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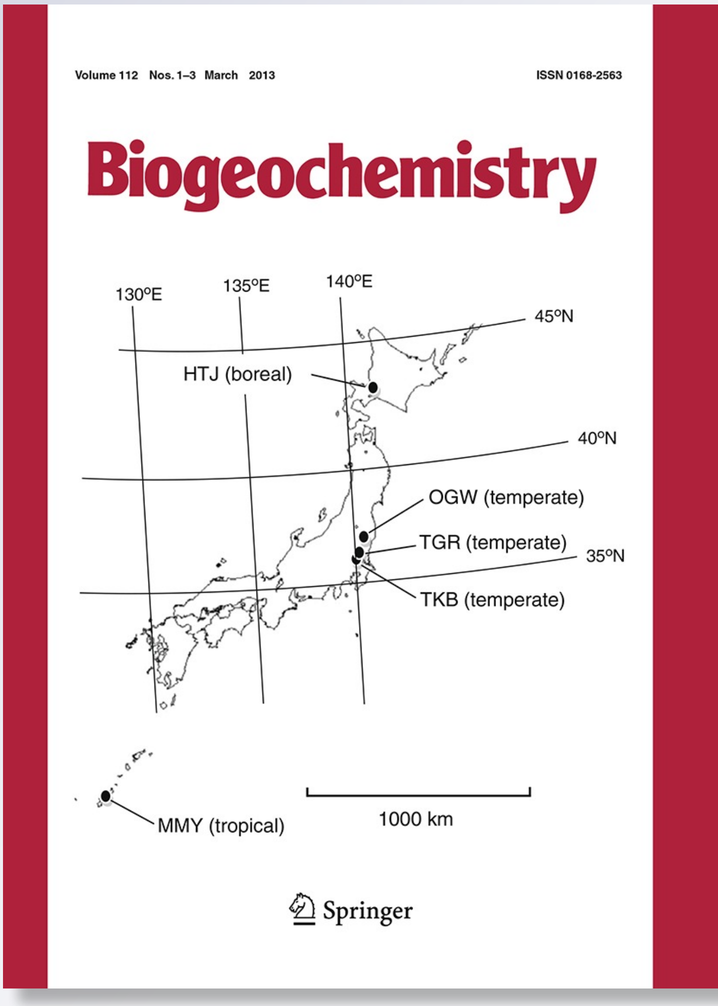

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Abstract Recent studies have shown that small mountainous rivers (SMRs) may act as sources of aged and/or refractory carbon (C) to the coastal ocean, which may increase organic C burial at sea and subsidize coastal food webs and heterotrophy. However, the characteristics and spatial and temporal variability of C and organic matter (OM) exported from tropical SMR systems remain poorly constrained. To address this, the abundance and isotopic character ($\delta^{13}C$ and $\Delta^{14}C$) of the three major C pools were measured in two Puerto Rico SMRs with catchments dominated by different land uses (agricultural vs. non-agricultural recovering forest). The abundance and character of C pools in associated estuaries and adjacent coastal waters were also examined. Riverine dissolved and particulate organic C (DOC and POC, respectively) concentrations were highly variable with respect to land use and sampling month, while dissolved inorganic C (DIC) was significantly higher at all times in the agricultural catchment. In both systems, riverine DOC and POC ranged from modern to highly aged (2,340 years before present), while DIC was always modern. The agricultural river and irrigation canals contained very old DOC (1,184 and 2,340 years before present, respectively), which is consistent with findings in temperate SMRs and indicates that these tropical SMRs provide a source of aged DOC to the ocean. During months of high river discharge, OM in estuarine and coastal waters had C isotope signatures reflective of direct terrestrial input, indicating that relatively unaltered OM is transported to the coastal ocean at these times. This is also consistent with findings in temperate SMRs and indicates that C transported to the coastal ocean by SMRs may differ from that of larger rivers because it is exported from smaller catchments that have steeper terrains and fewer land-use types.

Keywords Tropical small mountainous rivers · Dissolved organic carbon · Particulate organic carbon · Dissolved inorganic carbon · Carbon isotopes

Electronic supplementary material The online version of this article (doi:10.1007/s10533-012-9751-y) contains supplementary material, which is available to authorized users.

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Introduction

The delivery of organic and inorganic forms of carbon (C) from rivers to the coastal ocean is an important component of the global C budget (Hedges 1992; Siegenthaler and Sarmiento 1993; Benner 2004; Richey 2004; Sabine et al. 2004). Our understanding of the inputs and fates of terrestrially derived C discharged to the coastal ocean, while gradually improving due to a growing body of reliable river, estuarine, and seawater C geochemical measurements, is still not fully constrained. To date, most studies have focused on large temperate rivers (e.g., Raymond et al. 2004; Wang et al. 2004; Nagao et al. 2005; Raymond et al. 2008), with measurements from tropical rivers being dominated by the Amazon (e.g., Hedges et al. 1986; Richey et al. 2002; Mayorga et al. 2005) and its headwaters (e.g., Johnson et al. 2006; Saunders et al. 2006; Townsend-Small et al. 2007). Tropical small mountainous river (SMR) systems may transport as much as 50 % of the total terrestrial C delivered to the coastal ocean (e.g., Milliman and Syvitski 1992; Milliman et al. 1999; Lyons et al. 2002), however this export of terrestrial C appears to be sporadic, and linked to rain events and tectonic activity (Aufdenkampe et al. 2007; Alin et al. 2008; Townsend-Small et al. 2008; Sickman et al. 2010; Hatten et al. 2010; Wheatcroft et al. 2010). In addition, land-use change in the tropics has dramatically altered both the hydrology and the transport and cycling of C on land (Houghton et al. 2000) and in rivers (Mayorga et al. 2005). The paucity of information on C and organic matter (OM) characteristics and export by tropical SMRs to the ocean is therefore a major gap in our understanding of tropical land–coastal ocean linkages and biogeochemical cycles.

Rivers typically transport large amounts of terrestrial soil OM (Schlesinger and Melack 1981; Milliman and Meade 1983; Cole and Caraco 2001; Smith et al. 2001) and, along with their catchments and estuaries, are sites of intense OM processing. This internal processing influences the amount, composition, reactivity, and timing of C discharged to the coastal ocean. Soil OM may age significantly within river catchments prior to mobilization (Kao and Liu 1996; Cole and Caraco 2001; Masiello and Druffel 2001; Raymond and Bauer 2001a, b; Blair et al. 2003), and may be mobilized in part as dissolved organic C (DOC) (Hope et al. 1994; Aitkenhead-Peterson et al. 2003, 2005). Particulate organic C (POC) (Kao and Liu 1996; Masiello and Druffel 2001; Komada et al. 2004, 2005) and sedimentary OM deposits (Blair et al. 2003; Leithold et al. 2006) in SMRs are among the most highly aged among river systems globally. Still other studies have demonstrated that the age of OM exported by SMRs is quite variable, ranging from modern to highly aged within and between river systems (Masiello and Druffel 2001; Mayorga et al. 2005; Townsend-Small et al. 2007; Alin et al. 2008; Sickman et al. 2010). In addition, land-use change, dam and impoundment construction, and other anthropogenic impacts are speculated to have dramatically altered the abundance and transformations of C and OM transported from catchments to rivers and the coastal ocean (Hope et al. 1997; Oh and Raymond 2006; Worrall and Burt 2007; Raymond et al. 2008). These impacts are predicted to be manifested even more strongly in tropical SMR systems where most catchments have been heavily modified by anthropogenic activities (Houghton 1994).

