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journal homepage: www.elsevier.com/locate/chemgeo

# Dynamic of particulate and dissolved organic carbon in small volcanic mountainous tropical watersheds



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#### ARTICLE INFO

Article history: Received 20 March 2013 Received in revised form 8 May 2013 Accepted 14 May 2013 Available online 31 May 2013

Editor: David R. Hilton

Keywords: Carbon fluxes DOC POC DIC Small tropical rivers Watersheds

# ABSTRACT

In the tropical zone, small watersheds are affected by intense meteorological events. These events play an important role in the erosion of soils and therefore on the associated organic carbon fluxes to the ocean. We studied the geochemistry of three small watersheds around the Basse-Terre volcanic Island (French West Indies, FWI) during a four years period, by measuring dissolved organic carbon (DOC), particulate organic carbon (POC) and dissolved inorganic carbon (DIC) concentrations. The mean annual yields ranged between 8.1–15.8 tC km<sup>-2</sup> yr<sup>-1</sup>, 1.9–8.6 tC km<sup>-2</sup> yr<sup>-1</sup> and 8.1–25.5 tC km<sup>-2</sup> yr<sup>-1</sup> for DIC, DOC and POC, respectively. Floods and extreme floods (i.e., extremely high discharge associated to extreme meteorological events such as cyclones or tropical storms) account for 42.6% of the yearly water flux and represent 54.5% of the annual DOC flux, and more than 85% of the annual POC flux. The DIC flux occurs essentially during low water levels with 75% of the annual flux. During low water levels and floods, the dissolved carbon is exported in majority under the inorganic form (DIC/DOC =  $2.6 \pm 2.1$ ), while during extreme floods, the dissolved carbon transported is mostly organic (DIC/DOC =  $0.7 \pm 0.2$ ). The partial "residence time" taking into account only the physical processes (erosion and transport) in Guadeloupean soils has been estimated between 381 and 1000 years. These relatively short times could be linked to the intensity of meteorological events rather than the frequency of meteorological events. The total export of organic carbon coming from small tropical and volcanic mountainous rivers is estimated at 2.4  $\pm$  0.6 MtC yr<sup>-1</sup> for DOC and at  $5.9 \pm 2.4$  MtC yr<sup>-1</sup> for POC, emphasizing that these carbon fluxes are significant and should be included in global carbon budgets. In addition, the quality of terrestrial organic matter (POC/DOC, and C/N ratios) arriving to the ocean is different from the one of large river origin. These inputs are responsible for a fast transport of terrestrial organic matter to the ocean but their effect on regional and global carbon budget is still a matter of debate.

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# 1. Introduction

Soil organic matter contains 1400 to 1500 Gt of carbon and is one of the major pools of carbon at the Earth surface (Schlesinger, 1977; Gregory et al., 1999). Soil erosion represents a major input of organic carbon in aquatic ecosystems. During meteorological events, soil organic carbon (SOC) can be intensively either leached or eroded and transferred to aquatic ecosystems in dissolved and particulate forms, respectively (Lal, 2004). During its transport from rivers to the oceans, terrestrial organic carbon can be mineralized and/or exported into the ocean (DOC and POC), or deposited and stored (POC) in aquatic ecosystems under low discharge (i.e.: alluvial plains,

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mangroves; Meybeck, 1993; Hedges et al., 1997; Lal, 2003, 2004). Once in the ocean, this terrestrial organic matter is then mineralized, and/or buried in sediments, and/or transported offshore (Hedges et al., 1997; Hansell and Carlson, 2002; Benner, 2004; Burns et al., 2008). Having been subjected to microbial degradation in soils (Oades, 1988; Hedges et al., 1994) and aquifers (e.g. Nelson et al., 1993), riverine DOC and POC arriving in estuaries and coastal oceans can be recalcitrant and resistant to the degradation in these ecosystems. Terrestrial organic matter thus represents approximately one third of the organic matter buried in all marine sediments and is stored over geological timescales leading to atmospheric carbon dioxide sequestration (Berner, 1989; Hedges and Keil, 1995; Hedges et al., 1997; Schlünz and Schneider, 2000; Gordon and Goñi, 2004; Burdige, 2005; Galy et al., 2007).

