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Sources and main controls of dissolved organic and inorganic carbon in river basins: a worldwide meta-analysis

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Abstract

Despite dissolved carbon (C) exports from continents being crucial in the connection between terrestrial, atmospheric and oceanic C pools, the relative contribution and process controls on dissolved organic (DOC) and inorganic (DIC) fluxes within river basins are not fully understood. This paper presents an analysis of data from 843 sites worldwide from Web of Science SCI-Expanded (ex ISI) indexed papers that report both the DOC and DIC contents and fluxes in conjunction with chemical elements, such as Si, Na and ^{13}C abundance, to investigate the likely origin, pathways and fate of the dissolved C. The reviewed papers also report on selected environmental factors (e.g., MAP and MAT: mean annual precipitation and temperature respectively; Climate, LU: land use, A: basin surface area). Regarding dissolved C fluxes rivers transported on average, 8.4 GT C yr⁻¹ of dissolved C with 7.7 GT C yr⁻¹ (92%) being DIC and remaining (8%) DOC. Asia has the highest within-river dissolved C transport (5.8 GT C yr⁻¹) followed by Europe (2.0 GT C yr⁻¹), America (0.4 GT C yr⁻¹), and Africa (0.1 GT C yr⁻¹). The dissolved C fluxes tend to increase with river water fluxes and contribution of interflow as seen in the tropical climate, which results in the export of relatively fresh DOC with low aromaticity. In contrast, the lower river water fluxes in sub-tropical and temperate climates corresponds to high concentration of comparatively more decomposed DOC, which pointed to a high proportion of groundwater contribution to the water fluxes. The results also imply that surface area and morphology of the river basins, as well as land use, has insignificant impact on dissolved C dynamics. Such quantitative results, including on the important role of climate on the dynamics of dissolved C in river basins, are helpful in improving predictions on the impact of climate change on the global C cycle. New and innovative multidisciplinary research on the subject is called for.

Key words: C erosion, dissolved C, global C cycle, river water fluxes

1 Introduction

Rivers transport enormous amounts of carbon (C) from the land to the ocean. They are thus a key element in the connectivity between the terrestrial, atmospheric and oceanic C pools of the global C cycle with important consequences on the regulation of climate, soil and water quality and the overall ecological functioning. Despite that, the amount, quality and spatial patterns of riverine C fluxes are not very well understood. Land C can be exported in particulate, such as particulate organic C (POC) and inorganic C (PIC), and/or dissolved forms, such as dissolved organic C (DOC) and inorganic C (DIC). POC and DOC originate from organic matter (OM) eroded from soils or from aquatic plants. The DOC is a result of the decomposition of OM, while DIC is derived from rock weathering.

The exported C varies chemically from easily decomposable to more stable compounds, depending on sources and pathways (Lloret et al., 2016). Virtually all natural water contains some form of DOC, ranging from highly reactive freshly produced DOC to low reactive recalcitrant DOC that escaped remineralization for upwards of 6000 years (Druffel and Williams, 1992). Therefore, a thorough understanding of the riverine C fluxes and their controls is needed, particularly to assess their responses to current and future climatic change and influence of anthropogenic activities. Previous studies have shown that approximately 1 Pg C is exported each year from the land to the ocean with 65% of it being dissolved and 35% particulate. Sixty percent (60%) of the dissolved C export is inorganic, while 40% is organic (Probst et al., 1994). These data correspond to 0.22 Pg C yr⁻¹ DOC and 0.18 Pg C yr⁻¹ POC export; while 0.43 and 0.17 Pg C yr⁻¹ are DIC and PIC export, respectively.

Nevertheless, existing literature indicated the existence of large flux variations of these forms of riverine C (Meybeck, 1982; Ludwig et al., 1996; Huang et al., 2012; Regnier et al., 2013), resulting in different impacts on climate, aquatic and terrestrial ecosystems.

Humid tropical and subtropical regions of the world are characterized by large C exports (Galy et al., 2015; Hilton, 2017) with their rivers lying between 30°N and S latitudes transporting 62% of the global DOC export to the ocean (Dai et al., 2012). Their estimated export rates of 2.1 and 3.3 t C km⁻² yr⁻¹ for DOC and DIC, respectively, are far above the respective global export averages of 1.4 and 2.6 t C km⁻² yr⁻¹ (Huang et al., 2012). Yet the controls of their exports and ratios between them are scarcely investigated worldwide.

Results from the project named ‘Transport of Carbon and Minerals in Major World Rivers’ (SCOPE/UNEP) revealed that POC fluxes are a function of total suspended sediments, while DOC fluxes are linked to drainage intensity, basin slope, amount of soil C and C:N ratio (Ludwig et al., 1996). Li et al (2017) indicated that while DOC fluxes were primarily related to discharge ($r^2=0.93$) and soil organic C content ($r^2=0.60$), DIC fluxes correlated to CO₂ consumption by rock weathering ($r^2=0.66$) and river discharge ($r^2=0.63$). While several studies estimated the types of C exported by rivers, little is known about the global variations of the sources of the C, specifically dissolved C.

The major sources of riverine organic C are either autochthonous DOC produced by riverine biological activities or allochthonous C from detrital input (Aitkenhead-Peterson et al., 2003). In the case of allochthonous sources, the main driver of the organic C input into river systems is soil erosion. During erosive rainfall events, soil organic C is either intensively leached or eroded and transferred to aquatic ecosystems in dissolved and particulate forms. During low water stages, the DOC input can also be completed by soil water infiltration. The soil organic C (SOC) pool, which contains 1400–1500 Gt of C, is one of the major reservoirs of C (Schlesinger, 1977) storing twice the quantity of C in vegetation. Therefore, any change in

SOC abundance and composition has important effect on the global C cycle as well as soil ecosystems.

SOC is essentially regulated by biological production and decay rate of organic compounds (Tian et al., 2016). Plant litter falling onto the soil surface is gradually decomposed through physical fragmentation, faunal interactions, mineralization, and humus formation (Baudin et al., 2007). Overall, these processes induce variations in concentration and isotopic composition of total SOC in the soil profile. The decomposition of litter and SOM induces a differential decrease of SOC and nitrogen content in the soils. Carbon and nitrogen are not recycled at the same rate, hence the C/N ratios also vary throughout the soil profile. The C/N ratios are typically higher in the litter fall and lower in SOM due to humification (Yang et al., 2010). Selective degradation changes the stable C isotope ratios. Surface litter is more depleted in ^{13}C than SOM (Lichtfouse et al., 1995), which is progressively enriched with soil depth (Balesdent and Mariotti, 1996; Amiotte-Suchet et al., 1999, 2007). Therefore, highlighting the variations of concentrations and isotopic compositions of soil C (in solid and solute fractions) could help to track the origin of organic C in rivers with respect to their hydrological stages.

In their study of a tropical river using C isotopes, Lloret et al. (2016) indicated that DOC derived essentially from both the lixiviation of the soil surface layers during floods and groundwater flow during low water levels. Furthermore, DOC is extensively reworked within rivers through biotic processes such as bacterial degradation as well as abiotic processes such as photo-oxidation, and co-precipitate alongside inorganic minerals and salts. Albéric et al. (2018) further indicated that DOC transported in the Amazon basin exhibited higher $\delta^{13}\text{C}$ -DOC values, with a lower range in the upper than downstream reaches (-28.0 to -34.6%), which they attributed to increased proportion of fresh DOC from floodplains and open lakes.

111 These authors also reported higher $\delta^{13}\text{C}$ -DOC values during low flows, which they could not
112 fully understood.

113 Despite numerous studies on the C fluxes and the different forms from continents to the
114 ocean, little is known globally about the sources of this C, its pathways and fate, and the main
115 associated controls. Several questions including the following largely remain unanswered.
116 Does riverine DOC originate from top-soils, deep soil horizons or from within stream
117 production? What are the likely dominant pathways from overland flow to the river systems;
118 is it groundwater flow or interflow? How do sources and pathways vary from one climate to
119 the other, from one continent to the other?

