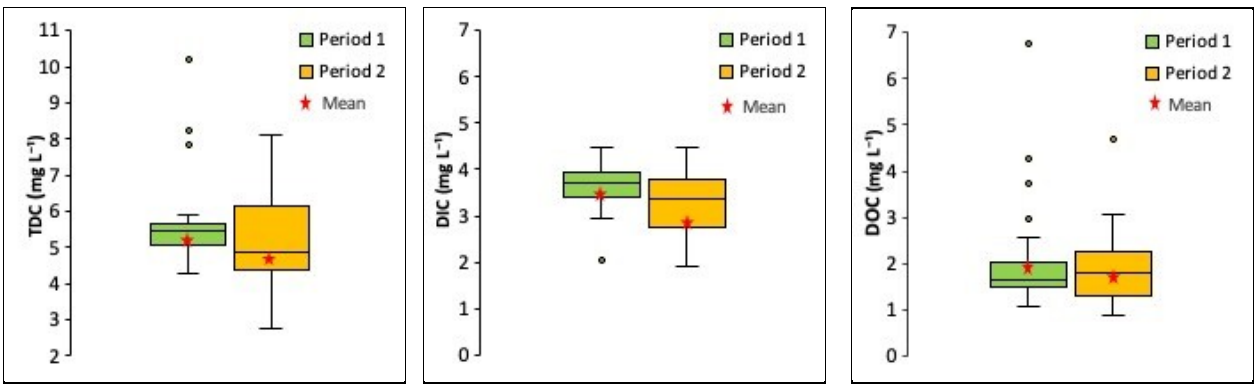

Fig. 1. Boxplots of dissolved carbon fractions for Period 1 and Period 2.

3.2. Outlier analysis of DOC and DIC concentrations

Across the analyzed periods, five outliers with the highest concentrations were identified for DOC (four from Period 1 and one from Period 2), alongside a single lower outlier for DIC in Period 1. These anomalous concentrations were defined statistically using the built-in 1.5 times the interquartile range (1.5 × IQR) rule via Microsoft Excel's exclusive quartile convention. Except for an outlier linked to in-stream processes, the ecohydrological interpretation of these anomalies is based on the water dynamics and hydroclimatic antecedent conditions (antecedent rainfall-AP-, initial discharge-Qb) previously documented for the study area. These outliers are described below by period; the four outliers in Period 1 are listed in descending order of concentration magnitude, followed by the single outlier from Period 2.

The maximum absolute DOC concentration (6.77 mg L^{-1}), which qualified as the most extreme upper outlier, occurred in early fall (October 6, 2005) under critical baseflow (0.02 m^3 s^{-1}) following a dry summer. Given the lack of catchment runoff and wetness, this maximum concentration was likely driven by in-stream processes.

Following in order of magnitude, the second highest upper DOC outlier (4.27 mg L^{-1}) was recorded just 16 days later (October 22, 2005) at the end of the recession limb of a major runoff event (total rainfall 47.4 mm; AP21 87.8 mm; Qmax 0.4 m^3 s^{-1}), when discharge had already returned to the initial baseflow level of 0.10 m^3 s^{-1} (event characterized by [36]). Previous studies on the hydrological response of this catchment [27, 28, 31, 37], as well as other well-vegetated catchments [38], indicate that subsurface flow dominates direct runoff and sustains the prolonged hydrograph recession. In this scenario, this delayed subsurface flow likely flushed DOC from the soil horizons. The lower concentration compared to the previous outlier resulted from a dilution effect driven by this five-fold increase in water volume. However, the total amount of carbon exported to the river system was much higher. Ultimately, this DOC outlier detected after the massive rainfall event represents a shift in catchment dynamics: the transition from summer accumulation to active hydrological export.

