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Comparison of dissolved inorganic and organic carbon yields and fluxes in the watersheds of tropical volcanic islands, examples from Guadeloupe (French West Indies)

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Abstract

Organic matter is an important factor that cannot be neglected when considering global carbon cycle. New data including organic matter geochemistry at the small watershed scale are needed to elaborate more constrained carbon cycle and climatic models. The objectives are to estimate the DOC and DIC yields exported from small tropical watersheds and to give strong constraints on the carbon hydrodynamic of these systems. To answer these questions, we have studied the geochemistry of eleven small watersheds around Basse-Terre volcanic Island in the French West Indies during different hydrological regimes from 2006 to 2008 (i.e. low water level versus floods). We propose a complete set of carbon measurements, including DOC and DIC concentrations, $\delta^{13}\text{C}$ data, and less commonly, some spectroscopic indicators of the nature of organic matter. The DOC/DIC ratio varies between 0.07 and 0.30 in low water level and between 0.25 and 1.97 during floods, indicating that organic matter is mainly exported during flood events. On the light of the isotopic composition of DOC, ranging from -32.8 to -26.2‰ during low water level and from -30.1 to -27.2‰ during floods, we demonstrate that export of organic carbon is mainly controlled by perennial saprolite groundwaters, except for flood events during which rivers are also strongly influenced by soil erosion. The mean annual yields ranged from 2.5 to $5.7 \text{ t km}^{-2} \text{ year}^{-1}$ for the DOC and from 4.8 to $19.6 \text{ t km}^{-2} \text{ year}^{-1}$ for the DIC and exhibit a non-linear relationship with slopes of watersheds. The flash floods explain around 60% of the annual DOC flux and between 25 and 45% of the DIC flux, highlighting the important role of these extreme meteorological events on global carbon export in small tropical volcanic islands. From a carbon mass balance point of view the exports of dissolved carbon from small volcanic islands are important and should be included in global organic carbon budgets.

Research Highlights

Source of DOC is mainly controlled by saprolite groundwaters, except for flood events.

The mean annual yields exhibit a non-linear relationship with slopes of watersheds.

The flash floods account for 60% of the annual DOC flux and 40% of the DIC flux.

The DOC input of small volcanic islands is similar to the Amazon flux to the ocean.

Keywords

Organic matter; Carbon fluxes; DIC; DOC; $\delta^{13}\text{C}$; Tropical rivers; Watersheds

1. Introduction

At the Earth's surface, a suite of chemical, physical and biological processes are closely combined to transform bedrock into soil. This complex engine regulates the rates of soil production through chemical weathering and organic productivity, and the rates of soil destruction through physical erosion at all temporal and spatial scales. Then it exerts a major control on the transport of the dissolved and particulate products of mechanical erosion and chemical weathering from continents to the oceans and influences the biogeochemical cycles of many elements, including carbon. As shown in pioneering works (Berner et al., 1983), chemical weathering of silicate rocks converts atmospheric CO_2 into bicarbonates within the stream. This process then strongly affects carbon cycle and many studies have focused on river geochemistry to quantify and characterize silicate weathering fluxes and associated inorganic carbon fluxes (e.g. [Stallard and Edmond, 1983], [Dupré et al., 1996], [Drever, 1997], [Gaillardet et al., 1999a], [Dessert et al., 2001] and [Viers et al., 2007]).

These previous studies mainly focus on the inorganic part of the carbon cycling and its role on weathering and its impact on climate change. A part of this cycle, however also concerns the organic carbon pool and cannot be neglected when considering the global carbon cycle at geological time scale. Indeed, total organic carbon flux (dissolved and particulate) from continents to the oceans represents globally 40% of the total carbon flux (i.e. 0.4 to 0.9 Gt yr^{-1} ; [Hedges et al., 1997], [Schlunz and Schneider, 2000] and [Aitkenhead-Peterson et al., 2003]). Moreover, soil organic matter with 1400 to 1500 Gt of carbon is one of the major pools of carbon at the Earth surface ([Schlesinger, 1977] and [Gregory et al., 1999]). The soil erosion is therefore the major input of organic carbon in aquatic ecosystems. During its transport to the oceans, the terrestrial organic carbon can be mineralized, or deposited and stored in aquatic ecosystems under low discharge (i.e.: alluvial plains, mangroves; Lal, 2004). This terrestrial organic matter is then mineralized or preserved in continental margins, and/or transported offshore (Hedges et al., 1997). Actually, an average of 20% of the flux of terrestrial dissolved organic carbon (0.25 Gt yr^{-1}) is removed in estuaries with a wide range of 4–60% that depends of the discharged organic matter ([Hedges et al., 1997], [Schlunz and Schneider, 2000] and [Burdige, 2005]). Previous works on the fate of dissolved organic matter have shown considerable mixing gradient and high short-term variability. In addition, slow photolysis and microbial degradation are major processes that will also contribute to dissolved organic matter removal in coastal and surface ocean waters ([Hedges et al., 1997] and [Benner, 2004]). Therefore, it is of major importance to understand the dissolved organic carbon dynamic within and along the river system (sources, fluxes and sinks) to better assess the global carbon cycle.

Currently, studies concerning the organic carbon cycle and its impact on global carbon cycle are often focused on soil erosion ([Lal, 2003], [Lal, 2005] and [Mills and Cowling, 2010])

and deposit of terrestrial particulate organic carbon in marine sediments ([France-Lanord and Derry, 1994], [Goñi et al., 1998], [Galy et al., 2008] and [Hilton et al., 2010]). Recent studies ([Waterloo et al., 2006], [Dawson et al., 2008], [Goldsmith et al., 2008] and [Hilton et al., 2008]) showed that the export of particulate organic carbon depends on the runoff and rainfalls. Indeed, during rainfalls, the top of soil profile enriched in organic carbon is lixiviated, and carbon is transferred into the rivers (Batjes, 1996).

Regarding rivers, studies are generally focused on large river systems like the Mississippi ([Bianchi et al., 2007] and [Duan et al., 2007]), the Ganga-Brahmaputra (Galy et al., 2008), tributaries of the Amazon river ([Moreira-Turcq et al., 2003], [Johnson et al., 2006] and [Aufdenkampe et al., 2007]), large Arctic rivers (Yenisey, Ob, Lena; [Ludwig et al., 1996a], [Dittmar and Kattner, 2003], [Gebhardt et al., 2004] and [Raymond et al., 2007]), ... which integrate differences in lithologies, vegetations, soils and climates. However, it was underlined that the small mountainous rivers could also be very important in transporting organic sediments to oceans, fluxes being inversely proportional to the watershed area ([Milliman and Meade, 1983], [Walling, 1983], [Degens and Ittekkot, 1985] and [Milliman and Syvitski, 1992]).

Moreover, it is difficult for studies about large rivers to constrain the different processes (natural vs land use; Amiotte-Suchet et al., 2007) influencing the organic carbon cycle as well as the weathering engine. For instance, the dissolved organic carbon can influence the bedrock weathering, since organic acids produced by microbially communities may accelerate mineral dissolution ([Bennett et al., 1988], [Drever, 1994], [Pittman and Lewan, 1994], [Drever and Stillings, 1997], [Viers et al., 1997], [Oliva et al., 1999], [Welch and Ullman, 2000] and [Millot et al., 2003]). The major sources of organic carbon in rivers are: soil organic matter, generated by the partial or total decomposition of living organisms (plants, animals and microorganisms); primary production in the river; the decomposition of living organism in the river (algae and aquatic animals); and groundwater (Battin et al., 2008). The organic carbon quality and concentrations in rivers depend therefore on different parameters (i.e. temperature, soil types, vegetation types and bedrock) controlling the distribution of these different sources. The recent study of Raymond et al. (2007) showed that arctic watersheds show a marked increase in dissolved organic carbon concentration with flow.

Wet tropical regions are ideal targets to study the organic carbon cycle. They have optimal climatic conditions for the volcanic rock weathering, including high temperatures and high runoff, promoting the transformation of rocks into soils ([Stallard, 1988], [Benedetti et al., 1994], [Louvat and Allègre, 1997], [Dessert et al., 2001], [Dessert et al., 2003], [Rad et al., 2006] and [Goldsmith et al., 2010]). Wet tropical regions also host the largest stock of organic carbon since 26% of the total global carbon in soils (depth from 0 to 200 cm) is found in these regions (Batjes, 1996). Moreover, the export of inorganic and organic carbon is estimated to be the highest in wet tropical regions ([Ludwig et al., 1996a], [Ludwig et al., 1996b], [Gaillardet et al., 1999b] and [Dessert et al., 2003]). Different authors have demonstrated the importance of oceanic “high standing” islands (HSIs) for sediments and total organic carbon export, for example in the southwest Pacific (i.e. 33% of total sediment entering the world's oceans annually, Milliman and Syvitski, 1992) and Oceania's small mountainous rivers (i. e. 21–38% of the total oceanic organic carbon inputs, Schlunz and Schneider, 2000). Therefore, these small mountainous rivers and HSIs are ideal settings to study geochemical fluxes. Moreover, previous studies on weathering rates of HSIs have shown some of the highest observed rates of chemical weathering and CO₂ consumption ([Jacobson et al., 2003] and [Lyons et al., 2005]). The Guadeloupe Island (French West Indies) is an ideal

location to study geochemical fluxes and the organic carbon geochemistry because its monolithologic volcanic composition helps to constrain the influence of other factors such as climate, soil composition, and age of the bedrock. In addition, its location in a wet tropical area implies that rates of chemical weathering and mechanical denudation are high ([Louvat, 1997], [Louvat and Allègre, 1997], [Dessert et al., 2001], [Dessert et al., 2003], [Rad et al., 2007] and [Goldsmith et al., 2010]). Previous works of [Rad et al., 2006] and [Goldsmith et al., 2010] were focused on stream geochemistry, weathering and CO₂ consumption in rivers of andesitic terrains without addressing the effect of the hydrological variability. Moreover, due to their small size, and steep slopes, the Guadeloupean rivers present a characteristic flash flood hydrological regime ([Ibiza, 1984–1985] and [Pagney, 1994]). The dynamic of carbon export could be different from one hydrological regime to another (i.e. low water level vs flood level). Our overarching goal is to obtain new data that will help to elaborate more constrained coupled modeling of biological and chemical weathering processes at the continental scale such as B-WITCH (Roelandt et al., 2010), that mostly focus on inorganic carbon. The collected data will also help to constrain the residence time of carbon in tropical soils and to understand the fate of terrestrial DOC in the ocean.