Generally greater soil OM turnover coupled with shorter residence times in tropical SMR catchments compared to other river systems, may result in the delivery of significant amounts of C and OM directly to the coastal ocean (Milliman and Syvitski 1992; Kao and Liu 1996; Lyons et al. 2002; Larsen and Webb 2009), especially during high-discharge events (Goldsmith et al. 2008; Wheatcroft et al. 2010). Terrestrial C and OM in larger tropical rivers also supports microbial heterotrophy, leading to large emissions of CO_2 to the atmosphere (Cole and Caraco 2001; Richey et al. 2002; Mayorga et al. 2005). Tropical SMRs may therefore have a disproportionately large impact on regional-scale coastal processes, despite their small size. To date, however, relatively few studies have examined simultaneously the sources, ages, and/or isotopic characteristics of C delivered to the coastal ocean by tropical SMRs (Goñi et al. 2006, 2008; Alkhatib et al. 2007; Townsend-Small et al. 2007; Alin et al. 2008), in the three major C pools (DOC, POC, and DIC). In addition, estuaries, which historically have not been considered adequately in riverine C studies (Raymond and Bauer 2001a, c; Wang et al. 2004), may also play an important role in the biogeochemical alteration of riverine OM in tropical SMR systems prior to its export to the coastal ocean.

The goals of the present study were to examine the abundances and isotopic character of the three major pools of C and OM in two tropical SMRs, their associated estuaries, and adjacent coastal waters of Puerto Rico. Measurements of DOC, POC, and dissolved inorganic C (DIC) concentration and stable- and radio-isotopic character ($\delta^{13}C$ and $\Delta^{14}C$, respectively) were made during historically wet and dry months in order to identify the potential sources of C and OM in the SMRs, the transformations associated with their estuarine transition zones, and inputs to adjacent coastal ocean waters. Therefore this study represents a first-order assessment of C in tropical SMRs and the adjacent coastal ocean for an understudied region of the globe, as no equivalent assessment has been conducted in Caribbean or Central American rivers.

Materials and methods

Study areas

The two study areas were located in Puerto Rico and consisted of the rivers, estuaries, and adjacent coastal waters of the Rio Loco and Rio Fajardo (Fig. 1a, b; Supplementary Table S1). The Rio Loco study area is located in the Lajas Valley in southwestern Puerto Rico (Fig. 1c), has a dry Mediterranean climate, and is dominated by actively farmed cropland and pastures (Supplementary Table S1). The valley is primarily drained by two man-made irrigation and drainage canals, which join to form the third-order Rio Loco a few kilometers north of the Bahia de Guanica. In 1952, a 1.3×10^6 m^3 reservoir (Presado Loco) and free-crest spillway dam were constructed $\sim$8 km upstream (Holmquist et al. 1998). The catchment size of the Rio Loco and its associated canals is $\sim$175 km^2 in total area. At its headwaters (elevation = 786 m), the Rio Loco drains igneous and metamorphic (serpentinite) rocks, while in the lowlands the bedrock is comprised of limestone and consolidated alluvium (Monroe 1980). The Rio Loco study area is located in the orographic rainshadow of the Cordillera Central, and receives an average of 860 mm $year^{-1}$ in rainfall (Lugo et al. 1978). Rainfall is generally greatest during the months of May through December, and significantly lower during the remainder of the year. Present land cover within the Rio Loco catchment consists of $\sim$60 % active cropland and pasture (largely vegetated by C_4 plants such as grasses, corn, and sugarcane), 33 % wooded wetland (C_3 plants, including mangroves), 5 % coniferous forests (C_3 plants), 2 % grassland (C_4 plants), and 0.2 % unclassified lands (United States Geological Survey 2001). The Rio Loco estuary is relatively large, semi-enclosed basin (Bahia de Guanica; Fig. 1c). A small mangrove forest grows at the mouth of the Rio Loco and in the northwest portion of the estuary (Bahia Noroeste; Fig. 1c). The remainder of the Rio Loco estuary coastline is bordered by rocky shorelines, and the mouth of the Bahia de Gauanica is incised between two limestone cliffs. Much of the seafloor in the Rio Loco estuary is vegetated by sparse to medium-density seagrass meadows.

The Rio Fajardo study area is located in northeast Puerto Rico, has a wet tropical climate, and is characterized by abandoned, reforested pastures (non-agricultural; Lugo and Helmer 2004) along the coastal plain and tropical moist broadleaf forests in the upland portions of the catchment (Fig. 1d; Supplementary Table S1). The third-order Rio Fajardo originates in the Luquillo Mountains and flows eastward, draining into Vieques Sound. The river is fed by numerous first-order mountain streams which drain the steep slopes of the eastern El Yunque National Forest, a tropical rain forest (Pike et al. 2010). The Rio Fajardo study area has a small catchment ($\sim$70 km^2), with the headwaters (elevation = 1,075 m) draining steep bedrock valleys composed of quartz-diorite and basaltic igneous rocks, while the downstream portion of the river drains recent alluvium to the head of the coastal plain where stream flow is tidally influenced (Clark and Wilcock 2000; Pike et al. 2010). Annual rainfall within the Rio Fajardo study area is spatially variable, with the mountainous headwaters receiving up to 4,500 mm $year^{-1}$, while the coastal plain receives about 1,500 mm $year^{-1}$ (Clark and Wilcock 2000). Peak rainfall generally occurs during the months of May, October, and November. Partial reforestation has occurred within the study area due to agricultural abandonment, and present land cover consists of $\sim$46 % partly developed or abandoned lands (now largely reforested by C_3 plants; Lugo and Helmer 2004; Moyer personal observation), 30 % active cropland and pasture (mixed C_3 and C_4 plants), 8 % coniferous forest (C_3 plants), 7 % lowland forest (C_3 plants), 4.0 % developed land, and 4 % grassland (C_4 plants) (United States Geological Survey 2001). For the purposes of this study, the Fajardo study area was considered to be non-agricultural compared to the Rio Loco study area. In contrast to the Rio Loco study area, the estuary of the Rio Fajardo consists of a relatively small area at the mouth of the river (Fig. 1d). Extensive mangrove forests line both sides of the banks of the Rio Fajardo from the mouth to 200 m upriver. Mangrove forest continues $\sim$600 m along the South bank of the

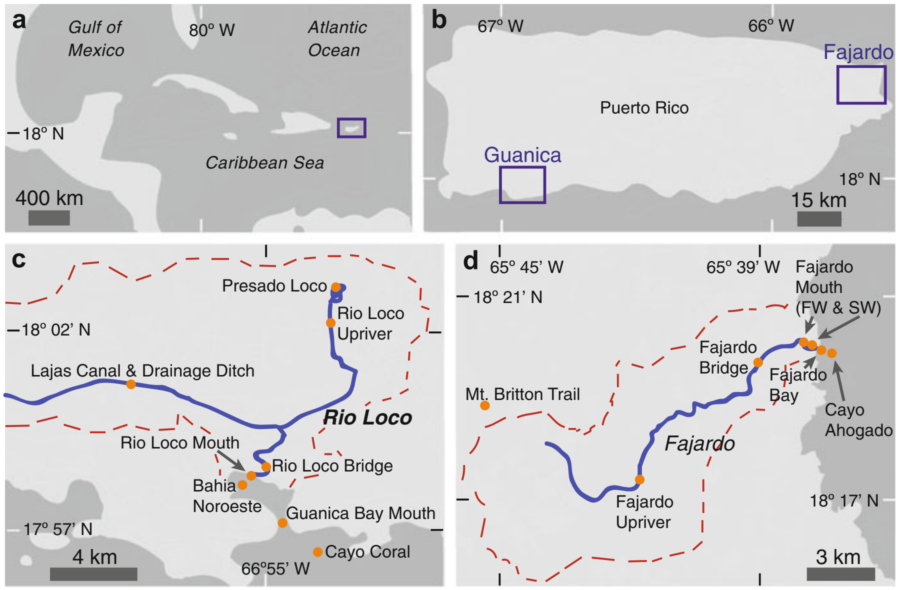

Fig. 1 Location of this study. **a** Map of Caribbean Sea and western Atlantic Ocean, showing location of Puerto Rico (indicated by *blue box*). **b** Location of the Rio Loco (Guanica region) and Rio Fajardo study areas within Puerto Rico (indicated by *blue boxes*). **c** Rio Loco and primary drainage channels shown with *blue lines*. Total catchment area (*red dashed line*) is 175 km^2. **d** Rio Fajardo shown with *blue line*. Total catchment area (*red dashed line*) is 70 km^2. Orange circles indicate sampling sites in each study area. (Color figure online)