120 Several studies reported disparities in DOC and DIC exports under different climates,
121 topographic conditions, land uses and water regimes; hence, there is no consensus yet on the
122 impact of these factors. Although C transformations and interactions between different
123 chemical and size fractions are important in influencing the chemistry and cycling of C in
124 aquatic environments, most studies focused on single C species, preventing a comprehensive
125 understanding of the C dynamics and export fluxes. Determining how the C dynamics vary as
126 flowing water increases in volume from first-order springs until they seep into the great rivers
127 of the world is a central problem in riverine ecology. Moreover, an improved understanding
128 of the pathways of the exported C may allow a better understanding of the origin and overall
129 dynamics of the exported C.

130 The existence of many studies across the world that reported data on DOC and DIC, and on
131 several water chemicals provides opportunities for comprehensive analyses of DOC and DIC
132 fluxes, and their pathways to draw a general understanding of the main controls of these
133 dissolved C dynamics. Therefore, the objective of the current study is to compile and analyze
134 available studies on river DOC and DIC and associated chemicals to assess and quantify their
135 dynamics at river basin level. The information on $\delta^{13}\text{C}$, together with water chemistry, might

allow to decipher the C dynamics. In pursuit of these objectives, the study compiled data from 843 sampling locations around the world.

2 Materials and Methods

2.1 Study setup

The study is based on data collected from available literature that reported on dissolved C exports to the ocean through major rivers around the world. The literature search targeted to identify and collect C exports, with specific focus on the dissolved forms (and associated data on isotope ^{13}C and water chemistry to inform on the sources, pathways and quality of dissolved C), from peer reviewed scientific articles published in Web of Science SCI-Expanded (ex ISI) indexed journals. Besides, a number of topic related key words and terms (such as “soil carbon exports from river basins”, “exports of carbon by river systems” and “dissolved carbon losses from landscapes”) were used to search for journal papers in Google, Google Scholar, Science Direct, Springer Link, Scopus and SciFinder.

In order to be accepted for inclusion in the analysis, the key criterion was that a paper had to report on the C content and the fluxes of the water exported by a river tied to a time scale. The river name and location had to be stated as well. The search yielded 48 research papers with 843 data points worldwide (Figure 1). Most of the observations ($n=223$) were in North America as reported by 14 papers. This was followed by 169 observation points (10 papers) in South America, 148 (14 papers) in Europe, 136 (4 papers) in Oceania, 84 (9 papers) in Africa and lastly 81 (7) in Asia. Nevertheless, data from Oceania were not considered in the analysis because 81 of the 84 observations came from Papua New Guinea.

Data from the 48 papers were captured and used to build a database with information such as paper author/s and year when paper was published, title of paper, locational details of river studied (i.e., country, continent, latitude, longitude and altitude), characteristics of the river

(i.e., length, river basin size, average slope, water temperature, discharge and content in selected chemicals, namely Si: Silicate, Na: Sodium, and ^{13}C isotope), environmental characteristics (climatic data: MAP and MAT, and major land uses) and C discharge (discharge rates of the different forms of C such as DOC, DIC, POC and PIC).

2.2 Definitions of environmental factors and variables

Mean annual temperature (MAT, $^{\circ}\text{C}$) and precipitation (MAP, mm yr^{-1}) are the long term (≥ 30 year) average values for the basins of the studied rivers, and they are captured MAT and MAP as presented in the source papers. The longitude (LONG), latitude (LAT) and altitude (Z) are for the observation points. In the event MAT and MAP are missing from source papers, data are retrieved either using other research papers in the area or global databases (see Mutema et al, 2015). Length (L, km) refers to the estimated length of the river from its source to the observation point (i.e., outlet to the ocean or to another major river) and Q ($\text{m}^3 \text{s}^{-1}$) its annual average discharge at the observation point; both are as reported in the source papers. The other factors, such as river water temperature (T_w , $^{\circ}\text{C}$) and pH, are also specific to the observation points used and as reported in the source papers.

The variables of interest are dissolved organic (DOCc, mg C l^{-1}) and inorganic C (DICc, mg C l^{-1}) and particulate organic C (POCc, mg C l^{-1}) content within rivers. DOCc and DICc are dissolved organic and inorganic carbon concentrations (mg C l^{-1}), respectively, of water samples from specific observation points as reported in the source papers. POCc is the corresponding concentration of particulate organic carbon (mg C l^{-1}) in the water samples. Therefore, total organic C (TOCc, mg C l^{-1}) is computed as a sum of DOCc and POCc, while total C (TCc, mg C l^{-1}) includes DICc. Si/Na is ratio of silicon to sodium concentration as reported for the water samples analysed.

Within-river fluxes were computed as follow:

$$DOC_F = \frac{DOC_c \times Q}{A} \quad (\text{Eqn. 1})$$

$$DIC_F = \frac{DIC_c \times Q}{A} \quad (\text{Eqn. 2})$$

where DOC_F and DIC_F ($\text{g C s}^{-1} \text{ km}^{-2}$) are dissolved organic and inorganic carbon fluxes respectively, DOC_c and DIC_c (g L^{-1}) are the corresponding average dissolved organic and inorganic carbon concentrations, Q (L s^{-1}) is the average discharge of the river at the observation point, and A (km^2) is the area discharge of the catchment draining at the observation point. DOC_F and DIC_F were finally expressed for main world regions in Giga Tons (GT C yr^{-1}) by extrapolating the data to the surface area of each region.

Several land use types were considered and the major ones were forests (natural and/or tree plantations), grasslands (include natural veld and planted grasses, and open Savannahs), wetlands (mostly natural, but also included cultivated wetlands such as paddy fields), urban and croplands. The most dominant land use, in terms of fractional area covered, was assigned to a river basin. The climatic regions used in the current study (polar, temperate, sub-tropical and tropical) were inspired by Mutema et al. (2015) and do not necessarily adhere to the Köppen (1936) classification system. These climatic regions are defined in Table 2, where the polar to tropical region transition represents a general increase in air temperature and precipitation.

2.3 Data analysis

2.3.1 Estimation of the sources and pathways of dissolved C

Stable water and C isotopes have been used to determine the origin, pathways and fate of organic substances in river systems (Mayorga et al., 2007; Trumbore, 2009, Zao et al., 2018). Isotopic tracers of hydrogen and oxygen are the most frequently used for estimating the sources of river waters (Lambs, 2004; Xu et al., 2017). However, the limited information on

them in conjunction with river water C content calls for alternatives. Easy to access hydrochemical parameters such as anions and cations make it possible to compare the contributions of groundwater versus surface water in river basins (Cook et al., 2003).

Si and Na can reasonably be considered as conservative elements and show large concentration differences between water compartments (Mutema and Chaplot, 2018; Chaplot and Ribolzi, 2014; Gomi et al., 2010; Ladouche et al., 2001). For example, water derived from melted snow and ice, and/or overland flow, which had low contact with soils and rocks, exhibits low Si and Na concentrations. As the duration of contact with rocks increases, the chemical content of the water increases. This explains groundwater enrichment, in most cases, in Ca and Na, as a result of the alteration of plagioclase, and interflow being Si enriched. The present study analysed the Si and Na content of the river waters as proxy for identifying the origin of the water transporting dissolved C.

In addition, available data on ^{13}C content of the dissolved C were considered to account the level of organic matter (OM) aromaticity, and thus its potential source and fate. In general, fresh OM is depleted in ^{13}C , while the older and decomposed OM is enriched due to selective preservation of plant lignin and lipids (Lichtfouse et al., 1995). Another important variation of ^{13}C abundance in dissolved C depends on the type of plant where it originated from (C_3 vs. C_4 photosynthetic pathway), which informs on the source of DOC.

Data for each sampling data point were confronted to types of climate such as for figure 7 and to ^{13}C data (Figure 8).