The aims of this paper are, with major elements, dissolved inorganic (DIC) and dissolved organic (DOC) carbon concentrations, (1) to calculate the DOC and DIC yields and fluxes in Guadeloupean rivers, (2) to characterize and identify the different sources of the organic carbon exported under different hydrological regimes (i.e. low water level vs flood level) and, (3) to evidence spatial and/or temporal variations. The comparison between two hydrological regimes is therefore needed for a better assessment of weathering processes and carbon fluxes and we emphasize the importance of DOC fluxes in the carbon mass balance in small mountainous tropical rivers.

2. General settings of Basse-Terre Island

The Basse-Terre Island is the volcanic part of the Guadeloupe archipelago, French West Indies, with an area of 950 km² (Fig. 1). The Lesser Antilles arc volcanism is generated by the subduction of the Atlantic seafloor beneath the Caribbean plate at a rate of about 2 cm yr⁻¹ (e.g. [Jordan, 1975], [Hawkesworth and Powell, 1980], [Wadge, 1984] and [DeMets et al., 2000]). The major part of the volcanic material of the Island is andesitic. The geology of the Basse-Terre was described by [De Reynal de Saint-Michel, 1966], [Westercamp and Tazieff, 1980] and [Boudon et al., 1988], and Westercamp (1988) and the ages of geological formations were recently reevaluated by Samper et al. (2007). The North of the island is characterized by a Pliocene volcanism (2.7–1.5 Myrs), with the series following: volcanic formations (lapillis, basaltic breccias...) and residual cover of red and ochre clays. Its center is characterized by volcanism occurring after a marine transgression between 1.6 and 0.9 Myrs, with volcanos imbricated into each other with different composition (labradoritic and andesitic flows versus dacitic and basaltic breccias). The East and the West of the island are composed by andesitic and labradoritic flows, andesitic breccias, andesitic pumices and pyroclastic sediments dating to Plio-Quaternary (900–550 kyrs). Two main massifs were identified in the southern part of the island. The Monts Caraïbes massif construction was initiated 500 kyrs ago by intensive effusive submarine activity. The Grande-Découverte Complex volcano construction ([Boudon et al., 1987] and [Boudon et al., 2008]), the youngest volcanic complex of Basse-Terre was initiated 205 kyrs ago, following three main stages: Grande-Découverte (200–42 kyrs), Carmichaël (42–11.5 kyrs) and La Soufrière (8.5 kyrs to present).

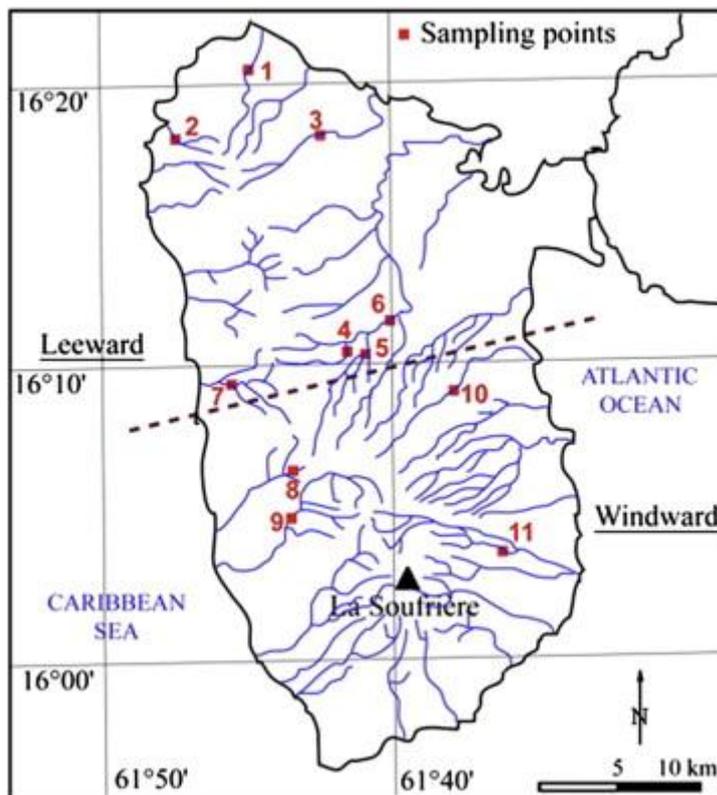


Fig. 1. Sampling location on Basse-Terre Island. The substratum ages range from 2.7 to 1.2 Myrs above the dotted line and are ≤ 900 kyrs below this line (Samper et al., 2007). 1. Desbonnes River, 2. Deshaies River, 3. Moustique Sainte-Rose River, 4. Bras-David River, 5. Corossol River, 6. Grande Rivière à Goyaves, 7. Lostau River, 8. Beaugendre River, 9. Grande Rivière de Vieux-Habitants, 10. Moustique Petit-Bourg River, 11. Grande Rivière de la Capesterre.

The Guadeloupe Island is characterized by a wet tropical climate, with a mean annual temperature and humidity around 23 °C and 75%, respectively. The average annual precipitation ranges from 1200 to 8000 mm yr⁻¹, depending on the topography (the highest at the top of La Soufrière massif). The island is characterized by a wet rainy season, corresponding to the maximum of precipitations and notably extreme meteorological events (i.e. tropical storms and cyclones, Zahibo et al., 2007), from June to November, and a drier season from December to May. The spatial distribution of precipitations is controlled by the orographic effect. Thus, the East coast receives high precipitations because of the strong influence of the Easterly and conversely, the West coast, protected by the topography, receives less water.

The steep slopes and the abundant precipitations generate a dense river network flowing through the volcanic substratum of Basse-Terre Island into the Atlantic Ocean or the Caribbean Sea. The island has about 55 independent rivers with watershed areas greater than 1 km² (25 on the East coast and 30 on the West coast), the largest river (130 km²) corresponding to the “Grande Rivière à Goyaves”. Valley slopes, resulting from the younger volcanic relief, exceed 49% in the southern part of the island, while they are smaller in the northern part of the island (Plaisir et al., 2003; Table 1). In the North, the water stocks are smaller than in the Center and in the South and during the dry season most of the northern rivers do not flow. Since 1950, discharges of major rivers have been monitored first by the

IRD (formerly the ORSTOM, French Research Institute for the Development) and now by the DIREN (French Water Survey agency) and data in Table 1 were obtained at the following web site: <http://www.hydro.eaufrance.fr>.

Table 1. Watersheds characteristics: sampling point geographic position (latitude and longitude), elevation above sea level, surface area and slopes of the watershed. Hydrologic characteristic: operating dates of gauging stations, discharges and runoffs during low water and flood levels calculated from DIREN data, and mean annual runoff, rainfalls and evapotranspiration.

Site	Latitude	Longitude	Elevation m	Watershed area km ²	% of watershed where the slopes are				Operating periods of hydrological stations	Low water level		Flood level		Mean annual			
					9- 24 %	25- 48 %	49- 99 %	>99 %		Discharge m ³ s ⁻¹	Runoff mm yr ⁻¹	Discharge m ³ s ⁻¹	Runoff mm yr ⁻¹	Mean annual runoff mm yr ⁻¹	Mean annual rainfall mm yr ⁻¹	Mean annual runoff mm yr ⁻¹	
<i>North</i>																	
Desbannes	N16°19' 34.4"	W61°44' 48.0"	136	5.50	34	59	7	0	1979- 1986	0.07 ± 0.05	400 ± 2 90	0.72 ± 0.56	4130 ± 3 200	780 ± 5 80	1790 ± 450	2.3 ± 1.4	
Deshai es	N16°18' 05.3"	W61°47' 29.8"	30	4.38	46	50	4	0	1979- 1982	0.04 ± 0.02	260 ± 1 40	0.28 ± 0.16	2030 ± 1 170	430 ± 2 50	1750 ± 440	4.0 ± 2.1	
Mousti que Sainte- Rose	N16°17' 54.9"	W61°42' 38.8"	114	6.16	52	45	3	0	1983- 2006	0.19 ± 0.10	970 ± 5 30	1.47 ± 0.93	7530 ± 4 770	1620 ± 950	2290 ± 570	1.4 ± 0.7	
<i>Center</i>																	
Bras- David	N16°10' 33.6"	W61°41' 34.8"	233	11.0	38	48	14	0	2001- 2010	0.59 ± 0.27	1680 ± 770	3.06 ± 1.27	8770 ± 3 640	2390 ± 1050	3410 ± 850	1.4 ± 0.6	
Corossol	N16°10' 48.8"	W61°40' 49.5"	179	12.5	39	33	26	2			1580 ± 940		10510 ± 4690				
Goyaves	N16°11' 27.7"	W61°39' 33.0"	125	14.4	48	28	23	1	1973- 2002	0.68 ± 0.51	1480 ± 1120	5.59 ± 2.61	12240 ± 5730	2560 ± 1580	3450 ± 860	1.3 ± 0.7	
<i>West</i>																	
Lostau	N16°09' 34.1"	W61°45' 35.9"	108	8.04	9	41	49	1	1979- 1987	0.29 ± 0.16	1130 ± 620	1.71 ± 0.78	6710 ± 3 070	1690 ± 860	2740 ± 680	1.6 ± 0.7	
Beauge ndre	N16°06' 27.6"	W61°44' 09.1"	225	8.17	6	37	53	4	1979- 1991	0.31 ± 0.26	1190 ± 990	2.71 ± 1.32	10450 ± 5100	2120 ± 1400	2720 ± 680	1.3 ± 0.7	
Vieux- Habitan ts	N16°05' 11.8"	W61°43' 31.3"	257	19.1	13	32	51	4	1980- 2009	1.50 ± 0.90	2480 ± 1490	9.81 ± 4.18	16190 ± 6900	3850 ± 2030	3830 ± 960	1.0 ± 0.5	
<i>East</i>																	
Mousti que Petit- Bourg	N16°09' 41.8"	W61°37' 37.8"	100	11.5	27	41	31	1	1984- 2010	0.72 ± 0.42	1970 ± 1150	4.44 ± 1.85	12160 ± 5080	2990 ± 1550	3990 ± 1000	1.3 ± 0.6	
Capeste erre	N16°04' 18.0"	W61°36' 34.1"	208	16.2	13	32	45	5	1983- 2010								

The climatic conditions promote the growth of abundant vegetation on Basse-Terre. The vegetation cover depends both on the meteorological conditions and the elevation (Rousteau, 1996). The vegetation on the island is represented by four levels from lower altitudes to higher altitudes: 1) a semi-deciduous forest on volcanic terrain, 2) a seasonal evergreen forest, 3) a mountain and sub-mountain rainforest and, 4) an altimountain forest.