Rio Fajardo, while the town of Fajardo boarders the North bank. The seafloor at the mouth of the Rio Fajardo is largely comprised of unstable sands, however the seafloor immediately offshore of the river mouth consists of a patchy framework of bare muds and sparse to high-density seagrass meadows.

Field sampling

River, estuary, and seawater samples were collected in September/October 2004, March 2005, October 2007, and March 2008 along transects extending from inland to the coastal ocean in each study area (Fig. 1; Supplementary Table S2). Sampling months represented relatively wet (September/October) and dry periods (March) in the hydrologic cycle of Puerto Rico, and all samples were collected under base-flow conditions (Fig. 2) (United States Geological Survey 2008). In 2004 and 2005, water samples were collected at four sites along each transect, including: (1) up-river (inland), (2) at the river mouth, (3) a site located intermediate to the river mouth and a nearby coral reef, and (4) directly overlying the coral reef. In 2007 and 2008 an additional sampling site was added in low-salinity coastal waters adjacent to the river mouth at each study area. In March 2008, representative headwater streams were also sampled. While headwaters within the Rio Loco study area were easily accessible and sampled, the headwaters of the Rio Fajardo were not easily accessible. Therefore a representative headwater stream from a neighboring north-draining catchment with similar lithology was sampled instead (Mt. Britton Trail; Fig. 1d). Shallow water samples were collected from ∼0.3 m below the surface in rivers, and ∼1.0 m below the surface at marine and estuarine sites using a portable peristaltic pump and filtered through pre-combusted Whatman QMA filters (0.8 µm nominal pore size). Duplicate DOC and DIC samples were collected at the inland and coral reef sites, while duplicate POC samples were collected at all sampling sites during each sampling year. Filtered DOC samples were collected in pre-cleaned (10 % HCl for 24 h) 0.50-L polycarbonate bottles, stored on ice in the dark while in the field and frozen at −20 °C upon return to the lab the same day. Filtered DIC samples were collected in pre-baked (550 °C for 4 h) 0.25-L borosilicate gas-tight serum bottles, poisoned with 200 µL anhydrous mercuric chloride, and stored in the dark. The amount of water filtered for POC samples varied depending on the suspended load and ranged from 0.30 to 3.25 L for river and estuarine waters and from 1.25 to 10.00 L for seawater samples. In all cases, samples were filtered until the flow decreased significantly, indicating filters were clogged. Detailed collection and storage methods for each sample type (DOC, POC, and DIC) can be found in Raymond and Bauer (2001b). Salinity at each sampling location was measured using a hand-held conductivity meter (YSI Inc.), and independently verified using a hand-held refractometer.

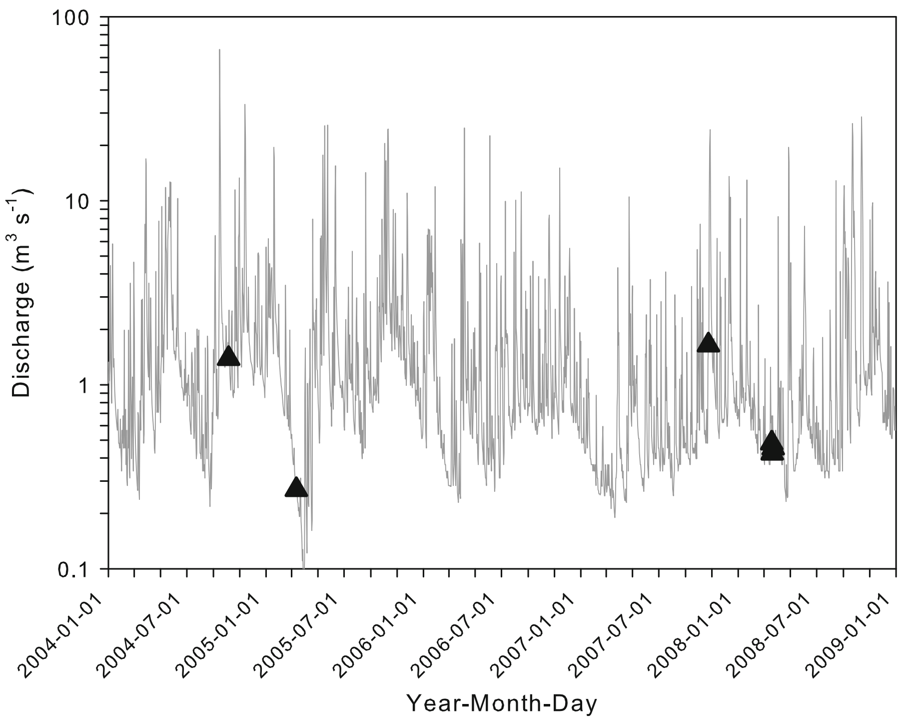

Fig. 2 Daily discharge of the Rio Fajardo during the study period. *Black triangles* represent daily discharge values for the sampling days of riverine sites in the Rio Fajardo study area. Discharge data available from USGS station 50071000 (United States Geological Survey 2008). Discharge data were not available for the Rio Loco, as no gauging station is currently maintained there

Sample processing and isotopic measurements

DOC samples collected in 2007 and 2008 were prepared for isotopic analysis using the methods described by Raymond and Bauer (2001b) and Bauer (2002). Briefly, 100 mL of sample was placed in a quartz reaction vessel, acidified to a pH of ~2 using 85 % phosphoric acid, and purged with 200 mL min^{-1} UHP He gas to remove DIC. Samples were then saturated with UHP O_2 and irradiated for 2 h using a 1,200 W medium-pressure ultraviolet lamp (Hanovia Corp.). This procedure was found to oxidize 100 % of the sample DOC. The CO_2 produced from DOC oxidation was then purged from the reaction vessel using UPH He and passed through a KIO_3 trap to remove any Cl_2 and Br_2 produced from the oxidation of seawater salts. The CO_2 was then purified cryogenically on a vacuum extraction line and split into two ampoules, one for $\delta^{13}C$ analysis and one for $\Delta^{14}C$ analysis. DOC concentrations for all samples were acidified and sparged, then measured as non-purgeable organic carbon using a Shimadzu TOC-5000A Pt-catalyzed high-temperature analyzer. A four-point calibration curve with glucose as a standard was used and blanks were run after every ten samples. The standard deviation (SD) of all replicate analyses ($n = 18$) was 8.1 µM.