2.3.2 Correlations between dissolved C content, fluxes and main controls

Units for similar factors of control and variables of interest differed from paper to paper. Sometimes the units depicted the spatio-temporal scales at which studies reported in the papers were carried out. Therefore, the first step in the data analysis process was to normalize

the data for each factor and/or variable to the same unit. The second step was an analysis for descriptive statistics, such as mean, median, minimum, maximum, standard deviation and standard error of mean, coefficient of variation, kurtosis and skewness. Skewness and kurtosis were used to test normality of dataset distribution. The mean values were tested for significance of differences using the *T-test*. The third step was an exploratory analysis of the main factors controlling the exports of dissolved C using correlation and Principal Component Analysis (PCA). Correlation analyses tested strengths of one-on-one relationships between factors and variables. The correlations were tested for statistical significance at $p < 0.05$. The PCA was used to evaluate multiple relationships between DOCc, DICc, Q and Si/Na on one hand, and factors of control (MAP, MAT, Z: altitude and A: river basin area) on the other. In general, a PCA converts factors and variables into their linear combinations (Jambu, 1991). The last step was a more in-depth analysis of the impacts of selected control factors on the variables using box-plots. Each box plot shows the quartiles for the non-outlier range. Data for each sampling data point were considered for computed the continental mean values displayed in (Table 3) or the worldwide mean values (Table 4).

3 Results

3.1 Environmental setting

Table 1 introduces summary statistics for the selected studies worldwide. The mean annual temperatures (MAT) of the river basins under the current study was 16.7°C, with a variation from -3.1°C (USA: Cai et al., 2008) to 27.0°C (Venezuela: Saunders and Lewis, 1988; Paolini et al., 1987, and Nigeria: Martins, 1983). The corresponding mean annual precipitation (MAP) varied from 224 (Pakistan: Arain, 1987) to 4341 mm yr⁻¹ (Costa Rica: Genereux et al., 2013), with a mean of 1456 mm yr⁻¹ (CV=71%).

Information on the river characteristics, such as river length, discharge, water temperature and pH, was generally scanty. Nevertheless, the available data showed large variations in the case of river length (CV=139%), with smallest length being 4 for Horonai River in Japan (Shibata et al., 2001) and longest 6290 km for the Amazon (Peru, Colombia and Brazil in South America). River discharge varied even more (CV=355%), but water temperature (37%) had low variation.

The DOC content (DOCc) averaged 5.30 mg C l^{-1} , with values from average 0.7 for some observations in Puerto Rico (Bhatt and McDowell, 2007) to 19.7 mg C l^{-1} in Venezuela (Paolini et al., 1987). The DIC content (DICc) average was $14.85 \text{ mg C l}^{-1}$, which was three times greater than DOCc. POC content (POCc) varied from 0.5 mg C L^{-1} in Japan (Shibata et al., 2001) to 24.2 mg C l^{-1} in France (Némery et al., 2013), with an average of 5.0 mg C L^{-1} . The corresponding total organic C content (TOCc) averaged 11.0 mg C l^{-1} . The DICc varied between 0.6 for observations in the UK (Neal and Hill, 1994) and 64.4 mg C l^{-1} for Belgium (Abril et al., 2000). The overall total C (TCc), the sum of all organic C forms and DIC, averaged 27.6 mg C l^{-1} , with a variation from 6.5 to 82.1 mg C l^{-1} (CV=73%).

3.2 Within-river DOC and DIC fluxes

3.2.1 Differences between global regions

Figure 2 shows the variability of DOCc, DICc and the respective DOCc/DICc ratios across global regions. Asian rivers show the highest within-river DOCc (Figure 2A), with an average of $8.7 \pm 1.4 \text{ mg C l}^{-1}$ (Table 3). The other regions do not appear to differ that much among themselves. The European rivers are the second highest with a significantly lower average value of $4.63 \pm 1.10 \text{ mg C l}^{-1}$, which is not significantly different from Africa ($4.2 \pm 1.1 \text{ mg C l}^{-1}$), North ($4.0 \pm 1.1 \text{ mg C l}^{-1}$) and South America ($3.9 \pm 1.3 \text{ mg C l}^{-1}$). DICc shows a

different trend (Figure 2B) with European rivers showing the highest average value of $24.1 \pm 0.8 \text{ mg C l}^{-1}$ (Table 3), which is not significantly different from the Asian rivers ($23.9 \pm 1.1 \text{ mg C l}^{-1}$). The North American rivers have significantly lower DICc ($14.0 \pm 1.1 \text{ mg C l}^{-1}$) than the Asian rivers, but significantly higher than the South American rivers ($12.0 \pm 0.9 \text{ mg C l}^{-1}$). The African rivers have the least significant DIC ($8.8 \pm 1.0 \text{ mg C l}^{-1}$). The corresponding DOCc/DICc ratios are depicted in Figure 2C.

Table 3 also show that DOC fluxes (DOC_F) descended in the following order: Europe ($0.5 \text{ g C s}^{-1} \text{ km}^{-2}$) > Asia ($0.3 \text{ g C s}^{-1} \text{ km}^{-2}$) > South America ($0.1 \text{ g C s}^{-1} \text{ km}^{-2}$) > North America ($0.1 \text{ g C s}^{-1} \text{ km}^{-2}$) > Africa ($0.04 \text{ g C s}^{-1} \text{ km}^{-2}$). DIC fluxes (DIC_F) show a similar trend, but with higher values than DOC_F at 5.7, 3.9, 0.4, 0.1 and $0.08 \text{ g C s}^{-1} \text{ km}^{-2}$ for Europe, Asia, South and North America, respectively. In terms of DOC (DOC_E) and DIC exports (DIC_E), Asia has the highest values at 0.4 and 5.4 GT C yr^{-1} , respectively, followed by Europe at much lower values (0.2 and 1.8 GT C yr^{-1} , respectively). The other continents have similar DOC_E (0.04 , 0.05 and $0.06 \text{ GT C yr}^{-1}$ for Africa, North and South America, respectively); however, South America show much higher DIC_E (0.2 GT C yr^{-1}) than both North America (0.1 GT C yr^{-1}) and Africa ($0.08 \text{ GT C yr}^{-1}$).

3.2.2 Differences due to climate

A comparison of DOCc and DICc in different climatic regions shows that DOCc tends to decrease from the cold polar region to the hot and wet tropical area (Figure 3). However, DOCc does not differ significantly among the climatic regions at 5.3 ± 1.1 , 4.3 ± 1.4 , 4.8 ± 1.1 and $3.6 \pm 1.5 \text{ mg C l}^{-1}$ for polar, temperate, subtropical and tropical region, respectively (Figure 3A). DICc behaves differently with a general increase from the polar to temperate region, followed by a decrease to the tropical through the subtropical region (Figure 3B). The temperate region rivers show the most significant DICc ($26.3 \pm 0.8 \text{ mg C l}^{-1}$), followed by the

subtropical ($17.4 \pm 0.7 \text{ mg C l}^{-1}$), polar ($14.0 \pm 0.9 \text{ mg C l}^{-1}$) and tropical region ($10.7 \pm 1.2 \text{ mg C l}^{-1}$). All the DICc regional average values are significantly different from each other. The corresponding DOCc/DICc ratios show a tendency to be higher in the polar region than the other regions. The average ratios decrease in the order polar (1.5) > subtropical (1.0) > tropical (0.9) > temperate region (0.3).

3.2.3 Land use/land cover

Urban rivers appear to have the highest DOCc; however, wetlands show the highest variation of DOCc (Figure 4A). The two land uses are not significantly different with average values of 6.6 ± 0.7 and $5.7 \pm 1.4 \text{ mg C l}^{-1}$ for urban and wetlands, respectively. Cropland rivers' DOCc ($4.3 \pm 1.7 \text{ mg C l}^{-1}$) does not differ significantly from urban and wetlands, but forest rivers are significantly lower ($4.1 \pm 1.2 \text{ mg C l}^{-1}$). Nevertheless, cropland and forest river DOCc are not significantly different. It is also interesting to observe that grassland ($3.6 \pm 0.9 \text{ mg C l}^{-1}$) and Savannah ($3.7 \pm 0.7 \text{ mg C l}^{-1}$) do not differ significantly with forest rivers, but the Savannah rivers show greater variation. Urban ($22.5 \pm 0.5 \text{ mg C l}^{-1}$) and cropland rivers ($26.7 \pm 0.9 \text{ mg C l}^{-1}$) show much greater DICc than the other land uses, with cropland being significantly greater (Figure 4B). Grassland rivers ($19.9 \pm 1.0 \text{ mg C l}^{-1}$) are significantly lower than urban areas, but significantly greater than forest ($11.0 \pm 0.8 \text{ mg C l}^{-1}$) and Savannah ($11.6 \pm 0.7 \text{ mg C l}^{-1}$), which is not significantly different. Wetlands had the least significant DICc ($7.8 \pm 1.0 \text{ mg C l}^{-1}$). The corresponding DOCc/DICc ratios (Figure 4C) show considerably higher values in wetlands (1.7), forests (1.2) and also grasslands (0.9). Urban and Savannah are similar (0.6), while croplands have the least average ratio (0.3). However, wetlands and Savannah show high variability in the ratios.