Different soil types have developed on the volcanic andesitic basement, depending on rock age, precipitations and topography ([Colmet-Daage, 1969], [Colmet-Daage and Bernard, 1979] and [Buss et al., 2010]). In the North, vertisols are characterized by high contents of montmorillonite and kaolinite typical of such old formations under tropical climate. The central part of the island is characterized by ferralitic soils with halloysites and iron oxides. East, West and South are characterized by andosols with allophanes, typical of volcanic rocks and wet tropical regions. Locally paleosols may occur.

The choice of the rivers was governed by their geological substratum, the pedology and the exposure to rainfalls. The water samples were collected during dry and wet seasons from 2006 to 2008, in order to assess the influence of the hydrological regime on surface water chemistry. In the South of the Basse-Terre, rivers were not sampled, because their chemistry is influenced by hydrothermal inputs, due to the Soufrière volcanic activity. They are characterized by high sulfate and cations concentrations (ex. Rivière Noire, Rad et al., 2007) and are not all perennial. This study focuses on 11 rivers located in the North (n = 3), the Center (n = 3), the West coast (n = 3) and the East coast (n = 2) (Fig. 1). The northern watersheds are characterized by less steep slopes (slope < 49%), rock older than 1 Myr and thick ferralitic soils and weak rainfalls; center watersheds have quite the same characteristics but higher rainfalls; western watersheds are characterized by steeper slopes (slope > 49%), an age less than 800 kyrs, thin andosols, weak rainfalls; eastern watersheds have also steep slopes, an age less than 800 kyrs, thin andosols and are subject to strong rainfalls.

3. Sampling and analytical methods

3.1. Hydrological data and calculation of rates and yields

The discharge was measured at gauging stations installed by the IRD or more recently by the DIREN. The water level is measured at gauging stations with a pressure detector. Gauging campaigns are regularly conducted to adjust the calibration curves relating discharge with water level (i.e. given by gauging scale). The different discharge values are available at: <http://www.hydro.eaufrance.fr>.

As some rivers are no longer equipped by gauging station (Table 1) discharge data at the time of sampling for all rivers is not available. We need however discharge values to calculate the riverine export rates. Based on the DIREN discharge dataset, we estimated, for each river a mean discharge value for low water and flood conditions. In Fig. 2, representing the discharge versus frequency for the Bras-David River, two hydrological periods are evidenced. The first part (before the break), corresponding to 90% of the annual flux is characteristic of low water level. The second part (after the break), corresponding to 10% of the annual flux, is characteristic of flood conditions. The distribution between both hydrological conditions is the same for all rivers, even if mean daily values vary from one river to the other. For rivers where present day gauging data were not available, their average discharge values corresponding to low water and flood conditions were calculated with the help of historical records of the DIREN.

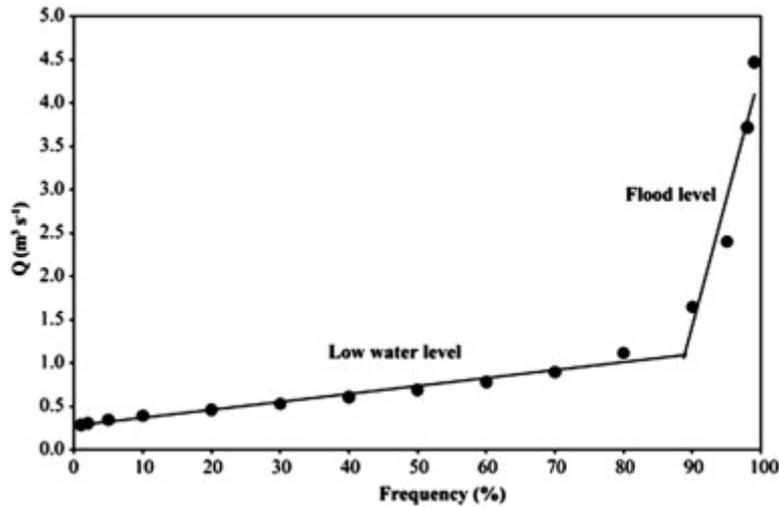


Fig. 2. Plot of frequency vs discharge ($\text{m}^3 \text{s}^{-1}$) for the Bras-David River (ORSTOM-IRD and DIREN data, Table 1). The lines represent the fits for the low water and flood periods. The flood regimes represent around 10% of the annual discharge. This trend is observed for all Guadeloupean rivers.

The runoff (in mm yr^{-1}) is defined by the following formula:

$$\text{Runoff} = \frac{\text{Discharge}}{\text{Area}_{\text{watershed}}}$$

The mean annual runoff is calculated with the following formula:

$$\text{mean annual runoff} = RLWL \cdot 0.9 + RFL \cdot 0.1$$

with R_{LWL} = mean runoff during low water level, and R_{FL} = mean runoff during floods.

The associated errors have been calculated with the minimal and maximal values during low water level or flood level. Using the rainfalls data from French meteorological survey agency (Météo-France), we estimated the mean annual rainfalls for each watershed. The mean annual evapotranspiration factor is the calculated ratio between rainfalls and runoff.

3.2. Sample collection

Pristine water samples were collected, upstream of the anthropogenic activities like the sugar cane and banana crops (Fig. 1). The sampling of surface water was done manually from 2006 to 2008 at different hydrological stages corresponding to low water levels (LWL) and flood levels (FL). Water samples used for the measurement of dissolved major ions concentrations were filtered through $0.2 \mu\text{m}$ cellulose acetate filters. For cations measurements, samples were acidified to $\text{pH} = 2$ with distilled nitric acid. Non-acidified samples were stored at 4°C in the dark for the measurements of anions and dissolved silica concentrations. Samples used for the measurement of dissolved organic carbon concentrations and $\delta^{13}\text{C}$ were filtered through glass fiber filters (GF/F Whatman® by Schleicher & Schuell cut off $0.7 \mu\text{m}$) acidified with concentrated H_3PO_4 in pre-cleaned and pre-burned Grasse amber glass bottles and stored at 4°C in the dark. A few sampled ($n = 25$) were collected in 2008 for the measurements of $\delta^{13}\text{C}$ of dissolved inorganic carbon in sealed glass vials.

3.3. Analytical methods

Temperature, pH and conductivity were measured in the field (Table 2). The precision of pH measurements was 0.05 pH units. Conductivity was measured with a Hanna HI9835 probe. The precision was 1%. Alkalinity values were measured in the laboratory with an automatic acid-base titration stand (Radiometer TIM840 with Schott probe) by the Gran method with a precision of 1%.

Table 2. Physico-chemical parameters and organic matter characteristics of water samples recovered on the Basse-Terre during low water levels and flood levels, *data calculated, NICB (Normalized Ionic Charge Balance), TDS_{cat} and TDS_w.

Site	Sampling date	Water temperature °C	pH	N μM	K μM	Mg μM	Ca μM	Si μM	Cl μM	NO ₃ μM	SO ₄ μM	Al μM	NiCB %	TDS _{cat} mg L ⁻¹	TDS _w mg L ⁻¹	DI C* μM	pCO ₂ Pa	DO μM	δ ¹³ C _{DOC} ‰	Aromaticity %	M _w D	DOC/DIC
<i>North</i>																						
Desbonnes	4/12/2006	22.9	7.11	54.9	26.7	10.7	86.8	49.9	53.1	5.94	51.0	32.7	-1.17	6.9	37.7	384	159	60	-31.5			0.16
	23/09/2007			61.8	31.2	11.4	10.9	56.4	59.8	0.16	67.9	41.6	-5.28	8.1	43.9	488	201	120	-30.5	48.3	33.14	0.25
Deshaies	10/09/2007			91.3	47.8	17.2	16.0	63.1	83.2	8.00	130.0	51.5	0.60	13.4	57.4	548	103	162	-30.0	31.0	21.60	0.30
Moustique Sainte-Rose	12/12/2006	22.6	7.30	37.3	19.5	84.7	78.8	38.9	37.0	0.00	42.7	22.6	4.72	5.6	30.2	251	70	51	-32.3			0.21
	23/09/2007			35.1	21.5	77.7	77.4	40.1	34.7	0.65	55.0	23.2	-1.80	5.5	32.2	261	83	75	-29.5	58.6	40.14	0.29
<i>Center</i>																						
Bras-David	11/12/2006	22.4	7.27	33.4	16.2	71.7	10.2	36.8	28.6	0.00	21.7	37.3	-1.11	7.2	29.3	418	125	59	-31.2	58.0	40.39	0.14
	13/07/2007	26.5	7.65	40.4	22.1	10.8	18.1	39.5	27.3	1.71	19.7	64.3	4.12	13.4	37.0	671	94	51	-30.9	52.4	36.28	0.08
Corosso	13/03/2008	22.8	7.88	33.6	15.6	68.2	13.0	41.0	20.8	0.00	12.5	46.3	7.46	10.3	34.5	475	38	51	-31.8	71.5	49.74	0.11
	19/08/2008	24.9	7.76	32.9	15.3	65.6	13.6	40.8	20.9	0.01	13.9	49.1	1.83	10.2	34.3	516	56	36	-28.9	51.1	35.59	0.07
Low water level	Goyaves 13/03/2008	25.3	8.04	34.0	14.8	78.6	14.6	35.6	23.1	0.00	16.9	48.1	7.01	10.5	31.8	488	28	57	-30.0	63.1	44.05	0.12
	19/08/2008	26.9	7.90	34.7	19.4	77.4	15.4	37.9	23.9	1.77	16.0	54.2	1.66	11.0	33.5	554	45	67	-26.2	48.4	34.01	0.12
<i>West</i>																						
Lostau	4/12/2006	22.4	7.71	43.2	25.6	12.6	22.6	54.8	30.8	0.00	74.0	65.0	4.68	15.7	53.3	676	78	167				0.25
	10/10/2007	24.0	7.77	37.5	21.2	97.8	17.8	49.3	25.1	3.87	56.9	56.4	1.66	12.9	46.1	583	60	144	-30.3	50.1	34.77	0.25
Beaugendre	26/09/2007	23.0	7.20	44.9	24.3	11.4	29.0	54.1	17.5	2.58	51.8	74.6	19.68	21.4	57.5	850	292	73	-31.9	48.7	33.43	0.09
	25/10/2007	23.2	7.87	38.6	19.9	93.3	25.3	51.6	20.7	6.67	76.1	75.0	-2.53	17.0	53.8	775	63	104	-31.7	45.7	31.58	0.13
Vieux-Habitants	11/07/2007	24.4	7.81	28.3	19.1	77.2	14.2	52.4	15.6	1.45	33.4	52.9	-2.34	11.1	44.6	545	52	47	-32.3	50.5	35.47	0.09
	14/03/2007	21.4	7.75	28.5	16.4	73.2	13.2	50.4	16.4	0.86	27.9	41.7	10.03	10.3	42.0	433	45	44		71.2	49.94	0.10
<i>East</i>																						
Moustique Petit-Bourg	11/12/2006	23.7	7.30	27.3	12.5	54.0	10.9	36.9	18.0	0.00	10.6	37.9	0.48	7.5	29.3	420	121	43	-30.8	74.5	51.65	0.10