Filters containing POC samples were air dried and then acid-fumed using concentrated HCl in order to remove any inorganic carbon in the samples (Lorrain et al. 2003). POC was measured using a Costech Analytical Elemental Analyzer. One of the duplicate filters was prepared for $\Delta^{14}C$ analysis by sealed quartz tube combustion (850 °C for 4 h) using CuO and Ag (Sofer 1980). All quartzware and reagents were precleaned by baking at 850 °C for 4 h prior to use. The resulting sample CO_2 gas was collected and purified on a vacuum extraction line and sealed in a pre-baked 6 mm Pyrex tube. The second filter from each duplicate set was used for $\delta^{13}C$ analysis (see below).

DIC samples were prepared for isotopic analyses using methods based on those of Raymond and Bauer (2001a, b). Briefly, each sample was acidified with 85 % ortho-phosphoric acid, purged with ultra-high purity (UHP) He gas at a rate of 200 mL min^{-1}, and the resulting CO_2 was then cryogenically collected and purified on a vacuum extraction line. The CO_2 gas was then split into two ampoules, one for $\delta^{13}C$ (the per-mil deviation of ^{13}C:^{12}C relative to the Vienna Pee Dee

Belemnite (VPDB) limestone standard) and one for $\Delta^{14}C$ (the per mil deviation of ^{14}C:^{12}C relative to the 95 % Oxalic Acid-I standard) analyses. Sample DIC concentrations were obtained from the amount of CO_2 collected using the pressure–volume relationship of a volume-calibrated section of the vacuum line. The SD of duplicate DIC sample measurements ($n = 8$) was <1.0 %.

The $\delta^{13}C$ of all DOC and DIC samples collected in 2007 and 2008 were measured using a Finnigan Delta Plus IV stable isotope ratio mass spectrometer (IRMS). Repeated measurements of an internal standard ($n_{DOC} = 12$, $n_{DIC} = 13$) had a SD of ±0.10 ‰ for $\delta^{13}C$-DOC, and ≤±0.02 ‰ for $\delta^{13}C$-DIC. For samples collected in 2004 and 2005, $\delta^{13}C$-DOC was measured using methods developed by Osburn and St-Jean (2007) in which a continuous-flow wet-chemical DOC oxidation (WCO) system was interfaced directly to a Finnigan Delta Plus XP high-amplification IRMS. The SD of repeated measurements of an internal standard using this method was ±0.30 ‰. Osburn and St-Jean (2007) found measured $\delta^{13}C$-DOC values of natural water samples to be consistent using both of the above methods. Samples for $\delta^{13}C$-POC analysis were combusted in a Costech Analytical Elemental Analyzer and the resulting CO_2 gas was transferred to a Finnigan Delta Plus IV IRMS. Repeated measurements of internal POC standards ($n = 85$) had a SD of ±0.14 ‰. At least 10 % of all $\delta^{13}C$ measurements were made in duplicate, and the SD of these measurements was ±0.19 ‰, ±0.06 ‰, and ±0.04 ‰ for $\delta^{13}C$-DOC, $\delta^{13}C$-POC, and $\delta^{13}C$-DIC, respectively.

DOC, POC, and DIC samples collected in 2007 and 2008 were submitted to the National Science Foundation-Arizona Accelerator Mass Spectrometry (AMS) Facility at the University of Arizona for analysis of $\Delta^{14}C$-DOC, $\Delta^{14}C$-POC, and $\Delta^{14}C$-DIC. DIC samples collected in 2004 and 2005 were submitted to the National Ocean Sciences AMS facility at Woods Hole Oceanographic Institution for $\Delta^{14}C$-DIC analysis. For all samples, CO_2 gas was reduced to graphite using H_2 gas and Fe as a catalyst and the ratio of $^{14}C/^{12}C$ was measured via AMS, blank-subtracted for background correction, and further corrected for fractionation using $\delta^{13}C$ values measured by IRMS standardized to modern wood. The SD of all $\Delta^{14}C$ measurements ($n = 96$) was <±7.0 ‰. All radiocarbon values were reported by the AMS laboratories as fraction modern and converted to $\Delta^{14}C$ and ^{14}C age according to the conventions of Stuiver and Polach (1977).

Data analysis

A fully factorial model III analysis of variance (ANOVA) was used to test for significant differences between end members in each study area (i.e., Rio Loco vs. Rio Fajardo), month (i.e., September/October vs. March), and salinity (S) (i.e., riverine vs. marine), as well as the interaction between each of those factors for DOC, POC, and DIC concentrations, and $\delta^{13}C$ and $\Delta^{14}C$ values. Only data from low-S river (S < 2) and marine end-member (S ≥ 34) sites were included in these analyses. A posteriori slice tests (e.g., tests of simple effects;

Winer et al. 1991) were used to explore significant interaction effects. Differences were considered statistically significant at $p \leq 0.05$. All statistical analyses were conducted using SAS version 9.1.3 of the SAS System for Windows (© 2000–2004 SAS Institute Inc. SAS and all other SAS Institute Inc. product or service names are registered trademarks or trademarks of SAS Institute Inc., Cary, North Carolina, USA).

Predicted conservative estuarine distributions of DOC and DIC concentrations were generated by fitting a linear distribution between the freshwater and marine end-member concentrations for each catchment. The predicted conservative estuarine distributions of $\delta^{13}C$-DOC, $\Delta^{14}C$-DOC, $\delta^{13}C$-DIC, and $\Delta^{14}C$-DIC were calculated using a simple two end-member mixing equation (Spiker 1980; Raymond and Bauer 2001b). A more complete description of these calculations is given in Supplementary Text S1. A constituent was considered to be non-conservative when its measured value deviated from the predicted conservative distribution by more than two SDs of the mean of all pooled measurements for that constituent. Simple three end-member mass balance equations were used to determine the proportionate contribution of C from each end-member to the riverine, estuarine, and marine DOC, POC, and DIC pools. A detailed description of this isotope mixing mass balance technique is provided in Supplementary Text S1.

Results

Dissolved and particulate organic carbon

DOC distributions were highly variable between site, season, and year for river versus marine end-members