3.2.4 Basin area

DOCc show a general tendency to increase with river basin area (Figure 5A). The DOCc increase from basin areas less than $1 \times 10^3 \text{ km}^2$ ($3.2 \pm 1.4 \text{ mg C l}^{-1}$) to 1×10^3 - $1 \times 10^4 \text{ km}^2$ ($3.9 \pm 0.9 \text{ mg C l}^{-1}$), before declining slightly to 1×10^4 - $1 \times 10^5 \text{ km}^2$ ($3.0 \pm 1.1 \text{ mg C l}^{-1}$). However, these three are not significantly different. Basin areas 1×10^5 - $1 \times 10^6 \text{ km}^2$ ($6.3 \pm 1.4 \text{ mg C l}^{-1}$) and $>1 \times 10^6 \text{ km}^2$ ($5.8 \pm 1.4 \text{ mg C l}^{-1}$) show significantly higher DOCc, but are not significantly different between themselves. DICc exhibits a different trend; it tends to increase with basin area up to 1×10^4 - $1 \times 10^5 \text{ km}^2$, followed by a general decrease (Figure 5A). The river DICc on the rising side are all significantly different at 12.3 ± 1.1 , 16.7 ± 0.8 and $18.6 \pm 0.7 \text{ mg C l}^{-1}$ for $<1 \times 10^3$, 1×10^3 - 1×10^4 and 1×10^4 - $1 \times 10^5 \text{ km}^2$, respectively. The other two basin sizes are not significantly different at 14.1 ± 1.2 and $13.7 \pm 1.4 \text{ mg C l}^{-1}$ for 1×10^5 - 1×10^6 and $>1 \times 10^6 \text{ km}^2$ respectively, which are not also not significantly different from basin area $<1 \times 10^3 \text{ km}^2$. It is important to observe that DICc on the rising side are characterized by greater variability in comparison to the falling side. The corresponding DOC/DIC ratios exhibit a general decrease followed by a rise (Figure 5C). The 1×10^5 - $1 \times 10^6 \text{ km}^2$ basin area show higher DOC/DIC ratio variability than the rest of the basin sizes.

3.2.5 Other important factors that control within-river DOC and DIC fluxes

Although many factors were initially considered, a general lack of quantitative data meant many of them could not be accepted for the current analysis. Table 4 shows the correlations between the accepted factors and C related variables. DOCc correlates positively with latitude and longitude ($r=0.27$), and negatively with both MAT (-0.41) and MAP (-0.29). On the other hand, DICc correlates positively with latitude (0.39) and Na (0.60) only, and negatively with river basin area (-0.25), MAP (-0.34), Q (-0.43), SiO_2 (-0.33) and Si/Na (-0.71). The corresponding DOCc/DICc correlates positively with basin area (0.32), MAP (0.31), Q (0.28) and Si/Na (0.50), but negatively with Na (-0.34). POCc, TOCc and TCc

correlate positively with longitude and Na; however, TCc also correlates negatively with MAP (-0.29), Q (-0.33) and Si/Na (-0.42). DOC_F and DIC_F correlate positively with MAP and Q. Nevertheless, DOC_F correlates negatively with Na (-0.35), while DIC_F also correlates negatively with SiO₂ (-0.35). Multiple correlations depicted by the PCA (Figure 6) suggest that DOCc and DICc tend to simultaneously increase with a combination of MAT and latitude, and to decrease with increasing MAP. In contrast, Q and Si/Na tend to increase with MAP, but tend to decrease with increasing MAT and latitude. The combined influence of river basin area and altitude on DOCc, DICc, Q and Si/Na appears to be very weak.

3.3 Potential sources of river dissolved carbon

The Si and Na for rivers of the different climatic zones (i.e. polar, temperate, sub-tropical and tropical region) are plotted on a simple Si-Na plane (Figure 7) in order to help in identifying the potential sources of the river waters. The data points from the polar region exhibit a low Si and Na content, which is indicative of diluted waters (Pradeep et al., 2016). The temperate region points are scattered over the Si-Na plane; however, they are in two distinct groups: one high in Na and low in Si, and the other one low in Na and high in Si content. The sub-tropical region points are scattered over the whole Si-Na plane, while those for the tropical region are enriched in Si compared to Na. Analysis of the relationship between Si/Na and δ DOC shows that δ DOC tends to decrease with increasing Si/Na ratios from -27.9‰ at Si/Na<50 to -31.8‰ at Si/Na>200 (Figure 8).

4 Discussion

4.1 Dissolved C fluxes within rivers: organic versus inorganic

Our current analysis revealed that riverine dissolved C fluxes are 8.4 GT C yr⁻¹. This amount is about 76 % of annual GES anthropogenic emissions, which is considerable. Past data from

a study by Probst et al. (1994) on the transport of C and minerals in major world rivers showed that approximately 0.65 GT C yr⁻¹ of dissolved C were exported by world rivers from landscapes to the ocean. Other authors reported dissolved C fluxes ranging from 0.58 GT C yr⁻¹ (Cai, 2011; Li et al., 2017), 0.60 GT C yr⁻¹ (Meybeck, 1982) to 0.9 GT C yr⁻¹ (Degens et al., 1991). Therefore, the current analysis estimated dissolved C fluxes within rivers are almost 12 times higher than estimated dissolved C exports to oceans.

One possible explanation for the big difference between current and past dissolved C fluxes is that much less dissolved C reaches the ocean than what the same rivers transport from upstream to downstream zones. Some of the dissolved organic matter decomposes and/or adsorb to some chemical elements/compounds and precipitate out of the within stream transport system (e.g., Chaplot and Robolzi, 2014). These processes can cause significant losses of dissolved C between the upstream and downstream zones of a river system. Another possible explanation could be the enhanced impact of (i) elevated atmospheric CO₂ on rock weathering (in the present study, DIC fluxes are 18 times higher than exports reported by Probst et al. (1994)) and (ii) increased temperature and urbanisation on DOC fluxes. Indeed, the intensification of human activities which has contributed to increased atmospheric CO₂ and climate change have likely accelerated DOC and DIC exports through organic matter decomposition and rock weathering in recent decades.

Our data also show that 92% of the 8.4 GT C yr⁻¹ dissolved C fluxes estimated in the current analysis is inorganic C (7.7 GT C yr⁻¹), while only and 8% is organic C (0.7 GT C yr⁻¹). Both estimates are significantly higher than 0.24 GT C yr⁻¹ reported for DOC (Ludwig et al., 1996), and 0.41 (Huang et al., 2012) and 0.38 GT C yr⁻¹ (Meybeck, 1982) for DIC. One possible explanation for the huge differences might be due to the different methodological approaches used to estimate the fluxes. For instance, Meybeck (1982) estimated global DIC fluxes (0.38 GT C yr⁻¹) based on discharge data at exit of 60 (i.e. 63% of global) rivers. The

estimations were not based on data derived from river water samples. They used average water temperature to obtain information regarding the dissolved C concentrations, which they used together with discharge data to estimate the dissolved C fluxes. Ludwig et al. (1996) used a similar methodology to estimate the global DOC export of 0.21 GT C yr⁻¹ on the basis of 29 major rivers. The current study used data from 249 rivers worldwide with most of them not discharging directly into the ocean. Therefore, most of the rivers used in the current study are tributaries and this might have affected the ratios between organic and inorganic C. In general, headwaters are likely to show greater DIC concentration, from rock weathering, than fresh waters exiting continents, which are generally characterised by low PCO₂ and thus DIC carrying capacity.