Laboratory measurements of major ions concentrations were done by ionic chromatography (Dionex DX120, precision 5%). The detection limits for Ca, Mg, Na and K were respectively 12.5 μM , 20.6 μM , 0.9 μM and 0.5 μM . The detection limits for SO_4 , Cl, NO_3 and F were respectively 4.2 μM , 8.5 μM , 3.2 μM and 5.2 μM . Dissolved silica concentrations were determined calorimetrically, with a Seal QUAATRO analyzer (detection limit 5 μM and precision 2%).

Dissolved organic carbon (DOC) concentrations were measured using a Shimadzu TOC-VCSH analyzer (Sugimura and Suzuki, 1988). The detection limit was 20 μM and the precision was 2%. The $\delta^{13}\text{C}_{\text{DOC}}$ was measured at the “Institut des Sciences de la Terre d'Orléans” (ISTO). The measurements were done with an IR-MS Delta V Advantage coupled with a LC-Isolink interface (both Thermo Scientific) and a HPLC system serving as a pump for the carrier flow (100 μL of filtered and acidified sample water were directly injected in bulk mode and monitored in continuous flow) (Albéric et al., 2010). The standards used for the $\delta^{13}\text{C}_{\text{DOC}}$ measurements were the internal standard from ISTO (NaHCO_3 , - 4.3‰), the benzoic acid (- 25.7‰), the USGS-40 (L-glutamic acid, - 26.389‰), the IAEA-C8 (oxalic acid, - 18.3‰) and the IAEA-C6 (sucrose, - 10.8‰). The precision of the isotopic measurements was 0.3‰. The $\delta^{13}\text{C}_{\text{DIC}}$ was measured at the Stable Isotopes Laboratory of IPGP. The measurements were done with a GC/IR-MS (Analytical Precision) (Assayag et al., 2006). The standards use for the $\delta^{13}\text{C}_{\text{DIC}}$ measurements were the Rennes II (CaCO_3 powder, - 9.766‰), the Merck (CaCO_3 powder, - 8.65‰), the Across (CaCO_3 powder, 0.264‰) and the NaHCO_3 (- 4.4‰). The precision of the isotopic measurements was 0.5‰.

Spectrophotometric analyses of samples were conducted with a dual beam Evolution 600 UV-Vis — Thermo Scientific spectrophotometer. An aliquot of acidified water sample taken for the DOC measurements was used for the spectroscopic characterization of the dissolved organic matter. Samples were placed in a 1 cm quartz window cuvette and scanned from 200 to 600 nm, with 1 nm resolution (Chin et al., 1994).

4. Results

4.1. Major elements

pH and concentrations of major elements are presented in Table 2. pH values are relatively homogeneous, according to the spatial location or hydrological regime of rivers and range from 6.72 to 8.10. Low water level samples have a higher ionic charge (from 1200 to 2300 μM) than flood level water samples (< 1200 μM), with ionic charge is the sum of anions (Σ^-) and cations (Σ^+) concentrations. The normalized ionic charge balance values ($\text{NICB} = ((\Sigma^+ - \Sigma^-)/\Sigma^+) \square 100$) are generally close to 8%.

The dissolved silica concentrations vary between 110 and 631 μM . These concentrations are evenly distributed around the Basse-Terre. The dissolved silica concentrations are systematically higher during the low water level than during flood events and are similar to results acquired previously by Rad et al. (2007) in Guadeloupe (from 391 to 654 μM), Rad et al. (2006) in Mont Serrat and by Goldsmith et al. (2010) in Dominica (from 135 to 1048 μM during wet season and from 365 to 2110 μM during dry season). Moreover, similar silica concentrations for rivers flowing over basaltic rocks in the Deccan Traps, the Mount Cameroun and the Réunion Island were reported by [Louvat and Allègre, 1997], [Dessert et al., 2001] and [Benedetti et al., 2003].

The alkalinity is given by the following simplified formula:

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

Within the pH range (from 6.72 to 8.10) of the rivers, the dominant ion in the alkalinity is HCO_3^- . Alkalinities range from 148 to 755 μM , and do not vary spatially. They are higher during low water level than during floods, and they are both similar to results obtained for the Guadeloupe (Rad et al., 2007), Mont Serrat and the Dominica (Rad et al., 2006), and to the lowest values measured in Mount Cameroun rivers (Benedetti et al., 2003) and the Réunion rivers (Louvât and Allègre, 1997).

HCO_3^- is the dominant anion under low water level conditions, while during floods Cl^- becomes the dominant anion, followed by SO_4^{2-} and F^- (Table 2). The high concentrations of NO_3^- for Deshaies (23rd September 2007) and Beaugendre (10th September 2007) are likely due to the lixiviation of soil horizons enriched in nitrates. The Cl^- concentrations increase from the southern part to the northern part of the island, and are the highest during low water level.

Among major cations, Na^+ is dominant (from 140 to 450 μM). Ca^{2+} and Mg^{2+} concentrations vary between 55 and 290 μM and 19 and 172 μM , respectively. K^+ concentrations range from 11.8 to 31.2 μM . The cations concentrations distribution is the same around the Basse-Terre. These concentrations are smaller during flood level than during low water level. These cations are in the range of those measured by [Rad et al., 2007] and [Goldsmith et al., 2010]. Cationic concentrations are systematically smaller than the ones reported for rivers flowing through basaltic rocks of the Réunion Island, the Deccan Trap or the Mount Cameroun ([Louvât and Allègre, 1997], [Dessert et al., 2001] and [Benedetti et al., 2003]).

4.2. Dissolved inorganic carbon

Calculated concentrations of DIC are reported in Table 2. The calculations are done with field pH, temperature values and with alkalinity and ionic strength measurements made in the laboratory. The calculated DIC values are obtained with the following simplified formula (neglecting concentrations of OH^- and H^+):

$$DIC = \frac{Alk}{\frac{1}{1 + \gamma_1 \cdot 10^{(pK_{A1} - pH)} + \frac{\gamma_1}{\gamma_2} \cdot 10^{(pH - pK_{A2})}} + \frac{2}{1 + \frac{\gamma_2}{\gamma_1} \cdot 10^{(pK_{A2} - pH)} + \gamma_2 \cdot 10^{(pK_{A1} + pK_{A2} - 2pH)}}$$

with Alk = alkalinity, γ_1 and γ_2 = activity coefficients of ions mono-charged or bi-charged respectively, K_{A1} and K_{A2} corresponding to the first and second acidity constants of carbonate system, respectively.

DIC values range from 149 to 850 μM of C. The distribution of DIC concentrations is homogeneous around the Basse-Terre. DIC concentrations are systematically the highest during low water level, and are similar to results obtained by Rivé (2008) in rivers of Martinique (from 319 to 978 μM), of Guadeloupe (from 292 to 817 μM) and of Dominica (from 235 to 962 μM) islands. The calculated partial pressures of the CO_2 (pCO_2) vary between 32 and 299 Pa. The pCO_2 variations are not related with hydrological regimes changes since for the northern rivers the values are the highest during low water level and for eastern rivers the values are the highest during floods. Guadeloupean rivers are oversaturated with respect to the atmospheric CO_2 according to NOAA (i.e. 39 Pa from 2006 to 2009,

www.noaa.gov). These results are similar to values obtained for rivers of Hawaii (Paquay et al., 2007) or for the Xijiang River characterized by a subtropical monsoon (Yao et al., 2007).

The isotopic compositions ($\delta^{13}\text{C}_{\text{DIC}}$) are obtained for the same rivers but sampled at different dates. $\delta^{13}\text{C}_{\text{DIC}}$ ranges from -16.7 to -6.8‰ , with an average value of -11.4‰ ($n = 20$) during low water level and from -24.4 to -9.6‰ , with an average value of -15.8‰ ($n = 16$) during floods. $\delta^{13}\text{C}_{\text{DIC}}$ values are similar to the one measured previously for the Guadeloupean rivers (i.e. from -17.2 to -7.3‰) by Rivé (2008).

4.3. Dissolved organic carbon

DOC concentrations fall into the range 43 to 601 μM of C. DOC concentrations are higher in the northern part than in the rest of the island. DOC concentrations are systemically the highest during flood levels. They are similar to the one measured for small mountainous rivers of New Zealand (from 8 to 630 μM , mean 30 μM for the Southern Alps and 200 μM for the southwestern North Island; Carey et al., 2005) and for tropical mountainous rivers of Puerto Rico (mean from 110 to 180 μM ; Mcdowell and Asbury, 1994).

The isotopic compositions of DOC ($\delta^{13}\text{C}_{\text{DOC}}$) in studied rivers are given in Table 2. The $\delta^{13}\text{C}_{\text{DOC}}$ ranges from -32.8 to -26.2‰ . The distribution of the isotopic composition of DOC is the same around the Basse-Terre. The $\delta^{13}\text{C}_{\text{DOC}}$ values are systematically more negative during low water level than during floods (Table 2). These values are characteristic of organic matter derived from Guadeloupean tropical forest C3 type plants (Deines, 1980).