The third upper DOC outlier (3.75 mg L^{-1}) was observed at the end of spring under baseflow (0.14 m^3 s^{-1}; AP15 15.4 mm) [39], coinciding with the single DIC outlier (a lower outlier) of the study period. Despite the lack of recent rainfall, this discharge was seven times higher than the discharge of the early fall outlier, which suggests that shallow subsurface flow from riparian soils remained active. Biogeochemically, this coupling could be explained by slow subsurface flow fed by catchment water storage, which continuously transferred soluble DOC into the channel, alongside potential in-stream biological production [40]. Simultaneously, at a near-neutral pH of 6.9 where bicarbonates dominate [35], the DIC maximum reflects enhanced soil respiration combined with silicate weathering [8, 18, 41] Consequently, this late-spring outlier highlights a seasonal transition where active subsurface pathways and restricted dilution simultaneously concentrate both carbon forms.

Concluding the anomalous events for Period 1, the minor upper DOC outlier (2.97 mg L^{-1}) and the lower DIC outlier — representing the minimum concentration (2.04 mg L^{-1})— were both identified concurrently in late fall (December 2, 2005) mid-way through the rising limb (Q 0.57 m^3 s^{-1}) of a large-magnitude storm event (44.6 mm of rainfall; AP7 49.2 mm; AP21 105.8 mm), which rapidly elevated discharge from 0.2 to 1.1 m^3 s^{-1} [37]. Given that the overall DIC dynamics in this catchment exhibit a strong linkage with baseflow—as suggested by the series boxplots (Fig. 1)—the occurrence of this minimum concentration during the rising limb could be attributed to baseflow dilution caused by the combined input of overland flow and fast subsurface flow into the stream. In contrast, fast subsurface flow, despite its short contact time with the soil matrix constraining the solubilization of organic carbon from upper horizons, could mobilize residual DOC unexhausted during preceding fall storms. Furthermore, overland flow, in synergy with this subsurface flow, might have acted as an indirect transfer mechanism for DOC via the solubilization of organic carbon bound to eroded sediments. This hypothesis is supported by the high suspended sediment concentrations from an agricultural plot hydrologically well-connected to the stream [37]. Indeed, this mechanism aligns with previous studies in the area that reported a strong correlation between DOC and suspended solids transported by overland flow during some rainfall events in fall and winter, that is, during the wet period [21, 22]

Shifting the focus to Period 2, the only upper DOC outlier (4.71 mg L^{-1}) occurred on October 6, 2006, mid-way through the rising limb of a 37.8 mm rain-runoff event (Qmax approx. 0.4 m^3 s^{-1}). This storm immediately followed a major event on October 1–3 (107.6 mm rainfall; AP23 70.2 mm; Qb: 0.10 m^3 s^{-1}; Qmax: 0.63 m^3 s^{-1}), triggering an immediate increase in stream discharge but yielding a reduced runoff coefficient, as the majority of the water input served to restore the soil water storage, which was depleted after the summer [28, 39]. In the context of an agroforestry catchment with high infiltration capacity [28], the occurrence of this outlier could be explained by a two-phase sequence: an initial chemical dissolution phase followed by a subsequent subsurface flow expulsion phase. During the summer dry season, the lack of connectivity of hydrological flow paths to the stream reduces the export of DOC [42-44]. This hydrological isolation, combined with microbial activity and the decomposition of plant residues—sourced from both forest cover and pastures or croplands—allows a labile organic carbon fraction to accumulate in the upper soil layers [33, 22, 45]. The volume of water infiltrated during the first event could have solubilized the accumulated summer carbon, transforming the water stored in the soil matrix into a DOC-enriched pool. Subsequently, this DOC was flushed from the soil into the stream via subsurface pathways triggered by the second rain event.

3.3. Dissolved Carbon Load and Specific Yield

Table 2 summarizes the observed daily mean load and specific yield. Figure 2 illustrates the individual contributions of carbon fractions to the daily mean TDC yield per period.

Tab. 2. Observed daily mean load (kg d^{-1}) and daily mean specific yield (kg km^{-2} d^{-1}, in parentheses) for DIC, DOC, and TDC. Values are presented as mean ± standard deviation.