4.2 Sources and quality of dissolved C

The present study points to high concentration in Si and low concentration in Na in rivers from tropical climates, which is indicative of the predominance of interflow water (i.e. water moving laterally in soils within hillslopes) in rivers. Tropical regions are characterised by high rainfalls through the whole year, hence interflow into the rivers is always high which correlates with low proportion of inorganic C and fresh and low aromaticity dissolved organic matter. Albéric et al. (2018), who used C isotopes in a tropical humid basin of the Amazon, suggested that although DOC might have originated from soils there were strong chances that it also came from flooded forests and plankton in flooded lakes due to its depletion in ¹³C.

A study in a tropical river from the French West Indies indicated that DIC concentration was higher dry spells when water level was low (Lloret et al., 2011). The DIC concentration was lower during rainy seasons due to partial dilution by rainwater. The same study suggested two possible sources of river DIC. The first one is respiration of plant roots and decay of soil

organic matter (SOM) characterised by low $\delta^{13}\text{C}$, while the other one characterised by high $\delta^{13}\text{C}$ is atmospheric CO_2 input. In contrast, DOC during low flows might be autochthonous to the rivers and derived from algal development because groundwater is generally depleted in DOC. Therefore, high DOC concentrations during floods might come from mineral desorption and/or solubilisation of SOM and its transfer into rivers via surface runoff and interflow.

Results from the current study also point to relatively low DOCc in tropical rivers, which suggests that these river flows are dominated by interflow. Interflow is characterised by depletion in DOC as large amounts of the DOC are adsorbed by clays and/or sesquioxides within soils. Adsorption is a more efficient process of DOC depletion than decomposition (Jardine et al., 1989). Polar region river water shows low Si and Na concentration, which is indicative of an overland flow origin (Pradeep et al., 2016). A study in Chena River, Alaska, revealed that most of the DOC fluxes occurred during Spring peak flows due to ice and snowmelt, which drove high runoff from C rich soils (Cai et al., 2008). The study also reported DIC enrichment of winter water due to higher groundwater contribution. Groundwater contribution might explain the higher Na content in polar than tropical region river observed in the current study (Pradeep et al., 2016). High DOCc/DICc ratios in polar regions might come from peatlands from boreal forest as shown for instance by Elder et al. (2000).

The DOC from polar rivers exhibits the lowest $\delta^{13}\text{C}$ among the climates under study, which is indicative of fresh organic matter (Dijkstra et al., 2006). Such organic matter originates not only from snowmelt events that flush elevated DOC from surface soils, but also from riverine primary production (e.g. algal blooms in rivers during summer) (Dijkstra et al., 2006).

The present study also points to significant impact of water fluxes, dominant land use and river basin surface area on DOC. For example, DOC increases by 2.5 fold from river basin

areas less than 1 million km² to those more than 4 million km². In a study of 109 rivers across the world, Li et al. (2017) reported a significant increase of dissolved C fluxes as water fluxes increased, which the present study confirms but with much lower correlation coefficients of 0.55 and 0.48 for DOC_F and DIC_F, respectively, as compared to respectively 0.97 and 0.84. While Li et al. (2017) did not present data on dissolved C content, the current study shows that as water fluxes in river basins increase, DOC_c and DIC_c decrease, which is indicative of a dilution effect as elaborated above. Drainage intensity, slope, sediment loads, soil C content and C/N ratio, which are not considered in the current study, also have significant impacts on riverine dissolved C fluxes (Li et al., 2017; 1996; McDowell, 2000). The impact of land use, especially vegetation cover, on dissolved C fluxes is intuitive for organic C. For instance, Mchunu and Chaplot (2012) showed that a decrease in grass basal cover in the process of grassland degradation increased DOC in surface runoff from 3.8 to 7.2 g l⁻¹. Other studies reported higher DOC contents under forest and tilled soils than no-tilled croplands (e.g. Mchunu et al., 2011). Furthermore, the anthropological impact on riverine dissolved C has been recognized. For example, Raymond et al. (2008) reported that DIC has dramatically increased in the Mississippi River during the last 70 years in response to the intensification of agriculture, while rivers crossing urbanized areas have notoriously high DOC_c. The enormous amount of dissolved C transported by Asian rivers as compared to other continental rivers is most probably a result of a combination of factors including high content of SOC, urbanisation and intensification of agriculture in the face of climate change.

Conclusions

Three main conclusions are drawn from this study involving 843 data points of dissolved C content and fluxes from 249 rivers worldwide. The first conclusion is that most of the dissolved C transported by world rivers is inorganic (92% or 7.7 GT C yr⁻¹); the organic form

is a much smaller fraction (8% or 0.67 GT C yr⁻¹). The Asian rivers transport the highest amount (5.8 GT C yr⁻¹) of dissolved C, followed by Europe (2.0 GT C yr⁻¹), America (0.4 GT C yr⁻¹) and Africa (0.1 GT C yr⁻¹). The second conclusion is that most of the tropical river water originates from interflow because the dissolved C in the rivers of this region is mostly young and of low aromaticity. Semi-arid region river water is dominated by groundwater contribution because the dissolved C is more stable, while the polar region rivers show a dominance of both groundwater and surface runoff. The third conclusion is the tendency for dissolved organic C fluxes to dramatically increase with increase in river basin surface area supporting the notion that within stream C production by algae, lixiviation of flooded soils and urbanised areas could be the most significant sources of dissolved organic and inorganic C fluxes. The results of the study also suggest that areas that are getting warmer and wetter, due to climate change, are more likely to experience increased dissolved organic and inorganic C exports due to increased organic matter decomposition and rock weathering as already seen in the polar region where massive amounts of DOC are released from peatlands. In contrast, drying areas will likely experience increased export of old and decomposed organic matter from the water table, which is more likely to be stable during riverine transportation to the ocean. More studies are still needed to confirm the trends observed by the study and their potential impact on the Global C Cycle and their retroactions to climate change. There is finally a need for studies on C fluxes within rivers to consider entire years.

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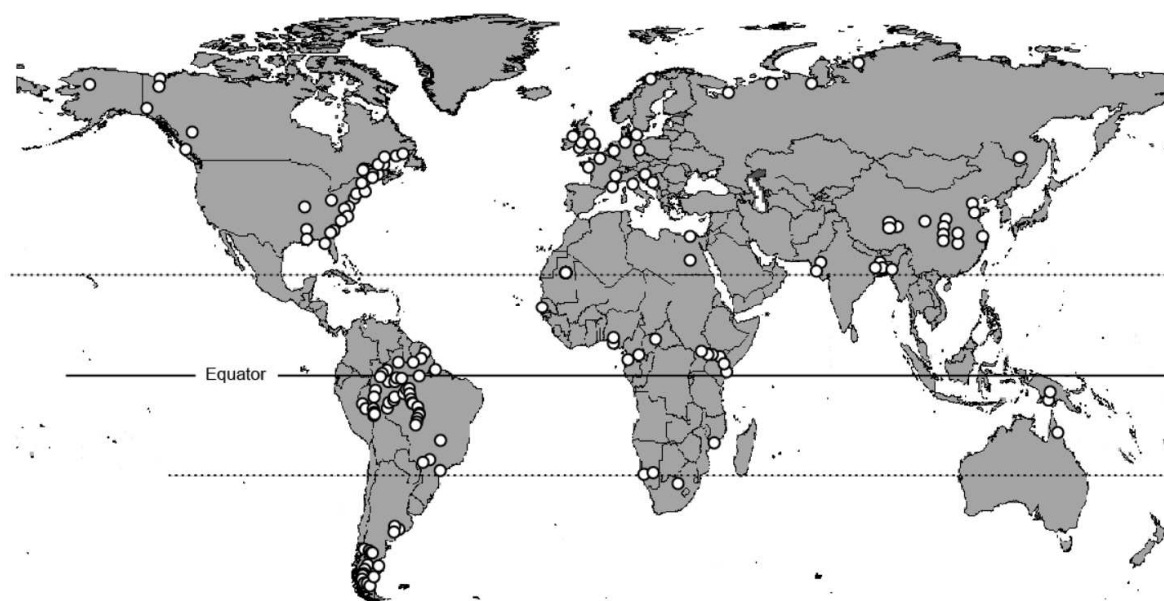