The parameters like aromaticity, weight (Mw) and number (Mn) average molecular weight and number and hydrophobic fraction can be estimated from the UV–Vis absorbance data, with empirical relationships (Chin et al., 1994). Different wavelengths are selected (254, 270, and 280) to underline the markers of organic matter. The absorbance at these different wavelengths defined as SUVA (Specific UV absorbance) is calculated with the following formula:

$$\text{SUVA}_{\text{XXX}} = \frac{\text{Absorbance at wavelength XXX} (\text{cm}^{-1})}{\text{DOC concentration} (\text{mgL}^{-1})}$$

(XXX corresponding to one of the following SUVA_{254} ;
 SUVA_{270} or SUVA_{280}).

The percentage of aromatic dissolved organic carbon or “aromaticity” is calculated by averaging the values obtained with the relationships proposed by [Chin et al., 1994], [Peuravuori and Pihlaja, 1997] and [Weishaar et al., 2003]. The percentage of aromatic carbon varies between 31 and 75% (Table 2). The weight averaged molecular weights (Mw) are calculated by averaging the data obtained with the relationships of [Chin et al., 1994] and [Zhou et al., 2001]. The Mw varies between 2521 and 5165 D. The values of the aromaticity and Mw are relatively similar for all rivers, but these values are higher during low water level than during floods. The percentages of aromatic carbon are similar to results acquired in water samples collected in 16 states of the USA by NASQAN sampling program (Weishaar et al., 2003) and in natural humic-water samples collected from two lakes in

Finland (Peuravuori and Pihlaja, 1997) using an identical spectroscopic approach. The weight averaged molecular weight values are similar to results obtained for colloidal organic matter from rivers of Amazonian basin (between 1126 and 2230 D, Alasonati et al., 2010). The polydispersity index calculated with ratio Mw on Mn was close to 2.0 ± 0.1 for all samples, and is identically for all rivers and during low water level and floods.

5. Discussion

The following discussion supported by the results presented above will first focus on the role of parameters included in models of watersheds weathering such as average slopes, precipitation and age of the geological substratum on the fluxes of both inorganic and organic carbon. Then the discussion will address the question of the sources of the dissolved organic carbon and their characteristics. Finally, we calculate average annual yields of both organic and inorganic carbon taking into account the spatial and temporal variability on the various studied watersheds the results of these calculations will emphasize the role of islands such as Guadeloupe in the overall global carbon budget.

5.1. Chemical composition

Considering our studied area, the global chemical composition of river waters mainly derives from water–rock interaction processes, soil lixiviation and atmospheric inputs. Indeed, samples have been collected upstream of agricultural areas and away from the active volcanic area (South) strongly impacted by hydrothermal springs.

The atmospheric inputs to the rivers can be classically estimated by looking at chlorine concentrations, which are mainly derived from rainwater in areas non-impacted by anthropogenic and geothermal inputs. We have plotted in Fig. 3 sodium concentrations as a function of chlorine concentrations for the different rivers. The Na/Cl ratios of rivers are systematically higher than those of rainwater, symbolized by the straight line with a slope of 0.8 ($\text{Na}/\text{Cl}_{\text{rain}}$), emphasizing the additional sources of sodium coming from water–rock interactions.

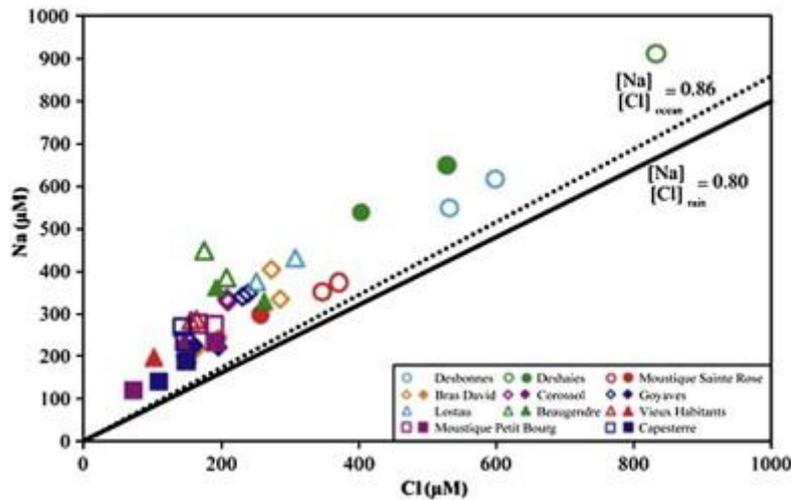


Fig. 3. Sodium concentrations as function of chlorine concentrations expressed in μM . The rainfall ratios were obtained from the average concentrations of rainwater sampled in the Southern part of Basse-Terre (Dessert, personal communication). The open and closed symbols correspond to low water level floods, respectively.

Northern rivers present higher concentrations than in the South, due to the highest evapotranspiration factor in the North (Table 1). The sea salt aerosols transported by the Easterly are scavenged by rainwater, which lead to a mean chlorine concentration about $200 \pm 110 \mu\text{M}$ in Guadeloupe (Dessert, personal communication). With evapotranspiration factor (f_{evap}) varying between 1 and 4 (Table 1), we estimate that the concentration of cyclic chlorine in rivers varies between $200 \mu\text{M}$ in the southern part and $800 \mu\text{M}$ for the Deshaies River in the northern part of the island ($[\text{Cl}]_{\text{river}} = [\text{Cl}]_{\text{rain}} \cdot f_{\text{evap}}$). We can thus assume that all the chlorine content has mainly an atmospheric origin. The content of other solutes having an atmospheric origin is determined using riverine chlorine concentrations and rainwater molar ratios ($\text{Na}/\text{Cl} = 0.8$, $\text{Mg}/\text{Cl} = 0.09$, $\text{SO}_4/\text{Cl} = 0.08$, $\text{Ca}/\text{Cl} = 0.06$, $\text{K}/\text{Cl} = 0.03$, Dessert, personal communication).

The remaining solutes are coming from water–rock interaction processes and are used in the determination of the different chemical weathering rates. TDS_{cat} (cationic total dissolved solid) is the sum of concentrations of major cations (Ca, Mg, Na and K) corrected for atmospheric inputs. TDS_{w} (weathering total dissolved solid) values are calculated from the concentrations of the major dissolved elements originating from andesitic weathering (SiO_2 , Ca, Mg, Na, K and SO_4) and corrected for atmospheric inputs. TDS_{cat} values vary between 3.7 and 21.4 mg L^{-1} and TDS_{w} concentrations range from 11.8 to 57.5 mg L^{-1} (Table 2). The TDS values are quite uniform from one area to the other and they are systemically lower during floods, because of a partial dilution effect. TDS_{cat} and TDS_{w} calculated for Guadeloupean Rivers are similar to those reported in Dessert et al. (2003) for Columbia Plateau, Hawaii, Iceland, the Massif Central and Sao Miguel.

With mean annual runoff, HCO_3^- (alkalinity), TDS_{cat} and TDS_{w} (Table 2) of each rivers, we estimate the mean annual regional rates of CO_2 consumption, cationic weathering and chemical weathering for each regions of Guadeloupe.

$$\text{mean regional CO}_2 \text{ consumption} = [\text{HCO}_3^-]_{\text{region}} * R_{\text{region}}$$

with $[\text{HCO}_3^-]_{\text{region}}$ = mean regional concentration in HCO_3^- and R_{region} = mean regional runoff;

$$\text{mean regional cationic weathering} = \text{TDS}_{\text{cat}/\text{region}} * R_{\text{region}}$$

with $\text{TDS}_{\text{cat}/\text{region}}$ = mean regional TDS and R_{region} = mean regional runoff;

$$\text{mean regional chemical weathering} = \text{TDS}_{\text{w}/\text{region}} * R_{\text{region}}$$

with $\text{TDS}_{\text{w}/\text{region}}$ = mean regional TDS_{w} and R_{region} = mean regional runoff and the regions correspond to the Northern, the Center, the Western and the Eastern part of the island.

The rates of CO_2 consumption, ranging from 0.26 to 1.36 $10^6 \text{ mol km}^{-2} \text{ year}^{-1}$ (Table 3), are similar to the data reported in Rad et al. (2006) for Guadeloupe and Martinique Rivers and in Goldsmith et al. (2010) for the Dominica Rivers. But they are different from the one reported for the Réunion Island (1.3–4.4 $10^6 \text{ mol km}^{-2} \text{ year}^{-1}$; Louvat and Allègre, 1997) under similar climatic conditions. This is most probably due to the different nature of parent rock (andesitic versus basaltic). The cationic weathering and chemical weathering rates, based on a compilation of TDS_{cat} and TDS_{w} , ranged from 7.8 to 34.0 and 38.9 to 114.5 $\text{t km}^{-2} \text{ year}^{-1}$ respectively (Table 3). These values are similar to those previously established for the andesitic terrains of Guadeloupe and Martinique (100–120 $\text{t km}^{-2} \text{ year}^{-1}$) by Rad et al. (2006) and Dominica (6–106 $\text{t km}^{-2} \text{ year}^{-1}$) by Goldsmith et al. (2010) and for the basaltic terrains under similar climatic conditions of Reunion Island (63–170 $\text{t km}^{-2} \text{ year}^{-1}$) by Louvat and Allègre (1997). These rates vary with geographical location around the Basse-Terre. Furthermore, all Guadeloupean watersheds had chemical weathering rates well in excess of the global mean value of 24 $\text{t km}^{-2} \text{ year}^{-1}$ (Gaillardet et al., 1999b). Such a difference is expected as large river systems integrate weathering processes occurring on different lithology, different runoff as well as temporary carbon storage or CO_2 consumption and production in floodplains ([Walling et al., 2006], [Bonnet et al., 2008], [Engle et al., 2008] and [Guyette et al., 2008]). The northern rivers of the Guadeloupe Island have the smallest rates compared to the rest of the Island. The smaller rates of the northern part could be due to lower annual precipitations combined with less steep slopes, related to oldest bedrocks. The central, western and eastern parts have higher rates than the northern part, reflecting the high rainfall inputs and the effect of the age of the geological substratum (Gislason et al., 1996). Moreover, for the eastern and western part of the island, the lack of soils will promote faster and stronger weathering as CO_2 acid interacts directly with fresh or physically eroded parent rocks.

Table 3. DOC and DIC yields for the two hydrological stages, and mean annual DOC and DIC yields, as well as calculated mean annual rates of CO₂ consumption, cationic weathering and chemical weathering for different part of the Guadeloupe.