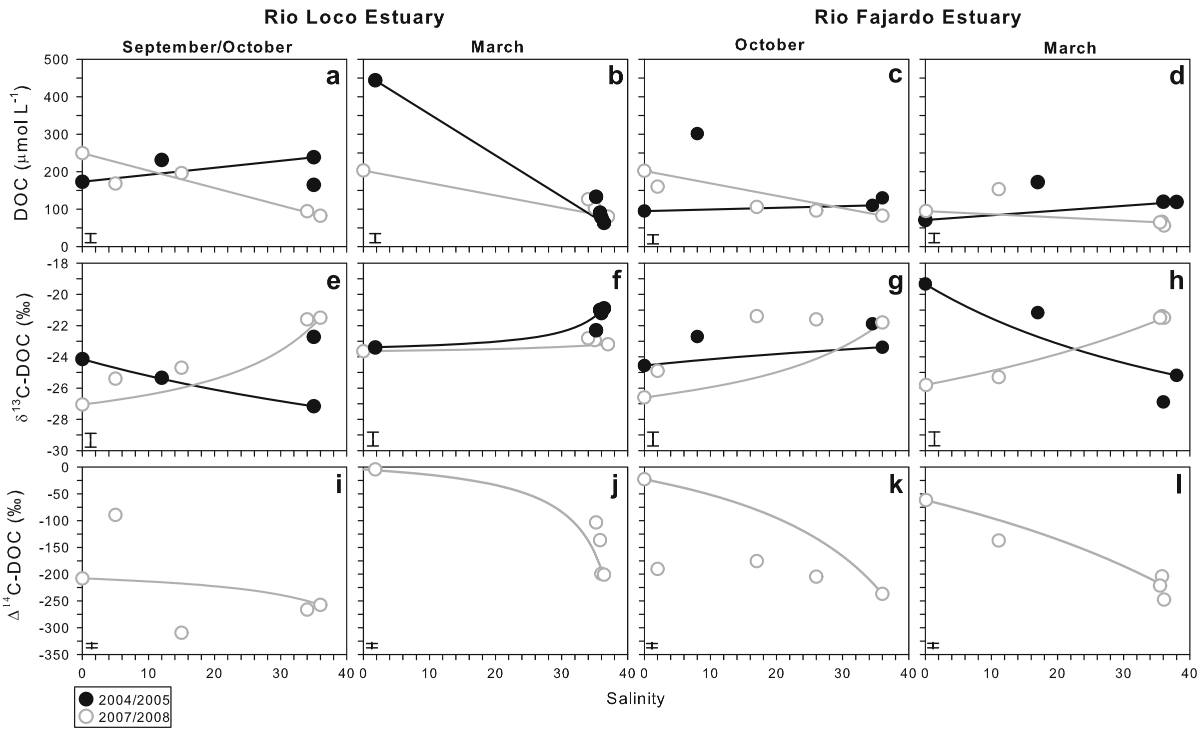

Fig. 3 DOC concentrations (**a**–**d**), δ^{13}C values (**e**–**h**), and Δ^{14}C (**i**–**l**) values versus salinity for the Rio Loco and Rio Fajardo estuaries. Data were sampled 2004/2005 (*black circles*) and 2007/2008 (*open grey circles*) during the months of September/October (**a**, **c**, **e**, **g**, **i**, and **k**) and March (**b**, **d**, **f**, **h**, **j**, and **l**) in both study areas. *Solid lines* show the calculated theoretical conservative mixing relationships of DOC, δ^{13}C, or Δ^{14}C between the riverine and seawater end-members for the 2004/2005 (*grey line*) and 2007/2008 (*black line*) sampling years. *Error bar* at bottom left of each panel represents two standard deviations of the mean of all replicate sample analyses within each panel

of both study areas (Fig 3a–d; Table 1). Riverine DOC concentrations in the Rio Loco ranged from 113 to 444 μmol L^{-1} and were significantly lower during September/October than during March (Fig. 3a, b; Table 1 and Supplementary Table S3). However during both March samplings, Rio Loco DOC concentrations were significantly higher than in the corresponding marine end-member samples (Fig. 3b; Supplementary Table S3). It is noteworthy that riverine DOC concentrations were lower than those of the marine end-member during September/October 2004 in the Rio Loco study area (Fig. 3a). Riverine DOC in the Rio Fajardo study area ranged from 57 to 301 μmol L^{-1} and was lower than marine end-member DOC in September/October 2004 and March 2005 (Fig. 3c, d, respectively; Table 1). Riverine DOC in the Rio Loco was significantly higher than in the Rio Fajardo study area during both March samplings (Fig. 3b, d).

DOC mixed non-conservatively in the Rio Loco estuary during both September/October samplings, with the estuary acting as a source of DOC in 2004, and acting as a sink in 2007 (Fig. 3a). A spatially compressed S gradient was present during both March samplings in the Rio Loco estuary, and all estuarine sites were dominated by either end-member (i.e., riverine or seawater) salinities. For this reason, it was not possible to collect mesohaline samples during March in this estuary, and mixing relationships of dry season DOC (Fig. 3b) or its isotopes (Fig. 3f, j—see below) within the Rio Loco estuary could not be unequivocally established. In the Rio Fajardo estuary, DOC mixed non-conservatively during September/October 2004 and both March samplings due to an estuarine source of DOC (Fig. 3c, d), but mixed conservatively during October 2007 (Fig. 3c).

No significant differences were found between September/October and March δ^{13}C-DOC or Δ^{14}C-DOC

Table 1 Concentrations and isotopic signatures ($\delta^{13}C$ and $\Delta^{14}C$) for dissolved organic carbon (DOC), particulate organic carbon (POC), and dissolved inorganic carbon (DIC), for all sites in the Rios Loco and Fajardo study areas. Sampling sites in each study area are listed in order from the uppermost (inland) site seaward to the coastal ocean

Site	Years	Salinity	Q[a] ($m^3\ s^{-1}$)	DOC (μM)	$\delta^{13}C$-DOC (‰)	$\Delta^{14}C$-DOC[b] (‰)	DOC ^{14}C age (years BP)	POC (μM)	$\delta^{13}C$-POC (‰)	$\Delta^{14}C$-POC[b] (‰)	POC ^{14}C age (years BP)	DIC (μmol kg^{-1})	$\delta^{13}C$-DIC (‰)	$\Delta^{14}C$-DIC[b] (‰)	DIC ^{14}C age (years BP)
Rio Loco Study Area—September/October															
Rio Loco Bridge	2004	0.0	–	173	−24.1	−6	9 ± 58	172	−24.7	–	–	1,955	−10.4	6	Modern
	2007	0.0	–	249	−27.1	−208	1,884 ± 56	3,328	−26.4	−92	718 ± 44	652	−11.8	21	Modern
Rio Loco Mouth	2007	5.0	–	168	−25.4	−90	754 ± 71	897	−20.0	−98	771 ± 44	1,375	−3.8	55	Modern
Bahia Noroeste	2004	12.0	–	231	−25.4	–	–	77	−23.3	–	–	2,176	−3.6	46	Modern
	2007	15.0	–	196	−24.7	−310	2,976 ± 53	2,448	−14.8	45	Modern	2,074	−1.1	66	Modern
Guanica Bay Mouth	2004	35.0	–	165	−22.7	–	–	64	−20.8	–	–	1,983	0.3	56	Modern
	2007	34.0	–	94	−21.6	−266	2,490 ± 56	126	−18.9	22	Modern	952	0.7	68	Modern
Cayo Coral	2004	35.0	–	238	−27.2	–	–	12	−19.4	–	–	1,980	0.9	53	Modern
	2007	36.0	–	82	−21.5	−258	2,393 ± 50	42	−17.7	−195	1,686 ± 258	1,297	1.2	60	Modern
Rio Loco Study Area—March															
Presado Loco	2008	0.1	–	113	−32.0	33	Modern	364	−37.9	–	–	2,535	−11.2	17	Modern
Rio Loco Upriver	2008	0.1	–	129	−29.2	28	Modern	–	−29.1	–	–	2,601	−12.6	16	Modern
Lajas Canal	2008	0.4	–	337	−26.9	16	Modern	711	−25.7	−13	52 ± 48	2,946	−9.8	31	Modern
Lajas Drainage Ditch	2008	0.0	–	712	−25.3	−258	2,340 ± 38	–	−28.7	−68	510 ± 51	3,882	−10.6	9	Modern
Rio Loco Bridge	2005	0.0	–	203	−23.6	−196	1,696 ± 76	868	−27.2	–	–	5,072	−10.7	45	Modern
	2008	1.8	–	444	−23.4	−4	7 ± 56	169	−32.4	−13	51 ± 40	3,646	−11.3	23	Modern
Rio Loco Mouth	2008	35.2	–	133	−22.3	−103	824 ± 62	1,514	−21.6	−36	240 ± 50	2,336	−1.8	62	Modern
Bahia Noroeste	2005	35.0	–	102	−22.9	−140	1,155 ± 78	2155	−16.7	–	–	2,221	−0.2	63	Modern
	2008	36.1	–	90	−21.0	−137	1,123 ± 77	901	−18.3	23	Modern	2,062	0.0	64	Modern
Guanica Bay Mouth	2005	34.0	–	126	−22.8	–	–	315	−17.4	–	–	1,819	0.2	67	Modern
	2008	36.0	–	78	−21.2	−199	1,733 ± 84	245	−21.9	2	Modern	1,841	0.0	67	Modern
Cayo Coral	2005	37.0	–	80	−23.2	–	–	20	−20.3	–	–	2,119	1.2	79	Modern
	2008	36.3	–	63	−20.9	−201	1,750 ± 70	10	−19.6	27	Modern	1,110	0.0	71	Modern
Rio Fajardo Study Area—October															
Rio Fajardo Bridge	2004	0.0	1.33	95	−24.6	–	–	19	−24.7	–	–	641	−8.8	59	Modern
	2007	0.0	1.59	202	−26.6	−23	185 ± 66	289	−25.2	−36	240 ± 50	390	−9.8	50	Modern
Rio Fajardo Mouth	2004	8.0	1.33	301	−22.7	–	–	813	−18.2	–	–	1,425	−3.3	59	Modern
FW	2007	2.0	1.59	160	−24.9	−190	1,707 ± 55	976	−22.2	−31	199 ± 41	1,263	−8.2	46	Modern
Rio Fajardo Mouth SW	2007	17.0	–	106	−21.4	−176	1,553 ± 56	3,157	−20.6	−13	51 ± 40	1,504	0.0	68	Modern
Fajardo Bay	2004	36.0	–	130	−23.4	–	–	114	−20.0	–	–	2,014	0.7	71	Modern
	2007	26.0	–	96	−21.6	−205	1,841 ± 58	1007	−18.9	29	Modern	1,878	0.9	71	Modern
Cayo Ahogado	2004	34.5	–	110	−21.9	–	–	60	−19.7	–	–	2,040	0.7	78	Modern