Figure 1. Location of the sampling data points

a

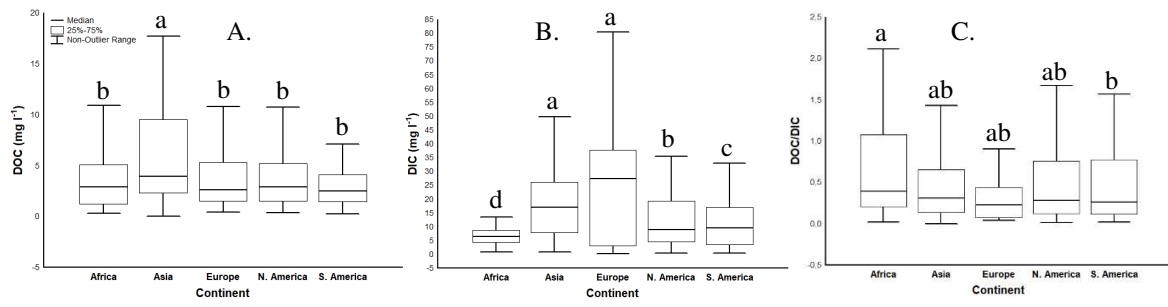


Figure 2. Comparisons of DOCc, DICc and DOCc/DICc from different continents. Box plots accompanied by similar small letters in each figure are not significantly different ($p < 0.05$).

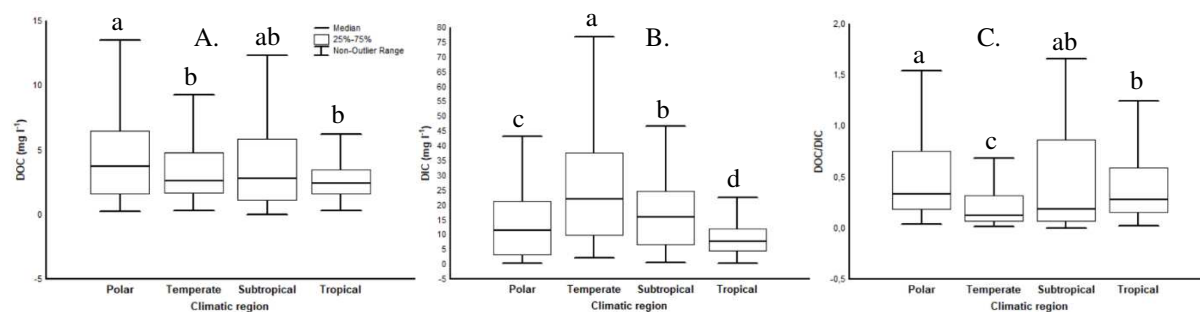


Figure 3. Comparisons of DOC_c, DIC_c and DOC_c/DIC_c from different climatic regions. Box plots accompanied by similar small letters in each figure are not significantly different ($p < 0.05$).

b

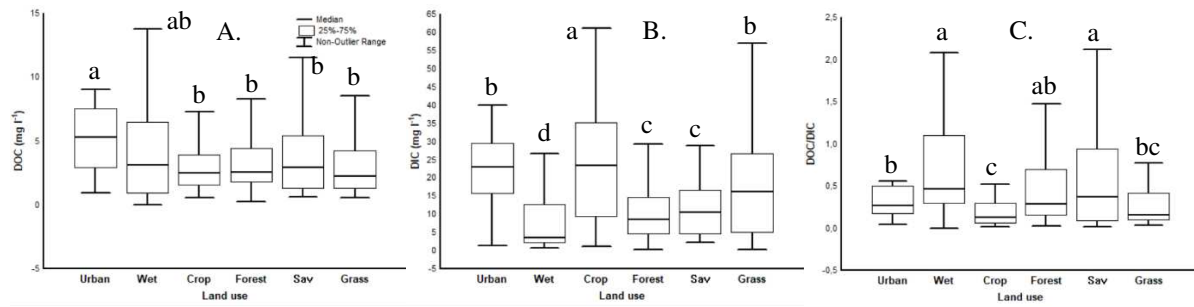


Figure 4. Comparisons of DOCc, DICc and DOCc/DICc in river basins from different land uses/land covers. Box plots accompanied by similar small letters in each figure are not significantly different ($p < 0.05$).

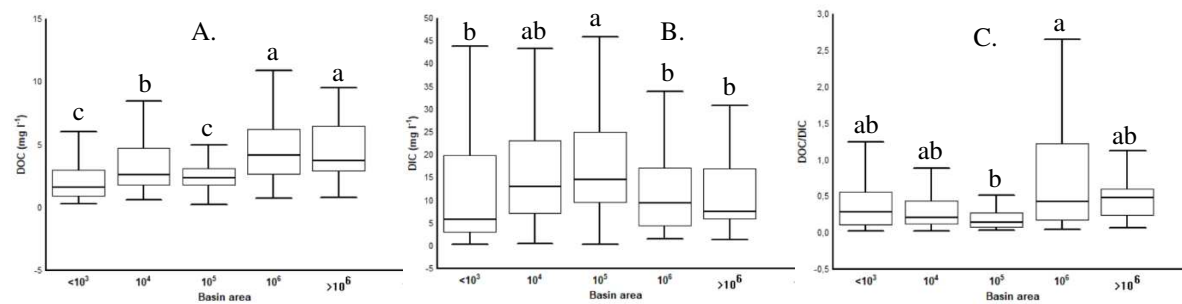


Figure 5. Comparisons of DOCc, DICc and DOCc/DICc from different basin areas. Box plots accompanied by similar small letters in each figure are not significantly different ($p < 0.05$).

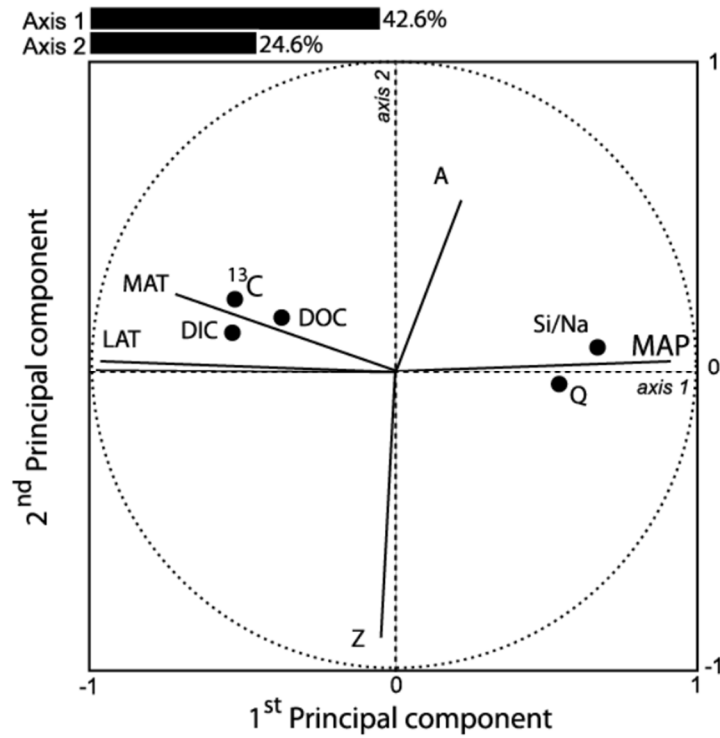


Figure 6. Principal Component Analysis (PCA) using mean annual precipitation (MAP), mean annual temperature (MAT), basin surface area (A), latitude (LAT), altitude (Z) as variables for the analysis and river dissolved organic carbon (DOCc), dissolved inorganic carbon (DICc) content and Si/Na ratio.