Site	Area km ²	Low water level		Flood level		Mean annual				
		Y _{DOC} km ⁻² year ⁻¹	Y _{DIC} km ⁻² year ⁻¹	Y _{DOC} km ⁻² year ⁻¹	Y _{DIC} km ⁻² year ⁻¹	Y _{DOC} km ⁻² year ⁻¹	Y _{DIC} km ⁻² year ⁻¹	CO ₂ consumption rate 10 ⁶ mol km ⁻² year ⁻¹	Cationic weathering rate t km ⁻² year ⁻¹	Chemical weathering rate t km ⁻² year ⁻¹
<i>North</i>										
Desbonnes	5.50	0.4 ± 0.3	2.1 ± 1.5					0.26 ± 0.16	7.8 ± 4.9	38.9 ± 22.6
Deshaies	4.38	0.5 ± 0.3	1.7 ± 0.9	11.3 ± 6.6	7.3 ± 4.2	1.6 ± 0.9	2.3 ± 1.3			
Moustique Sainte-Rose	6.16	0.7 ± 0.4	3.0 ± 1.6	25.4 ± 16.1	21.9 ± 13.9	3.2 ± 2.0	4.9 ± 2.9			
<i>Center</i>										
Bras David	11.00	1.1 ± 0.5	11.0 ± 5.0	15.1 ± 6.3	32.8 ± 13.6	2.5 ± 1.1	13.2 ± 5.9			
Corossol	12.52	0.8 ± 0.5	9.4 ± 5.6	25.5 ± 11.4	40.3 ± 18.0	3.3 ± 1.6	12.5 ± 6.8	0.95 ± 0.51	20.8 ± 11.0	69.7 ± 37.0
Goyaves	14.40	1.1 ± 0.8	9.3 ± 7.0	21.1 ± 9.9	44.3 ± 20.7	3.1 ± 1.7	12.8 ± 8.4			
<i>West</i>										
Lostau	8.04	2.1 ± 1.2	8.5 ± 4.7					1.36 ± 0.76	34.0 ± 19.0	114.5 ± 64.1
Beaugendre	8.17	1.3 ± 1.1	11.6 ± 9.7	31.0 ± 15.1	75.7 ± 36.9	4.2 ± 2.5	18.0 ± 12.4			
Vieux-Habitants	19.10	1.4 ± 0.8	14.6 ± 8.8	27.2 ± 11.6	65.2 ± 27.8	3.9 ± 2.0	19.6 ± 10.7			
<i>East</i>										
Moustique Petit-Bourg	11.50	1.1 ± 0.7	11.5 ± 6.7	24.5 ± 10.2	43.2 ± 18.0	3.5 ± 1.6	14.6 ± 7.8	1.11 ± 0.59	24.7 ± 13.1	84.8 ± 44.9
Capesterre	16.20	1.7 ± 1.1	14.8 ± 9.4	42.4 ± 16.9	47.1 ± 18.8	5.7 ± 2.6	18.0 ± 10.4			

5.2. The dissolved carbon: spatial and temporal distribution

DIC concentrations are systematically the highest during low water level (Table 2), and represent more than 75% of the total dissolved carbon in rivers. During floods, the DIC is partially diluted by rainfall inputs as the lowest calcium and magnesium concentrations cluster in the lower part of Fig. 4. Moreover, the different $\delta^{13}\text{C}_{\text{DIC}}$ values for the two hydrological stages reflect the variable contribution of two end-members. The first one with less negative $\delta^{13}\text{C}_{\text{DIC}}$ corresponds to atmospheric CO₂ inputs (− 5 to − 10‰, Trumbore and Druffel, 1995), and the second one corresponds to depleted biogenic CO₂ produced during the decomposition of soil organic matter as decomposers used preferentially ¹²C (Lichtfouse et al., 1995). In Guadeloupean rivers, the major source of the riverine DIC is the CO₂ from soils (respiration of plant roots and the decay of organic matter) and atmospheric CO₂, both consumed during rock weathering processes (Worall et al., 2005). This hypothesis is supported by the good correlation between divalent cations (Ca and Mg) concentrations and DIC concentrations given by the Fig. 4. Elementary ratios of rocks are 0.13 for K/Si, 0.40 for

Ca/Si, 0.30 for Mg/Si, 1.33 for Ca/Mg, 3.00 for Ca/K and 2.30 for Mg/K for the 1440 AD eruption of the Soufrière (Poussineau, 2005). In the river waters corrected by the rainfall inputs, the average ratios are 0.03, 0.31, 0.14, 2.23, 9.80 and 4.43 for K/Si, Ca/Si, Mg/Si, Ca/Mg, Ca/K and for Mg/K, respectively. The differences between water and rock element ratios can be explained by the plant uptake for nutrient elements like potassium (Hinsinger et al., 2001) or by the mixing between of solutions seeping from the weathered soil horizons and the geological substratum. Indeed, the soils have elementary ratios smaller than those of parent rocks (Buss et al., 2010). Moreover, field observations show that the northern and center rivers flow on the soils and not directly on the parent rocks. In addition changes could also be due to the incorporation of Si in secondary minerals such as kaolinite, halloysite, allophane or montmorillonite during incongruent reactions of silicate minerals weathering ([Colmet-Daage, 1969] and [Colmet-Daage and Bernard, 1979]).

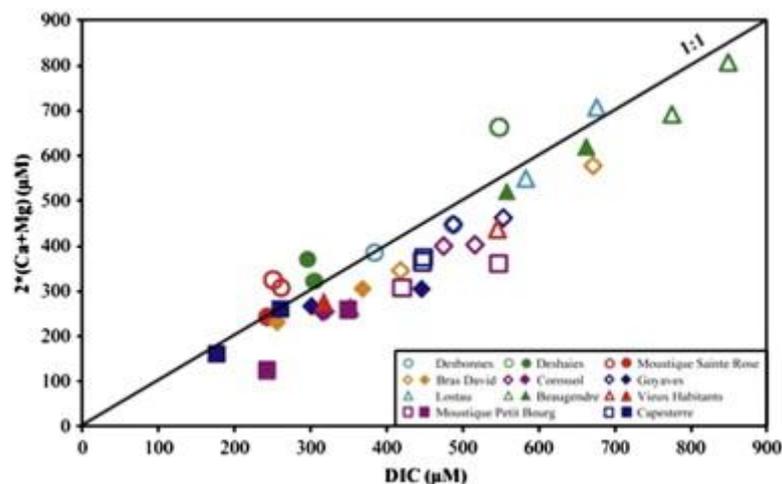


Fig. 4. $2 \times (\text{Ca} + \text{Mg})$ concentrations as function of DIC concentrations expressed in μM . The 1:1 line corresponds to a control of both Ca and Mg by weathering processes. DIC is also controlled by the weathering processes of the parent rocks.

Conversely to DIC, DOC concentrations are systematically higher during the flood level than during low water level (Table 2). For the later, the DOC represents from 10 to 30% of the total carbon, while during floods it accounts for more than 50% of the total carbon concentration. An input of water enriched with DOC is therefore needed to account for this difference. In Fig. 5, a general negative trend between $\delta^{13}\text{C}_{\text{DOC}}$ versus $1/\text{DOC}$ could correspond to the mixing between two end-members. Data points cluster reasonably along a mixing line with the highest concentrations characterized by less negative $\delta^{13}\text{C}_{\text{DOC}}$ corresponding to flood level and the lowest concentrations associated to the most negative $\delta^{13}\text{C}_{\text{DOC}}$ corresponding to low water level. Variable sources and weathering processes might have obscured that broad relationship between quality and quantity of DOC. One hypothesis would be that during low water level, the rivers could be fed in DOC by autochthonous algal development ([Kuserk et al., 1984], [Romani et al., 2004], [Sachse et al., 2005] and [Liang et al., 2008]) or by saprolite groundwater ([Sachse et al., 2005] and [Liang et al., 2008]). Conversely, the high DOC concentrations (116–601 μM , Table 2) during floods, could reflect an intense desorption or solubilisation of soil organic matter and its transfer into rivers by surface runoff during these extreme hydrological events. The values of $\delta^{13}\text{C}$ of litter obtained by Rivé (2008), vary between -30.4 and -27.8‰ and are in agreement with those obtained for refractory soil organic carbon (Lichtfouse et al., 1995). In fact, during the decomposition of the C3 plants ($\delta^{13}\text{C} = -20$ to -35‰ , Deines, 1980), the

soil organic matter is enriched by 1.5 to 4.3‰ in ^{13}C (Lichtfouse et al., 1995). The $\delta^{13}\text{C}_{\text{DOC}}$ of flood level was in the range of soil litter carbon indicating that the rivers were therefore probably fed by litter layers.

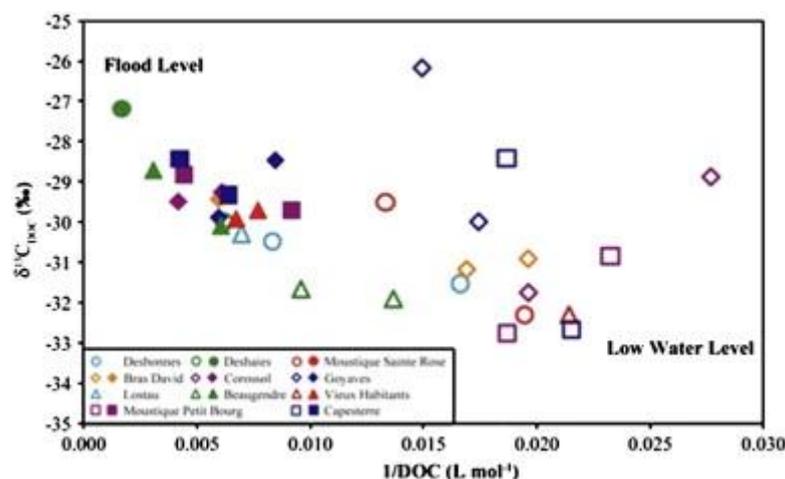


Fig. 5. Isotopic composition of dissolved organic carbon as function of 1/DOC. The general trend suggests a mixing process between two end-members.