Table 1 continued

Site	Years	Salinity	Q[a] (m^3 s^{-1})	DOC (μM)	δ^{13}C-DOC (‰)	Δ^{14}C-DOC[b] (‰)	DOC ^{14}C age (years BP)	POC (μM)	δ^{13}C-POC (‰)	Δ^{14}C-POC[b] (‰)	POC ^{14}C age (years BP)	DIC (μmol kg^{-1})	δ^{13}C-DIC (‰)	Δ^{14}C-DIC[b] (‰)	DIC ^{14}C age (years BP)
	2007	36.0	–	82	−21.8	−237	2,176 ± 54	107	−20.8	−69	517 ± 60	1,779	0.9	74	Modern
Rio Fajardo Study Area—March															
Mt. Britton Trail	2008	0.0	0.59	67	−25.8	43	Modern	254	−28.5	21	Modern	238	−12.2	81	Modern
Rio Fajardo Upriver	2008	0.0	0.59	57	−29.3	13	Modern	–	−26.4	17	Modern	620	−10.4	75	Modern
Rio Fajardo Bridge	2005	0.0	0.27	71	−19.3	−40	272 ± 65	225	−26.8	–	–	692	−8.2	27	Modern
	2008	0.1	0.59	95	−25.8	−62	457 ± 71	70	−26.8	–	–	494	−9.0	27	Modern
Rio Fajardo Mouth	2005	17.0		172	−21.2	−20	108 ± 51	1,316	−20.4	–	–	1,644	−6.3	21	Modern
FW	2008	11.1	0.59	153	−25.3	−138	1,133 ± 55	623	−21.8	−10	27 ± 48	995	−6.2	40	Modern
Rio Fajardo Mouth SW	2008	35.8	–	66	−21.4	−204	1,780 ± 70	812	−22.1	−20	108 ± 49	2,004	0.6	63	Modern
Fajardo Bay	2005	36.0	–	120	−26.9	–	–	202	−21.1	–	–	2,101	0.9	65	Modern
	2008	36.1	–	56	−21.5	−248	2,231 ± 76	165	−22.9	−21	116 ± 57	1,938	0.9	72	Modern
Cayo Ahogado	2005	38.0	–	119	−25.2	–	–	95	−19.8	–	–	2,117	0.9	71	Modern
	2008	36.0	–	65	−21.5	−222	1,958 ± 71	89	−20.7	−5	7 ± 48	1,342	0.9	68	Modern

[a] Rio Fajardo discharge values taken from USGS Station 50071000 (United States Geological Survey 2008)

[b] Errors ($\pm 1\sigma$) associated with radiocarbon ages are based on measurement errors of Δ^{14}C values, which averaged ±7.0 ‰ for all measurements

for riverine or marine end-members among or between either study area (Supplementary Table S3). However, several noteworthy patterns were observed in the δ^{13}C-DOC and Δ^{14}C-DOC signatures (Fig. 3e–l). In the Rio Loco study area, δ^{13}C-DOC ranged from −27.2 to −22.7 ‰ and generally decreased from the river to the coastal ocean while mixing conservatively within the estuary during September 2004. However, in October 2007, δ^{13}C-DOC ranged from −27.1 to −21.5 ‰ and generally increased while mixing non-conservatively (Fig. 3e). In the Rio Fajardo estuary, δ^{13}C-DOC ranged from −26.6 to −21.4 ‰ and mixed non-conservatively due to an estuarine source of enriched δ^{13}C-DOC during both September/October sampling periods (Fig. 3e, g). During March 2005, δ^{13}C-DOC ranged from −26.9 to −19.3 ‰ in the Rio Fajardo estuary, and generally decreased from the river to the coastal ocean while mixing non-conservatively due to an estuarine source of enriched δ^{13}C-DOC (Fig. 3h). Conversely, in March 2008, the opposite isotopic distribution and mixing patterns were observed for δ^{13}C-DOC in the Rio Fajardo estuary (Fig. 3h).

Riverine Δ^{14}C-DOC measurements in the Rio Loco study area were characterized by high variability both spatially and temporally, and yielded values with corresponding ^{14}C ages of modern to 2,340 years before present (Table 1). However, in both study areas, Δ^{14}C-DOC generally decreased from river to the coastal ocean during both sampling months (September/October and March; Fig. 3i–l). In the Rio Loco estuary Δ^{14}C-DOC mixed non-conservatively, and a source of Δ^{14}C-enriched DOC was present in low-S ($S < 10$) waters during September/October, while Δ^{14}C-depleted DOC was present in mid-S ($10 < S < 20$) waters during the same months in both 2004 and 2007 (Fig. 3i). In the Rio Fajardo estuary, Δ^{14}C-DOC ranged from −237 to −23 ‰ mixed non-conservatively during September/October, when a strong source of Δ^{14}C-depleted DOC was present in the estuary (Fig. 3k). However, during March 2005 and 2008, Δ^{14}C-DOC ranged from −222 to −40 ‰ and mixed conservatively in the Rio Fajardo estuary (Fig. 3l).

Concentrations of POC in the Rio Loco study area ranged from 10 to 3,328 μmol L^{-1} and were highly variable among and between both riverine and coastal marine end-member sites (Fig. 4a, b; Table 1). However, POC concentrations in the Rio Fajardo study area ranged from 19 to 3,157 μmol L^{-1} and were generally low in both river and marine end-member sites, and were highest within the estuary (Fig. 4c, d; Table 1). No significant differences in POC concentrations were found between study areas, months, or S (Supplementary Table S3). Average δ^{13}C-POC values were significantly lower in the rivers (−27.6 ‰) than at marine end-member sites (−19.8 ‰) in both study areas, and were significantly higher during September/October (avg. = −20.9 ‰) versus March (avg. = −23.9 ‰; Fig. 4e–h; Tables 1 and Supplementary Table S3). Δ^{14}C-POC signatures ranged from −195 to 45 ‰ and were also highly variable between the rivers and their respective marine end-member sites in both study areas (Fig. 4i–l; Table 1). No significant differences were found between Δ^{14}C-POC values with respect to catchment, season, or S (Supplementary Table S3).