Period	DIC	DOC	TDC[a]
Period 1 (n = 31)	56.15 ± 30.53 (3.51 ± 1.91)	30.20 ± 25.55 (1.89 ± 1.60)	86.35 ± 51.07 (5.40 ± 3.19)
Period 2 (n =26)	62.03 ± 43.35 (3.88 ± 2.71)	39.29 ± 40.09 (2.45 ± 2.51)	101.32 ± 81.16 (6.33 ± 5.07)
Total Study Period (n = 57)	58.83 ± 36.70 (3.67 ± 2.29)	34.35 ± 32.98 (2.15 ± 2.06)	93.18 ± 66.29 (5.82 ± 4.14)

[a]TDC represents the sum of the DIC and DOC fractions.

Mass export analysis demonstrates that Period 2 recorded the highest exportation of the study. For Period 1, the observed daily mean load of TDC was 86.35 kg d^{-1}, equivalent to a daily mean specific yield of 5.4 kg km^{-2} d^{-1}; of this total, DIC represented 65% and DOC accounted for 35% (Fig. 2). In contrast, during Period 2, TDC increased by 17.3%, reaching a load of 101.32 kg d^{-1} and a daily mean specific yield of 6.33 kg km^{-2} d^{-1}, composed of 61% DIC and 39% DOC. This net increase in total kilograms transferred per day confirms a more active carbon transport dynamic during Period 2 compared to Period 1. For the total study period, calculated as the average of all collected grab samples, the observed daily mean load of TDC was 93.18 kg d^{-1}, which represents a daily mean exportation of 5.82 kg km^{-2} d^{-1}. Within this global balance, DIC was the clearly dominant fraction, representing 63% of the total flux compared to 37% for DOC (Fig. 2).

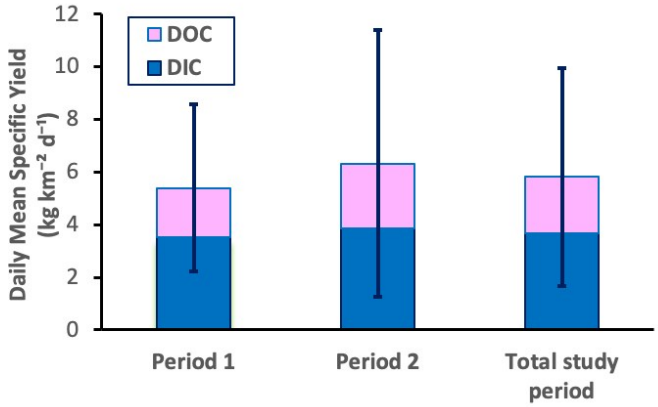

Fig. 2. Contribution of carbon fractions to the daily mean TDC specific yield per period. Bars represent the mean, and error bars represent the TDC standard deviation.

4. Conclusions

During the total study period, DIC concentrations were clearly higher than DOC concentrations, indicating that most of the dissolved carbon in the stream water is in its inorganic form. Regarding interannual variability, the central tendencies of TDC, DIC, and DOC showed stability due to dominant baseflow conditions; however, a clear contrast in baseflow concentrations was observed, as Period 2 exhibited a much wider interquartile range across all carbon fractions. In terms of fraction-specific behavior, DOC exhibited high variability with multiple upper outliers, which are primarily associated with episodic flushing events from the upper soil horizons due to rainfall-runoff events, and only occasionally to in-stream processes. In contrast, DIC remained stable across both periods, although it presented a single lower outlier corresponding to its minimum value in Period 1, which is attributed to a rainfall-runoff event that caused the dilution of stream water DIC. Given the near-neutral pH of the stream, DIC exists primarily as bicarbonate ion. Regarding dissolved carbon export, the total study period was characterized by an observed daily mean TDC load of 93.18 kg d^{-1} (specific yield of 5.82 kg km^{-2} d^{-1}), dominated by DIC. However, interannual variability in export loads was observed.