Organic matter characteristics (i.e. aromaticity and molecular weight) are reported in Table 2. The DOC aromaticity and the molecular weight estimated for the low water level are higher than the ones corresponding to flood level. These observations are valid for all rivers except the Deshaies river that was not perennial. These parameters combine with isotopic data can help us to decipher between the two potential sources of DOC under low water level conditions (i.e. autochthonous vs saprolite). The trend observed in Fig. 6, between the $\delta^{13}\text{C}_{\text{DOC}}$ and aromaticity has been previously reported (Violleau, 1999). The $\delta^{13}\text{C}_{\text{DOC}}$ decreases as DOC aromaticity increases. In the saprolitic horizons, longer water residence time and smaller saprolite–solution ratio prevail. Under such conditions, the more aromatic, more hydrophobic and heavier organic carbon pool could also be desorbed (Muller et al., 2009). In addition at large water fluxes after heavy rainfall events DOM contains more carbohydrates, is less aromatic and more hydrophilic than at small water fluxes (Kaiser and Guggenberger, 2005). Moreover, the autochthonous organic matter production (algal or bacterial production) has, according to Croue (2004), a molecular structure similar to the hydrophilic fraction of natural organic matter. This autochthonous organic matter is generally enriched in ^{13}C and less aromatic.

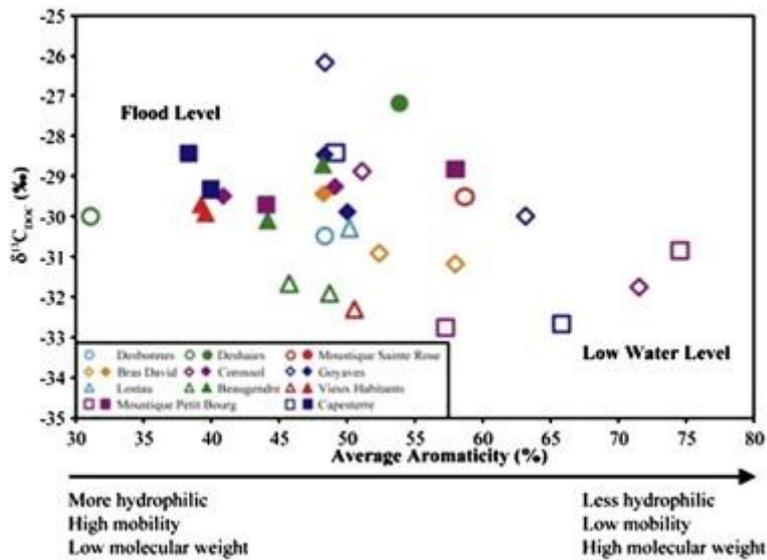


Fig. 6. Isotopic composition of dissolved organic carbon as function of the calculated average % of aromatic organic carbon. Percentages were obtained by averaging the values calculated with the relationships proposed by [Chin et al., 1994], [Peuravuori and Pihlaja, 1997] and [Weishaar et al., 2003].

In Fig. 7, we summarize the various processes accounting for the observed trends between low water level and floods. During low water level, the rivers are fed by ground flow from the saprolite. The ground flow is depleted in DOC. The organic matter molecules are larger (Mw), more aromatic, less hydrophilic, ^{13}C depleted and less mobile (Cabaniss et al., 2000). Conversely, during floods, the rivers are fed by surface runoff of solutions enriched with DOC. These DOC molecules are smaller, less aromatic, more hydrophilic, ^{13}C enriched and more mobile (Cabaniss et al., 2000).

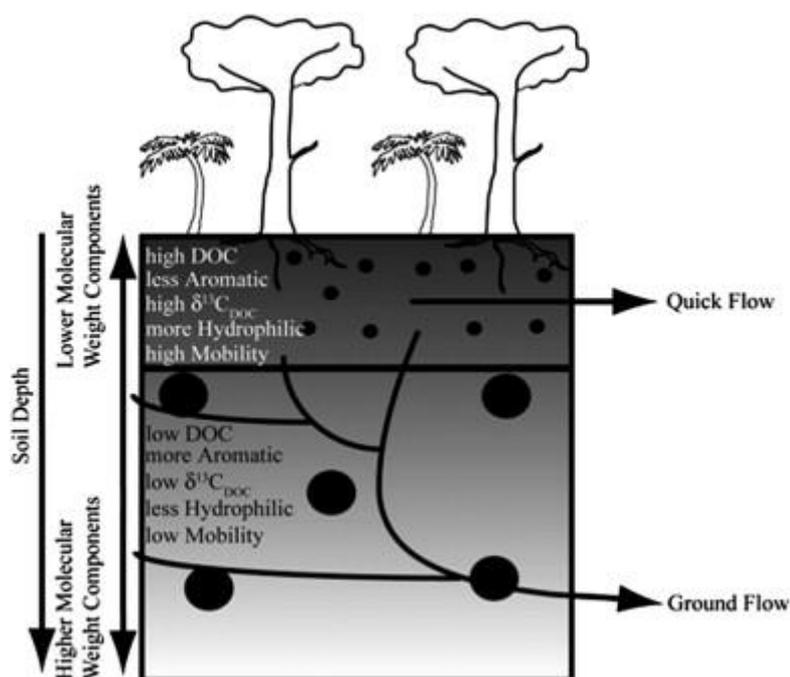


Fig. 7. Summary of the dissolved organic carbon characteristics and potential flowpath in the weathering profile developed on andesitic bedrock of the Basse-Terre Island. During flood events the quick flowpath dominates and the freshly deposited organic carbon is feeding the rivers. Under low water conditions the ground flowpath is the major source of organic matter for rivers.

The ratio DOC/DIC varies between 0.09 and 0.29 during low water level and between 0.37 and 1.97 during floods (Table 2). The increase of the DOC/DIC ratio for the flood water level is related to the massive input of rainwater that will modify the chemical equilibrium established during the low water level conditions. Both the lower ionic strength of the rainwater and the decrease of soil to pore water ratio will favor the desorption of soil organic matter and its release into the soil solution (Arnarson and Keil, 2000). Under conditions where mineral surfaces become limited and competitive anions are present, such as in surface horizons, newly formed mineral–organic associations are weaker and the OM is more susceptible to desorption. In contrast, once the availability of mineral surfaces increases in deeper soil horizons, the stabilization of OM upon sorption will increase and only a small portion of dissolved organic matter will eventually feed the rivers. This scenario will prevail under low water level conditions and justify the lower DOC/DIC ratios. In Fig. 8, the DOC/DIC values are plotted as function of the percentage of the total watershed area with slopes higher than 49% (Plaisir et al., 2003). The figure shows that there is a non-linear relationship between the two parameters for both water level conditions. The DOC/DIC ratio decreases as the watershed area is dominated by surfaces with slopes steeper than 49%. The steep slopes will prevent the development of deep soils on the geological substratum and therefore the accumulation of organic matter in the upper horizons that would generate higher DOC in the soil solutions. In addition beyond a threshold value of 10%, the decrease of the DOC/DIC is much smaller. The unknown distribution of organic matter in the soils of the studied watershed might however obscure that broad relationship.

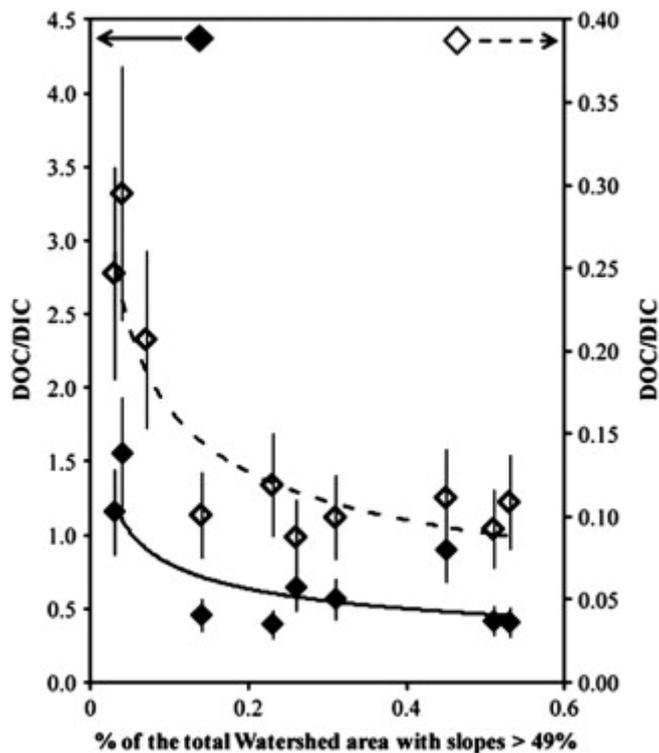


Fig. 8. [DOC]/[DIC] ratio as a function of percentage of the total area of watersheds with slopes > 49%. The open symbols correspond to low water level of rivers and the closed symbols to flood level. Curves are trend lines that correspond to the best fit ($R > 0.8$) between the average slopes of the watersheds. The best fits were obtained for slope above 49%.

5.3. DOC and DIC yields

The yields of carbon have been calculated from the mean runoff values and mean carbon concentrations for each river (Table 3). During low water level, the carbon yield varies between 0.4 and $2.1 \text{ t km}^{-2} \text{ year}^{-1}$ for the DOC and between 1.7 and $14.8 \text{ t km}^{-2} \text{ year}^{-1}$ for the DIC. The carbon yield during floods varies between 11.3 and $42.4 \text{ t km}^{-2} \text{ year}^{-1}$ for the DOC and between 7.3 and $75.7 \text{ t km}^{-2} \text{ year}^{-1}$ for the DIC (Table 3).

The mean annual yields of DOC and DIC were calculated using the following equation:

$$\text{mean annual yield} = Y_{LWL} * 0.9 + Y_{FL} * 0.1$$

where Y_{LWL} is the yield during low water level (related to 90% of the annual discharge; Fig. 2), and Y_{FL} is the yield during floods (related to 10% of the annual discharge).