Dissolved inorganic carbon

In the Rio Loco study area, all September/October riverine DIC concentrations (avg. = 1,304 μmol kg^{-1}) were significantly lower than March values (avg. = 4,359 μmol kg^{-1}; Fig. 5a, b; Table 1 and Supplementary Table S3). Similarly, all September/October season marine end-member DIC concentrations (avg. = 1,549 μmol kg^{-1}) were also significantly lower than March values (avg. = 1,722 μmol kg^{-1}) in the Rio Loco study area (Fig. 5a, b; Table 1 and Supplementary Table S3). In the Rio Fajardo study area, DIC concentrations were significantly lower in the river (avg. = 554 μmol kg^{-1}) than at marine end-member sites (avg. = 1,901 μmol kg^{-1}) during both September/October and March (Fig. 5c, d; Supplementary Table S3). March riverine DIC concentrations in the Rio Loco study area (avg. = 602 μmol kg^{-1}) were also significantly higher than those in the Rio Fajardo study area (avg. = 3,773 μmol kg^{-1}) during the same month (Fig. 5b, d; Supplementary Table S3). In both study areas, DIC mixed conservatively within the estuary during September 2004, but non-conservatively during October 2007 when an estuarine source of DIC was present (Fig. 5a, c). Similar to March DOC values ("Dissolved and particulate organic carbon"), DIC concentration (Fig. 5b) and isotopic (Fig. 5f, j—see below) mixing relationships in the Rio Loco estuary could not be determined due to the lack of mesohaline samples caused by the spatially compressed S gradient during that month. In the Rio Fajardo estuary, DIC

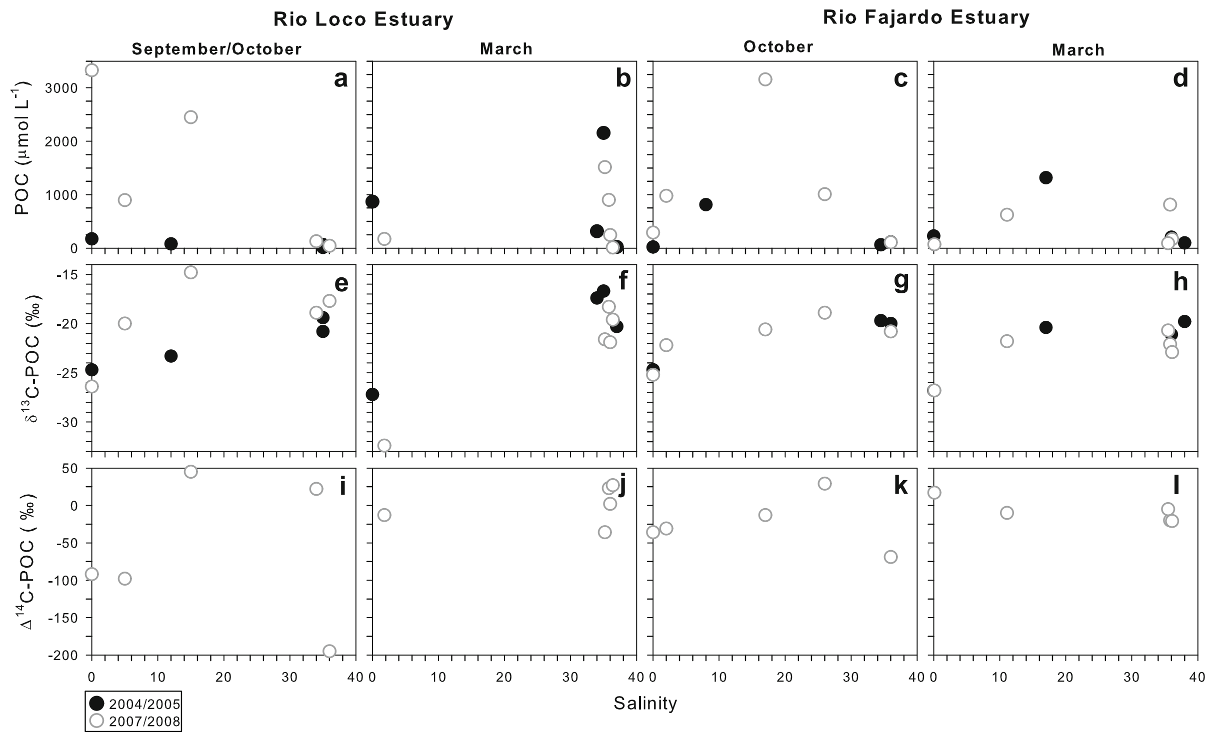

Fig. 4 POC concentrations (**a–d**), δ^{13}C values (**e–h**), and Δ^{14}C (**i–l**) values versus salinity for the Rio Loco and Rio Fajardo estuaries. Data were sampled 2004/2005 (*black circles*) and 2007/2008 (*open grey circles*) during the months of September/October (**a**, **c**, **e**, **g**, **i**, and **k**) and March (**b**, **d**, **f**, **h**, **j**, and **l**) in both study areas. Unlike dissolved solutes such as DOC and DIC, POC represents a heterogeneous solid phase, and therefore plotting theoretical mixing distributions against the raw data is not appropriate

mixed conservatively during both March samplings (Fig. 5d).

Average riverine δ^{13}C-DIC and Δ^{14}C-DIC values (−10.0 ‰ and 31 ‰, respectively) were significantly lower than at their corresponding marine end-member sites (0.7 and 68 ‰, respectively) during all months in both study areas (Fig. 5e–l; Table 1 and Supplementary Table S3). Average Rio Loco Δ^{14}C-DIC (14 ‰) was also significantly lower than Rio Fajardo Δ^{14}C-DIC (55 ‰) during September/October (Fig. 5i, k; Supplementary Table S3). In the Rio Fajardo study area, average riverine Δ^{14}C-DIC values (55 ‰) were significantly higher during September/October (55 ‰; Fig. 5k) than during March (27 ‰; Fig. 5l). Both δ^{13}C-DIC and Δ^{14}C-DIC mixed non-conservatively in the Rio Loco estuary during September/October (Fig. 5e, i). In the Rio Fajardo estuary, δ^{13}C-DIC and Δ^{14}C mixed conservatively during September/October (Fig. 5g, k). During March, δ^{13}C-DIC mixed non-conservatively in the Rio Fajardo estuary due to an apparent source of δ^{13}C-depleted DIC (Fig. 5h). Similarly, Δ^{14}C-DIC mixed non-conservatively in March 2005 in the Rio Fajardo estuary due to an apparent estuarine source of Δ^{14}C-depleted DIC. However, Δ^{14}C-DIC mixed conservatively during March 2008 in the Rio Fajardo estuary (Fig. 5l).