Finally, these findings highlight the critical importance of episodic events in carbon dynamics. Consequently, future monitoring programs must encompass both high- and low-flow regimes to accurately capture the full range of fluvial carbon transport.

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References

1. M. Meybeck, “Carbon, nitrogen, and phosphorus transport by world rivers”, Am. J. Sci., 282, 401–450 (1982).
2. M. F. Billett, C. M. Deacon, S. M. Palmer, J. J. C. Dawson and D. Hope, “Connecting organic carbon in stream water and soils in a peatland catchment”, J. Geophys. Res., 111, G02010 (2006).
3. T. Lambert, C. R. Teodoru, F. C. Nyoni, S. Bouillon, F. Darchambeau, P. Massicotte and A. V. Borges, “Along-stream transport and transformation of dissolved organic matter in a large tropical river”, Biogeosciences 13, 2727–2741 (2016).
4. K. Kalbitz, S. Solinger, J. H. Park, B. Michalzik and E. Matzner, “Controls on the dynamics dissolved organic matter in soils: A review”, Soil Sci., 165 (4): 277–304 (2000).
5. P. Massicotte and J. J. Frenette, “Spatial connectivity in a large river system: resolving the sources and fate of dissolved organic matter”, Ecol. Appl., 21, 2600–2617 (2011).
6. B. Stewart, W. Zhi, K. Sadayappan, G. Sterle, A. Harpold and L. Li, “Soil CO2 controls short-term variation but climate regulates long-term mean of riverine inorganic carbon”, Global Biogeochem. Cycles 36 (8) (2022).
7. J. J. Cole and Y. T. Prairie, “Dissolved Inorganic Carbon,” in Reference Module in Earth Systems and Environmental Sciences. Amsterdam. Elsevier, 2014.
8. J. Gaillardet, B. Dupre, P. Louvat, and C. J. Allegre, “Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers”, Chem. Geol. 159 (1–4), 3–30 (1999).