The mean annual yields range from 2.5 to $5.7 \text{ t km}^{-2} \text{ year}^{-1}$ for the DOC and from 4.8 to $19.6 \text{ t km}^{-2} \text{ year}^{-1}$ for the DIC (Fig. 9). The actual yields of DOC and DIC to the ocean could be different from these calculated yields because our estimation does not take into account extra organic matter inputs from cultivated soils and mangroves located below our sampling points. The erosion of cultivated soils will release organic matter into rivers ([Bellanger et al., 2004], [Quinton et al., 2006], [Martinez-Mena et al., 2008] and [Gilles et al., 2009]). The real inputs to the ocean are even more difficult to forecast because mangrove can favor the

accumulation of organic matter from rivers (sink) as well as contribute to the flux of the later by degradation of organic residues issued from the mangrove itself (source) ([Chen and Twilley, 1999], [Bouillon et al., 2003], [Bouillon et al., 2008], [Chmura et al., 2003] and [Marchand et al., 2006]). The DOC and DIC yields are the most important in the South of the Basse-Terre (Fig. 9). This is likely due to the exposure to rainfalls and steep slopes (related to the younger age of the substratum) which implicate that the erosion of soils is more intense in the southern part than in the northern part of the island. The DOC yield is the most important for the Capesterre River with $5.7 \text{ t km}^{-2} \text{ year}^{-1}$. The Capesterre watershed is the most exposed to rainfalls and therefore its soils were prone to the erosive power of the extreme meteorological events. The DIC yield is the highest for the Vieux-Habitants River, due to higher weathering rates. The dissolved carbon yield is mainly in the form of DIC ($\text{DOC/DIC} < 1$). However, if we could take into account the particulate organic carbon then the yield of organic carbon would be higher than the yield of inorganic carbon. For instance, the particulate organic carbon represents about 10–30% of the total organic carbon in the Puerto Rico rivers (McDowell and Asbury, 1994). If similar percentages are applied to our samples, the yield of organic carbon in the Basse-Terre could represent between 18 and 47% of the total carbon yield. Noteworthy, more than 60% of the DOC export and 25–45% of the DIC export occurred during flash floods.

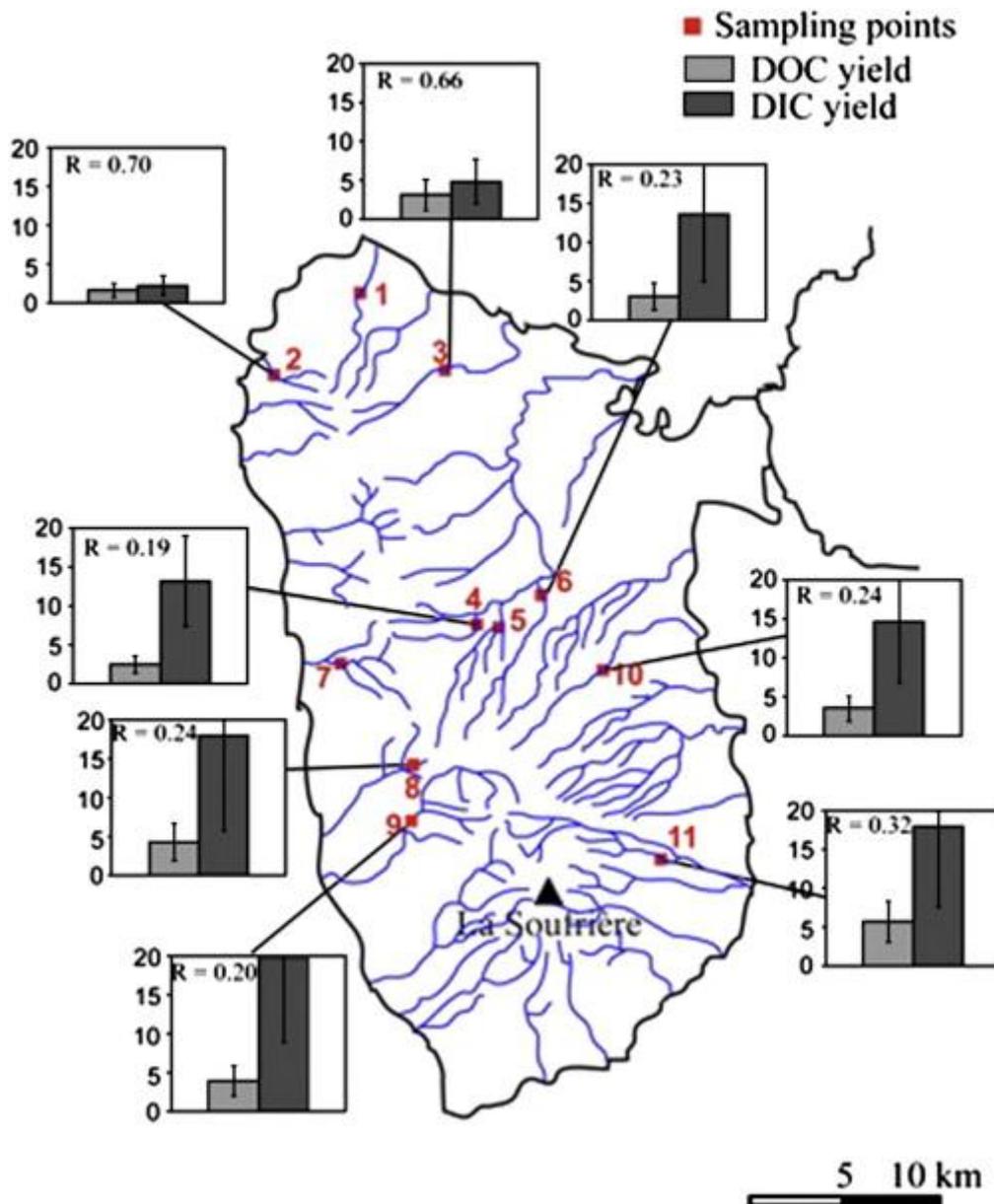


Fig. 9. Average annual DOC and DIC yields ($\text{t km}^2 \text{ year}^{-1}$; Table 3) for 8 watersheds in the Basse-Terre Island. $R = [\text{DOC}]/[\text{DIC}]$.

The DOC yields are close to the yields calculated at Puerto Rico (Mcdowell and Asbury, 1994) and the yields of New Zealand rivers under temperate climate (Carey et al., 2005). Moreover, the DOC yields are also similar to the yields determined for the large rivers under wet tropical climate like Zaire with $2.5 \text{ t km}^{-2} \text{ year}^{-1}$ (Nkounkou and Probst, 1987), Parana with $1.4 \text{ t km}^{-2} \text{ year}^{-1}$ (Depetris and Cascante, 1985), Changjiang with $5.7 \text{ t km}^{-2} \text{ year}^{-1}$ (Gan et al., 1983), Orinoco with $4.8 \text{ t km}^{-2} \text{ year}^{-1}$ (Lewis and Saunders, 1989). The DIC yields calculated for the Guadeloupean rivers are more important than the yields determined for the large rivers under wet tropical climate like Zaire with $9.9 \text{ t km}^{-2} \text{ year}^{-1}$ (Probst, 1992), Parana with $2.0 \text{ t km}^{-2} \text{ year}^{-1}$ (Cai et al., 2008), Changjiang with $11.2 \text{ t km}^{-2} \text{ year}^{-1}$ (Cai et al., 2008), Orinoco with $5.5 \text{ t km}^{-2} \text{ year}^{-1}$ (Cai et al., 2008). The large rivers integrate the yields of several watersheds which present different lithologies and therefore different

chemical weathering rates and DIC yields. The DIC yields calculated for the Guadeloupean rivers could be the analogue of one kind of sub-catchment in the large rivers systems.

The surface area of volcanic arc islands under wet tropical climate was calculated ([Louvat, 1997] and [Dessert et al., 2003]) and would represent about $3.29 \cdot 10^6 \text{ km}^2$. We assume that the DOC and DIC yields of Guadeloupean Rivers ($1.6\text{--}5.7 \text{ t km}^{-2} \text{ year}^{-1}$ and $2.3\text{--}19.6 \text{ t km}^{-2} \text{ year}^{-1}$, respectively; Table 3) are representative of DOC and DIC yields export for volcanic arc islands and we estimate therefore the annual DOC and DIC exports of these islands. The DOC and DIC exports from volcanic arc islands under wet tropical climate are about $0.005\text{--}0.019 \text{ Gt yr}^{-1}$ and $0.008\text{--}0.065 \text{ Gt yr}^{-1}$ respectively. The DOC export is similar to the DOC export calculated for large tropical rivers like the Amazon (0.034 Gt yr^{-1} ; Moreira-Turcq et al., 2003), the Orinoco and the Parana (0.005 and 0.004 Gt yr^{-1} , respectively; Ludwig et al., 1996b and references there in) or for the whole African continent (0.025 Gt yr^{-1} ; Lal, 2003). The DIC export is close to the DIC export calculated for Africa (0.009 Gt yr^{-1} ; Lal, 2003) or South America (0.059 Gt yr^{-1} ; Lal, 2003). Therefore, the exports of dissolved carbon from small volcanic islands are important and should be included in global carbon budget budgets.

6. Conclusion

This study examined the rivers of the volcanic Guadeloupe Island (FWI) to characterize the yields of dissolved organic (DOC) and inorganic (DIC) carbon during weathering in a tropical context. The small rivers present a characteristic hydrological regime where flash floods explain around 10% of the annual water flux. Dissolved carbon yields were constrained by taking into account this hydrological variability with samples collected during both low water and floods for eleven rivers distributed over the island.

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Differences in carbon origin during the two hydrological stages were confirmed with DOC and DIC concentrations as well as DOC characteristics and isotopic compositions. During low water level the rivers were mainly fed by soil ground flow while during floods level the rivers were fed by runoff and quick flow.

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DOC and DIC yields were estimated with data acquired for both hydrological stages of rivers. Noteworthy, more than 60% of the DOC export and 25–45% of the DIC export occurred during flash floods. Neglecting these flash floods leads to an underestimation of the global carbon export from these islands.

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A spatial variation of DOC and DIC yields is evidenced around the Basse-Terre Island. Indeed, the DOC and DIC yields are higher in the southern part of the island where the bedrock is younger and the slopes are steeper than in the northern part. Moreover, the southern part receives the maximum of precipitations.

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Therefore, for a carbon mass balance perspective, the exportation of organic carbon by small tropical rivers can no longer be neglected.

As the particulate organic carbon represent a non negligible fraction of the total organic carbon yield in other similar hydrological systems (Puerto Rico), future studies should include particulate organic carbon characterization from samples taken along the whole year to obtain a full mass balance for the carbon and a better estimation of the organic carbon yields. In addition organic matter from soils and soil solutions should be characterized to validate the organic carbon pools proposed in this study to account for the trends between the two hydrological periods.

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