Organic carbon transport from continents to oceans represents around 40% of the global continental carbon flux (DOC, DIC, POC and particulate inorganic carbon), varying between 400 and 900 Mt  $yr^{-1}$ 

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<sup>0009-2541/\$ –</sup> see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.chemgeo.2013.05.023

(Hedges et al., 1997; Schlünz and Schneider, 2000; Aitkenhead-Peterson et al., 2003). For large rivers, the portion of DOC exported is around 60% of the total organic carbon export. Uncertainties on the estimation of the global organic carbon transfer are partly due to the lack of holistic quantitative studies taking into account all sizes of watersheds as well as all type of climatic regimes. Indeed studies generally focus on large river systems like the Mississippi (Bianchi et al., 2007; 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; Aufdenkampe et al., 2007; Bouchez et al., 2010) and, large Arctic rivers (Yenisei, Ob, Lena Rivers; Ludwig et al., 1996a; Dittmar and Kattner, 2003; Gebhardt et al., 2004; Raymond et al., 2007), which integrate differences in lithology, vegetation, soils and climate. Small mountainous rivers directly connected to the oceans are less studied than large rivers, although they play an important role in transport in organic matter, their yields and runoff being inversely proportional to the watershed area (Milliman and Meade, 1983; Walling, 1983; Degens and Ittekkot, 1985; Milliman and Syvitski, 1992). Recent works have demonstrated that these small rivers are major sources of POC (Kao and Liu, 1996; Schlünz and Schneider, 2000; Lyons et al., 2002; Carey et al., 2005; Hilton et al., 2008b), DOC (Lloret et al., 2011) and dissolved major elements to the oceans (Louvat and Allègre, 1997; Dessert et al., 2009; Goldsmith et al., 2010; Calmels et al., 2011; Lloret et al., 2011). Due to their location in the tropical zone, numerous small mountainous rivers are affected by aperiodic intense precipitation events such as cyclones or tropical storms that can play an important role on soil erosion and can potentially increase total organic carbon fluxes released by these systems (Waterloo et al., 2006; Dawson et al., 2008; Goldsmith et al., 2008; Hilton et al., 2008a; Bass et al., 2011; Lloret et al., 2011; Jeong et al., 2012; Wohl et al., 2012).

The Guadeloupe Island (French West Indies) provides an unique opportunity to study the yield and the flux of carbon from such small watersheds as well as the impact of these meteorological events on inorganic and organic carbon fluxes. Its monolithologic volcanic composition, combined with its lack of fossil organic carbon, helps to constrain the influence of other factors such as climate, soil composition, and age of the bedrock. In addition, high rates of chemical weathering and mechanical denudation are reported for volcanic lithology (Louvat and Allègre, 1997; Dessert et al., 2001, 2003; Goldsmith et al., 2010; Gaillardet et al., 2012). Moreover, Guadeloupean soils (Andosol and ferralitic soils; Colmet-Daage and Bernard, 1979) present surface horizons enriched in organic matter (10-15 %; Colmet-Daage and Lagache, 1965; Duchaufour, 2001; Lloret, 2010). Guadeloupean coasts are impacted by numerous meteorological events like tropical storms and cyclones (Zahibo et al., 2007), that can accentuate the soil erosion (Waterloo et al., 2006; Dawson et al., 2008; Hilton et al., 2008a; Lloret et al., 2011). Lloret et al. (2011) focused on spatial and temporal distribution of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) concentrations in the Guadeloupean rivers. This study underlined the importance of floods on carbon export, more than 50% of the annual DOC export being transported during these hydrologic events. During floods, rivers are fed by surface solutions enriched in DOC resulting from leaching of freshly deposited organic matter. Under low water conditions, the ground flow path is the major source of organic carbon and is characterized by low DOC concentrations in rivers. Lloret et al. (2011) also estimated that DOC yields by small volcanic and mountainous islands under tropical climate range between 2.5 and 5.7 t  $km^{-2} yr^{-1}$  and are similar to the DOC yields calculated for large tropical rivers like the Amazon (5.8 t  $\text{km}^{-2}$   $\text{yr}^{-1}$ ; Moreira-Turcq et al., 2003), the Orinoco and the Parana (4.8 and 1.4 t km<sup>-2</sup> yr<sup>-1</sup>, respectively; Ludwig et al., 1996b and references therein). However, the DOC yields calculated in Lloret et al. (2011) were based on a discrete sampling (2 low water and 2 flood levels only) and probably are an underestimation of these yields. Indeed Bass et al. (2011) showed that the DOC and the POC fluxes could be underestimated by 49 to 78%, respectively if high temporal resolution sampling is not performed. Moreover, Lloret et al. (2011) did not report POC fluxes and did not compare carbon with other particulate macronutrients, like nitrogen which, when it is combined with C/N ratio, can be a good indicator of organic matter origin.