9. Z. H. Liu, W. Dreybrodt, and H. Liu, “Atmospheric CO2 sink: Silicate weathering or carbonate weathering?” Appl. Geochem., 26, S292–S294 (2011).
10. A. Marx, J. Dusek, J. Jankovec, M. Sanda, T. Vogel, R. van Geldern, J. Hartmann and J. A. C. Barth, “A review of CO2 and associated carbon dynamics in headwater streams: A global perspective”, Rev. Geophys., 55, 560–585 (2017).
11. H. P. Jarvie, C. Neal, D. V. Leach, G. P. Ryland, W. A. House and A. J. Robson, “Major ion concentrations and the inorganic carbon chemistry of the Humber rivers”, Sci. Total Environ., 194, 285–302 (1997).
12. R. P. A. Raymond and J. E. Saiers, “Event controlled DOC export from forested watersheds”. Biogeochemistry 100 (1–3), 197–209 (2010).
13. T. S. Bianchi, F. Garcia-Tigreros, S. A. Yvon-Lewis, M. Shields, J. H. Mills, D. Butman, C. Osburn, P. Raymond, G. C. Shank, S. F. DiMarco, N. Walker, B. K. Reese, R. Mullins-Perry, A. Quigg, G. R. Aiken and E. L. Grossman, “Enhanced transfer of terrestrially derived carbon to the atmosphere in a flooding event”, Geophys. Res. Lett., 40, 1–7 (2013).
14. C. Zhao, G. Yang, L. Meng, H. Chen, S. Li, F. Chen, Z. Bian, J. Chen, J. Zhou, Q. Jiang, T. Huang, H. Yang and C. Huang, “ Extreme precipitation amplified the cumulative effects of DOM availability on organic-sourced DIC in the Yangtze River”, Water Res., 287, 124312 (2025).
15. Y. Cai, L. Guo and T. A. Douglas, “Temporal variation in organic carbon species and fluxes from the Chena River, Alaska”, Limnol. Oceanogr., 53, 1408–1419 (2008).
16. P. A. Raymond, N. H. Oh, R. E.,Turner and W. Broussard, “Anthropogenically enhanced fluxes of water and carbon from the Mississippi River”, Nature, 451, 449–452 (2008).
17. W. Ludwig, P. Amiotte Suchet and J. L. Probst, “River discharges of carbon to the world’s oceans: Determining local inputs of alkalinity and of dissolved and particulate organic carbon”. Sci. Terre Des. Planètes Comptes Rendus L’académie Des. Sci. 323, 1007–1014 (1996).
18. M. Meybeck, “Global chemical weathering of surficial rocks estimated from river dissolved loads”. Am. J. Sci. 287 (5), 401- 408 (1987).
19. A. Baker, S. Cumberland and N. Hudson, “Dissolved and total organic and inorganic carbon in some British rivers”, Area 40, 117–127 (2008).
20. H. He, T. Li, C. He, J. Chen, H. Chu and B. Dong, “Removal of natural organic matter in full-scale conventional and advanced water treatment plants: Assimilable organic carbon and its precursors”, Chem. Eng. J. Adv. 8, 100183 (2021).
21. M. M. Taboada-Castro, M. L. Rodríguez-Blanco, J. Andrade and M. T. Taboada-Castro, “Geochemical Behavior of Dissolved Organic Carbon under Baseflow Conditions at the Corbeira Stream Water, Spain”, Commun. Soil Sci. Plant Anal., 43:17, 2202-2208 (2012).
22. J. A. Figueiredo, E. A. Menor, M. T. Taboada-Castro, M. M. Taboada-Castro and L. D. Lacerda, “Hydrogeochemistry approach to the identification of flow components under the descending limb conditions of a hydrograph (Corbeira stream, Spain)”, Appl. Geochem., 27, 753–759 (2012).
23. J. A. Figueiredo, E. A. Menor, M. T. Taboada-Castro, M. M. Taboada-Castro, M. L. Rodríguez-Blanco and E. S. Braga, “Using hydrogeochemical signatures of stream water to assess pathways for rainfall events: towards a predictive model”, Hydrol. Process., 28, 2302–2311 (2014).
24. IGME (Instituto Tecnológico y Minero de España), Mapa Geológico de España, 1:50,000. Hoja 45. Betanzos. Spain (1981).
25. J. Samper, A. Naves, B. Pisani, J. Dafonte, L. Montenegro and A. García-Tomillo, “Sustainability of groundwater resources of weathered and fractured schists in the rural areas of Galicia (Spain)”. Environ Earth Sci. 81:141 (2022).
26. IUSS Working Group WRB. World Reference Base for Soil Resources. International soil classification system for naming soils and creating legends for soil maps. 4th edition. International Union of Soil Sciences (IUSS), Vienna, Austria (2022).
27. M. L. Rodríguez-Blanco, M. M. Taboada-Castro and M. T. Taboada-Castro, “An Assessment of the Recent Evolution of the Streamflow in a Near-Natural System: A Case Study in the Headwaters of the Mero Basin (Galicia, Spain)”, Hydrology 7 (4), 97. doi:10.3390/hydrology7040097 (2020).
28. M. L. Rodríguez-Blanco, M. M. Taboada-Castro and M. T. Taboada-Castro, “Rainfall–runoff response and event-based runoff coefficients in a humid area (northwest Spain)”, Hydrological Sciences Journal, 57 (3) 445-459 (2012).
29. F. Soto-Varela, M. L. Rodríguez-Blanco, M. M. Taboada-Castro and M. T. Taboada-Castro, “Identifying environmental and geochemical variables governing metal concentrations in a stream draining headwaters in NW Spain”. Appl. Geochem., 44, 61–68 (2014).
30. M. L. Rodríguez-Blanco, M. T. Taboada-Castro and M. M. Taboada-Castro, “Improving the understanding of N transport in a rural catchment under Atlantic climate conditions from the analysis of the concentration–discharge relationship derived from a high-frequency data set”, Hydrol. Earth Syst. Sci., 27, 1243–1259, (2023).