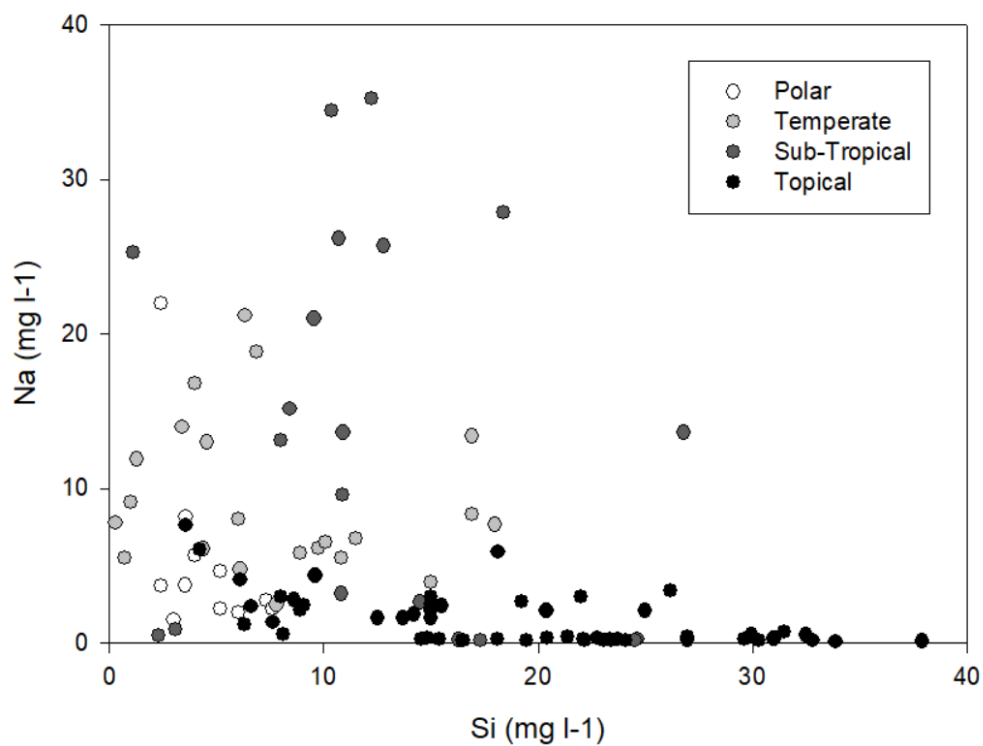


Figure 7. Si and Na content in rivers for the different climatic regions of the world (polar, temperate, sub-tropical and tropical).

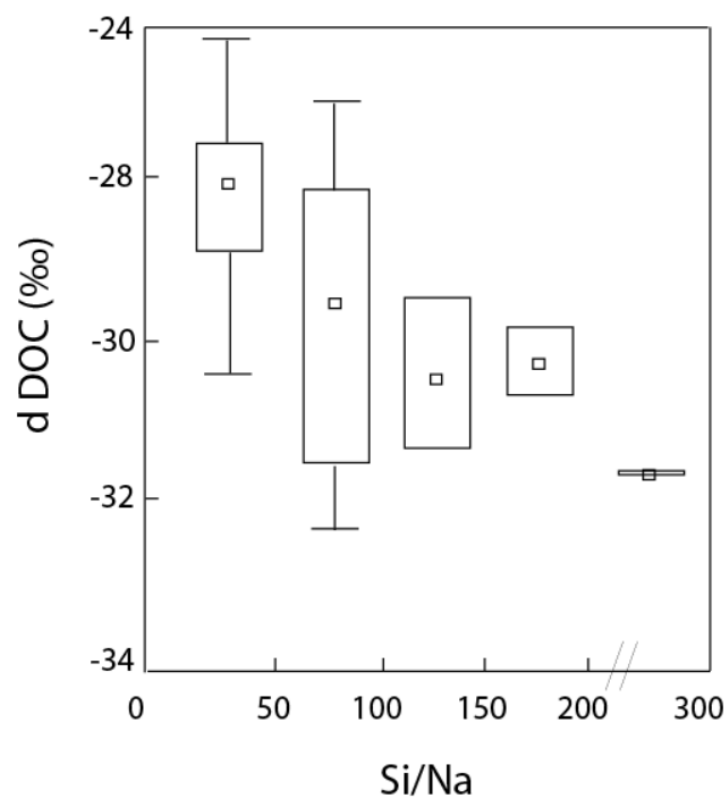


Figure 8. Relationship between river Si/Na and δDOC (‰).

Table 1. Summary database showing author name/s and year source paper was published, number of sampling data points (n); mean upstream surface area of sampling points (A); mean annual temperature (MAT) and precipitation (MAP) for the river basin; and mean dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) content of the river water at the sampling points.