The aim of this paper is to supplement existing knowledge on small mountainous rivers and further demonstrate their important role in global carbon budget. To achieve this goal, we used new data (with notably POC and particulate nitrogen (PN) concentration data) acquired at high temporal resolution to (1) calculate the annual yields of different carbon fractions and PN, (2) determine processes controlling dissolved carbon and particulate fraction distributions, (3) estimate the impact of meteorological events on the annual carbon fluxes, (4) calculate the carbon mass balance at Guadeloupean watershed scale, (5) estimate the carbon organic export by small and tropical mountainous islands to the world ocean. To address these issues we have selected three watersheds hydrologically monitored for several decades with various size, elevation, ages, slope, and exposure to rainfall. One river was monitored intensively with an automatic water sampler equipped with pressure sensors activated during flood events, increasing significantly the time resolution of sampling.

### 2. Study area

Guadeloupe is part of the Lesser Antilles volcanic arc generated by the subduction of the North American plate beneath the Caribbean plate. The volcanic island of Basse-Terre, part of the Guadeloupe archipelago, belongs to the central segment of the arc (e.g., Feuillet et al., 2011) (Fig. 1). The main characteristics of the studied watersheds are given in Table 1 and summarized in Fig. 2. The three watersheds are studied as part of the ObsErA (INSU-CNRS) observatory devoted to the study of weathering and erosion in the French West Indies. The observatory belongs to the French network of monitored watersheds (RBV supported by INSU-CNRS and AllEnvi).

#### 2.1. Vegetation cover, geology and soils

The three watersheds are located in the National Park of Guadeloupe in the central part of the volcanic Basse-Terre Island. The vegetation is mainly dominated by tropical rainforest and by altitude forest type at the head of watersheds (Rousteau et al., 1994; Rousteau, 1996).

The Bras-David watershed located in the center of the Basse-Terre Island is essentially composed of Pleistocene andesitic and dacitic formations (Samper et al., 2007), covered by a very thick ferralitic soil (>15 m; Colmet-Daage and Bernard, 1979). These soils were previously studied (Buss et al., 2010; Lloret, 2010; Sak et al., 2010) and consist of highly weathered volcanoclastic debris flows containing rocky clasts at various stages of weathering. Clays, dominantly halloysite, represent about 75 wt.% of the mineralogy and nonclays are almost entirely Fe(III)-hydroxides and quartz/cristobalite. The average C/N ratio (expressed as %wt:%wt) is  $12.9 \pm 3.4$  (Lloret, 2010). The slopes observed for this watershed are essentially included between 25 and 48% (Plaisir et al., 2003). The Capesterre and the Vieux-Habitants watersheds, located respectively in the southeast and southwest parts of the Basse-Terre Island, are underlain by andesitic rocks linked to late Pleistocene volcanism (Samper et al., 2007) and covered with thin Andosol (<1 m; Colmet-Daage and Bernard, 1979; Cattan et al., 2007), related to the steep slopes of the young volcanic rocks. The average C/N ratio is 11.8  $\pm$  1.6 (Lloret, 2010). The slopes observed for these two watersheds are higher than 49% (Plaisir et al., 2003).

#### 2.2. Climate and hydrology

The Basse-Terre Island is characterized by a wet tropical climate, with a mean annual temperature around 23 °C and 75% humidity (Plaisir et al., 2003). The average annual precipitation for the last 20 years ranges from 1200 to 8000 mm yr<sup>-1</sup>, depending on the

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