31. M. L. Rodríguez-Blanco, M. M. Taboada-Castro and M. T. Taboada-Castro. “Long-Term Suspended Sediment Concentrations and Loads from a Relatively Undisturbed Agroforested Catchment in the Northwest of the Iberian Peninsula”. Water, 10, 1302 (2018).

32. E. M. Thurman, Organic Geochemistry of Natural Waters (Springer Science & Business Media, Kluwer Academic Publishers Group, Dordrecht, The Netherlands, 1985), pp. 497.

33. E. W. Boyer, G. H. Hornberger, K. E. Bencala and D. M. McKnight, “Response characteristics of DOC flushing in an alpine catchment”. Hydrol. Processes 11(12), 1635-1647 (1997).

34. T. Lambert, C.R. Teodoru, F. C. Nyoni, B. Bouillon, F. Darchambeau, P. Massicotte and A. V. Borges, “Along-stream transport and transformation of dissolved organic matter in a large tropical river”, Biogeosciences 13, 2727–2741 (2016).

35. W. Stumm and J. J. Morgan, Aquatic chemistry: chemical equilibria and rates in natural waters (John Wiley & Sons., 3rd edn. A Willy-Interscience Publication, New York 2012).

36. M. L. Rodríguez-Blanco, M. M. Taboada-Castro, L. Palleiro-Suárez, and M. T. Taboada-Castro, “Effect of runoff on suspended sediment and phosphorus loading in a headwater stream of a rural catchment (NW Spain)”, Rev. de Ciências Agrárias 33(1) 329-337 (2010).

37. M. L. Rodríguez-Blanco, M. M. Taboada-Castro and M. T. Taboada-Castro, “Sources and sediment yield from a rural catchment in humid temperate environment, northwest Spain”, Earth Surf. Process. Landforms 35, 272–277 (2010).

38. J. D. Hewlett and A. R. Hibbert, “ Factors affecting the response of small watersheds to precipitation in humid areas” in Forest Hydrology, edited by W. E. Sopper and H. W. Lull (Pergamon Press, New York, 1967), pp. 275-290.

39. M. L. Rodríguez-Blanco, M. M. Taboada-Castro, L. Palleiro, M. T. Taboada-Castro, “Temporal changes in suspended sediment transport in an Atlantic catchment, NW Spain”, Geomorphology 123, 181–188 (2010).

40. O. Izagirre, U. Agirre, M. Bermejo, J. Pozo, and A. Elosegi, “Environmental controls of whole-stream metabolism in a Mediterranean-Atlantic forested catchment”, Journal of the North American Benthological Society, 27(1), 42-55 (2008).

41. E. A. Davidson and I. A. Janssens, “Temperature sensitivity of soil carbon decomposition and feedbacks to the climate system”. Nature, 440 (7081) 165-173 (2006).

42. B. Glaser, M. Antonelli, L. Hopp and J. Klaus, “Intra-catchment variability of surface saturation – insights from longterm observations and simulations”, Hydrol. Earth Syst. Sci., 24, 1393-1411 (2020).

43. K. Blaurock, B. Beudert, B. S. Gilfedder, J. H. Fleckenstein, S. Peiffer, L. Hopp, “Low hydrological connectivity after summer drought inhibits DOC export in a forested headwater catchment”, Hydrol. Earth Syst. Sci., 25, 5133–5151 (2021).

44. R. Harrison, J. van Tol, P. A. Suchet, M. Thevenot and M. Olivier, “Environmental Factors Influencing Dissolved Organic Carbon Concentrations in Afromontane Catchments”. Int. J. Environ, Res. 19, 78 (2025).

45. A. Senatore, G. A. Corrente, E. L. Argento, J. Castagna, M. Micieli, G. Mendicino, A. Beneduci and G. Boter, “Seasonal and storm event-based dynamics of Dissolved Organic carbon (DOC) concentration in a Mediterranean headwater catchment”, Water Resour. Res., 59, e2022WR034397 (2023)