Author/s and Year	Country	n	A Km ²	MAT °C	MAP mm yr ⁻¹	L km	Q ×10 ⁻³ m ³ s ⁻¹	T _w °C	pH	DOCc	DICc	POCc mg C L ⁻¹	TOCc	TCc
1. Abril et al., 2000	Belgium	5	3612	10.0	771		9.1			10.1	64.4	7.6	17.7	82.1
2. Kanduč et al., 2007	Slovenia	14	713	8.2	1218	74	1189	10.7	8.3	3.1	31.6			
3. Pall et al., 2011	Estonia	10	629	5.0	797	58	11.8			19.7	43.2		22.6	65.8
4. Paolini et al., 1987	Venezuela	2	465500	27.0	967		46.4		6.4	4.4	1.4	1.1	5.5	6.9
5. Zheng et al., 1987	China	4	260000	17.0	510		0.1			16.3	37.5		23.8	61.3
6. Alin et al., 2008	Papua NG	7	75000	26.0	1300	1000	7.3	27.5	7.8	3.8	15.3	2.1	5.9	21.2
7. Arain, 1987	Pakistan	26		26.0	224					8.6	11.0	5.6	14.2	25.2
8. Bass et al., 2014	Australia	2		23.5	2784	7			6.1	6.4	4.7			
9. Bhatt and McDowell, 2007	Puerto Rico	3	3	21.0	4200			19.4	6.4	0.7	5.8			
10. Boeglin et al., 2005	Cameroon	6	5890	25.0	1745		11.2			14.0	1.1	2.1	16.1	17.2
11. Bouillon et al., 2009	Kenya	21	120000	21.5	1027		33.3	23.7	7.9	1.0	14.0	2.0	3.0	17.0
12. Bouillon et al., 2012	DR Congo	28	489000	25.0	1540	489	7.7	28.7	7.3	5.1	5.2	1.1	6.2	11.4
13. Bradley et al., 2007	UK	4	38	8.0	770					13.4	32.2			
14. Brunet et al., 2005	Argentina	65	27229	10.1	253		14.4	12.7	7.7	2.7	18.1			
15. Cai et al., 2008	USA	28	5200	-3.1	313	118	8.3	5.0	7.4	4.5	19.1	1.0	5.5	24.7
16. Degens et al., 1991	Various	19	1618895	17.8	943		9.5			13.5	31.9	20.8	32.4	64.3
17. Depetris and Cascante, 1985	Argentina	1	2800000	18.0	955	900	5.4			9.3	4.9	2.1	11.4	16.3
18. Ferguson et al., 2011	Papua NG	124	23825	26.0	3309		110	29.0	8.0	2.2	12.2			
19. Genereux et al., 2013	Costa Rica	2	0	25.1	4341		239			1.4	30.8			
20. Giesler et al., 2013	Sweden	6	124	-1.0	321	115	20.0			1.5	2.0			
21. Hart, 1987	South Africa	3		18.0	361			15.8	7.8	2.5	6.9	1.1	3.5	10.4
22. Hunt et al., 2011	USA & Canada	14	72	4.6	1096				6.4	7.4	4.7			
23. Jantze et al., 2015	Sweden	32	59	0	304		1521		7.5	1.2	3.5			
24. Kempe, 1988	Germany & Brazil	4	5385003	20.8	2139		28.3		5.4	2.9	3.3	1.3	4.2	7.5
25. Lalah and Wandiga, 2006	Kenya	4		20.0	1234				7.5	4.6	14.6			
26. Lloret et al., 2011	Guadeloupe	35	12	23.4	3151		122	23.7	7.6	1.7	5.3			
27. Lloret et al., 2013	Guadeloupe	10	15	23.6	3474		94.2			1.7	3.6	15.1	16.8	20.3
28. Lloret et al., 2016	Guadeloupe	2	22	24.0	3410		69.5	26.5	7.5	1.3	5.6			
29. Lu et al., 2014	USA	36		14.0	1284			14.5	5.9	4.7	22.3	0.9	5.6	27.9
30. Martins, 1983	Nigeria	13	1240000	27.0	1484	4200	0.3			3.3	7.2			
31. Mayorga et al., 2005	Various	88	370272	20.9	1774			25.4	6.6	4.9	9.1	2.4	7.2	16.4
32. Meybeck and Ragu, 1995	Various	55	797329	11.7	1008	2365	12.6	14.6	7.2	6.2	17.4	6.4	7.4	24.7
33. Moyer et al., 2013	Puerto Rico	42	125	25.5	2593		13.0			1.9	21.1	7.6	9.5	30.6
34. Neal and Hill, 1994	UK	7	1	7.5	2336		59.3		4.7	1.6	0.6			
35. Némery et al., 2013	France	6	5570	22.0	800		57.9			2.3	19.3	24.2	26.5	45.7
36. Raymond and Bauer, 2001	USA	2	4350	14.0	1118		11.2			6.9	5.5	0.6	7.5	12.9
37. Raymond et al., 2013	USA	5	155	9.0	1155		15.4			9.1	9.8	0.8	9.9	19.7
38. Safuillah et al., 1987	Bangladesh	22	82	25.0	1823		5228		7.9	3.1	30.7			
39. Saunders and Lewis, 1988	Venezuela	2	167000	27.0	1545		11.4			6.2	12.2	3.7	9.9	22.1
40. Sempéré et al., 2000	France	35	97800	14.0	574	816	29.7			2.6	36.2	6.1	8.7	44.8
41. Shibata et al., 2001	Japan	1	9	6.0	1189	4	31.9			1.6	4.3	0.5	2.2	6.5
42. Sholkovitz, 1976	UK	4		8.0	1271				6.8	8.0	0.9			
43. Teodoru et al., 2015	Mozambique	1	1379423	25.0	940	3083	2.7	30.1	7.3	2.2	30.8	2.6	4.8	35.6
44. Tipping et al., 1997	UK	11	1927	8.8	992		23.4			6.5	26.9	11.0	17.5	44.4
45. Tweed et al., 2015	Australia	3	1833	24.0	481		21.5	21.1	6.8	3.0	3.6	2.5	5.5	9.1
46. Vihermaa et al., 2014	Peru	12	4003	26.0	2000	210			6.2	2.9	2.9	3.8	6.7	9.5
47. Walsh and Vigneault, 1986	Canada	3	14314	1.3	1007	400			6.4	5.2	0.6			
48. Wang et al., 2010	China	14		13.8	1062					7.3	17.7			
	Mean			16.7	1456	923	259	20.6	7.0	5.3	14.9	5.0	11.0	27.6
	Median			19.0	1137	400	20.0	23.7	7.3	4.1	10.4	2.4	7.5	21.1
	Minimum			-3.1	224	4	0.1	5.0	4.7	0.7	0.6	0.5	2.2	6.5
	Maximum			27.0	4341	4200	5228	30.1	8.3	19.7	64.4	24.1	32.4	82.1
	CV%			53	71	139	355	38	12	81	93	121	71	73

Table 2. Definitions of the climatic regions used in the current analysis

Climatic region	Characteristics
Polar	Cold and frigid region Temperature $<10^{\circ}\text{C}$ Precipitation $<800\text{ mm yr}^{-1}$
Temperate	Cool and arid to moist Temperature $10\text{-}20^{\circ}\text{C}$ Precipitation $<800\text{ mm yr}^{-1}$
Sub-tropical	Warm and arid to humid Temperature $>20^{\circ}\text{C}$ Precipitation $300\text{-}1000\text{ mm yr}^{-1}$
Tropical	Hot and wet Temperature $>20^{\circ}\text{C}$ Precipitation $>1000\text{ mm yr}^{-1}$

Table 3. Mean annual temperature (MAT), mean annual precipitation (MAP), mean of dissolved organic (DOC_c) and inorganic C concentration (DIC_c), mean of dissolved organic (DOC_F) and inorganic C fluxes (DIC_F) within rivers, drainage basin area (A) and estimated within-river DOC_F and DIC_F per world region. Data computed for the whole Africa, Asia, North and South America. Numbers accompanied by similar letters in the same column are not significantly different (p<0.05).

Continent	MAT	MAP	DOC _c	DIC _c	DOC _F	DIC _F	Si/Na	A			
	°C	mm yr ⁻¹	-----mg C L ⁻¹ -----		---g C s ⁻¹ km ⁻² ---			×10 ⁶ km ²	--GT C yr ⁻¹ --		
Africa	23.80	1277	4.19 b	8.84 d	0.04	0.08	5.87	30.37	0.04	0.08	
Asia	24.40	2355	8.73 a	23.90 a	0.30	3.86	1.01	44.58	0.42	5.43	
Europe	7.80	761	4.63 b	24.12 a	0.53	5.73	0.39	10.18	0.17	1.84	
North America	6.90	943	3.95 b	14.04 b	0.07	0.13	1.53	24.71	0.05	0.10	
South America	20.60	1877	3.87 b	11.97 c	0.10	0.42	77.77	17.84	0.06	0.24	
Mean	17.50	1591	5.08	16.57	0.25	2.50	31.05	Sum	127.68	0.74	7.68

Table 4. Correlations between variables (DOC: dissolved organic carbon, DIC: dissolved inorganic carbon, DOC/DIC ratio, POC: particulate organic carbon, TOC: total organic carbon, TC: total carbon, and DOC_F and DIC_F for DOC and DIC fluxes, respectively) and factors of control (LAT: latitude, LONG: longitude, Z: altitude, MAT: mean annual temperature, MAP: mean annual precipitation, Q: discharge and L: river length). Correlations accompanied by a star (*) are significant (p<0.05).

Variable	DOC _c	DIC _c	DOC _c /DIC _c	POC _c	TOC _c	TC _c	DOC _F	DIC _F
	----- mg C L ⁻¹ -----					-mg C L ⁻¹ s ⁻¹ km ² -		
LAT (°)	0.27*	0.39*	-0.24	0.04	0.08	0.22	0.05	0.24
LONG (°)	0.27*	0.23	-0.02	0.29*	0.32*	0.35*	0.11	0.23
Area (km ²)	0.12	-0.25*	0.32*	-0.05	-0.03	-0.12	0.18	-0.22
Z (masl)	-0.19	-0.13	0.02	-0.10	-0.13	-0.15	-0.01	-0.04
MAT (°C)	-0.41*	-0.21	0.11	-0.05	-0.10	-0.17	-0.17	-0.14
MAP (mm yr ⁻¹)	-0.29*	-0.34*	0.31*	-0.15	-0.19	-0.29*	0.34*	0.33*
Q (m ³ s ⁻¹)	-0.18	-0.43*	0.28*	-0.17	-0.19	-0.33*	0.55*	0.48*
L (km)	0.11	-0.03	0.05	0.22	0.23	0.18	-0.01	-0.22
SiO ₂ (mg L ⁻¹)	-0.19	-0.33*	0.07	0.03	0	-0.13	-0.19	-0.35*
Na (mg L ⁻¹)	-0.10	0.60*	-0.34*	0.29*	0.27*	0.46*	-0.35*	-0.05
Si/Na	-0.17	-0.71*	0.50*	-0.16	-0.18	-0.42*	0.23	-0.24