Discussion

Variability in the concentrations and isotopic signatures of C and OM in catchments and rivers is driven by numerous interactions between biological, chemical, geological, and hydrological processes. In the two tropical SMRs studied here, significant spatial and temporal differences were observed in the abundance and isotopic character of the three major C pools in river and coastal waters, as well as within their dynamic estuarine mixing zones (Figs. 3–5; Table 1 and Supplementary Table S3). Elucidating the processes that control the quantities, characteristics and fates of inorganic and organic C in the continuum from

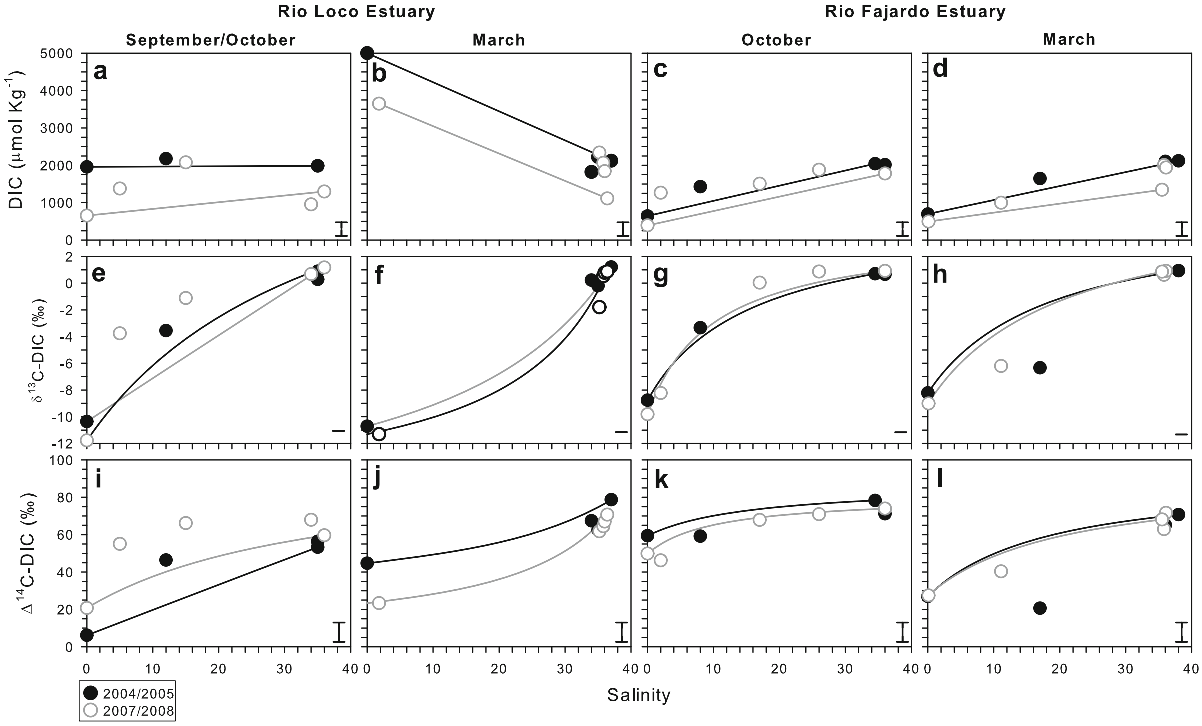

Fig. 5 DIC concentrations (**a–d**), δ^{13}C values (**e–h**), and Δ^{14}C (**i–l**) values versus salinity for the Rio Loco and Rio Fajardo estuaries. Data were sampled 2004/2005 (*black circles*) and 2007/2008 (*open grey circles*) during the months of September/October (**a**, **c**, **e**, **g**, **i**, and **k**) and March (**b**, **d**, **f**, **h**, **j**, and **l**) in both study areas. *Solid lines* show the calculated theoretical conservative mixing relationships of DIC, δ^{13}C, or Δ^{14}C between the riverine and seawater end-members for the 2004/2005 (*grey line*) and 2007/2008 (*black line*) sampling years. *Error bar* at bottom right of each panel represents two standard deviations of the mean of all replicate sample analyses within each panel

catchment to coastal ocean is therefore a key consideration for evaluating: (1) similarities and differences between tropical SMRs and other types of rivers and estuaries and (2) the role of tropical SMRs in both regional and global land-to-ocean C budgets and cycling. While it is unlikely that the sampling regime of this study captured the full range of natural variability in C abundance and isotopic character (i.e., McDowell and Asbury 1994; Goldsmith et al. 2008; Townsend-Small et al. 2008; Wheatcroft et al. 2010), the data set presented here is one of the most comprehensive for tropical SMRs to date, in terms of characterizing the three major C pools (DOC, POC, and DIC). The large range in variability observed in this study demonstrates that single samples from single years may not effectively capture the full range of natural variability of tropical SMRs (Table 1). This is especially true given the highly variable nature of discharge common to most tropical SMRs (Fig. 2), and the fact that the data presented here are only representative of base-flow conditions within the two SMR systems. Therefore, higher frequency sampling (~weekly to monthly) in consecutive years over a range of hydrologic conditions is necessary in tropical SMRs, in order to best constrain the range of natural variability in the abundance, isotopic character, and flux of terrestrial carbon to the coastal ocean in these systems. Despite these limitations, the data represents a strong baseline for evaluating the inventory and biogeochemistry of C in tropical SMR catchments within the Caribbean and Central American region.

Potential sources of OM to tropical SMRs

The main sources of OM (i.e., DOC and POC) to rivers include degraded plant biomass (Onstad et al. 2000; Benner and Opsahl 2001), surface soil OM (Hope et al. 1994; Raymond and Bauer 2001b, 2001c; Aitkenhead-Peterson et al. 2003, 2005), autochthonous production by phytoplankton and submerged and aquatic vegetation (Thorp and Delong 2002; Raymond et al. 2004), and, when present in the catchment, sediments eroded

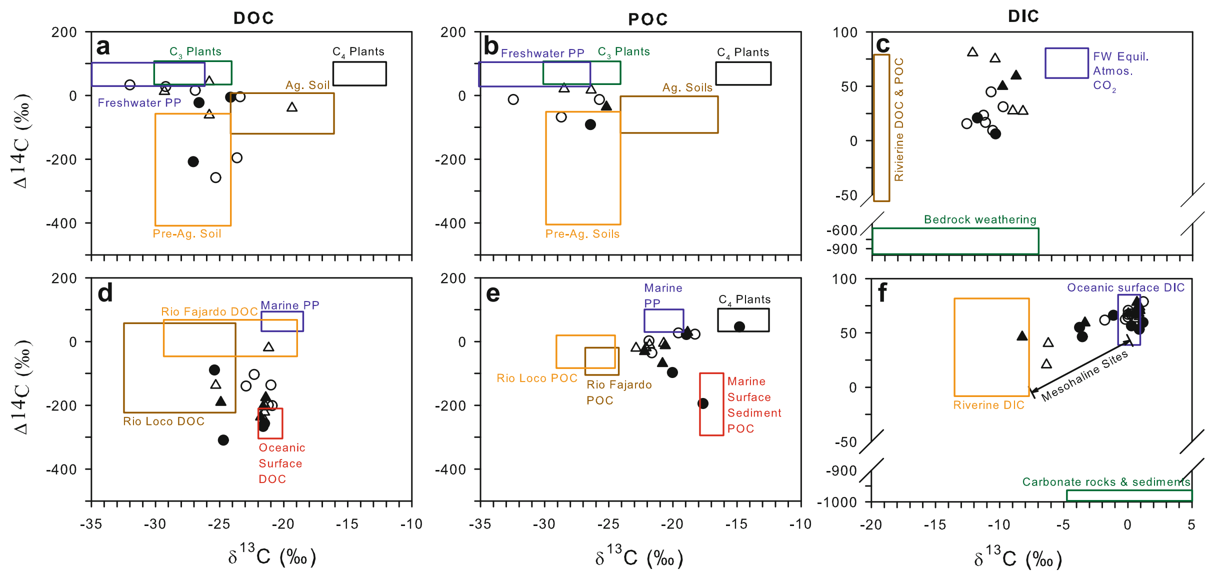

Fig. 6 Carbon isotope (δ^{13}C vs. Δ^{14}C) source diagrams for DIC, DOC, and POC in riverine (panels **a**–**c**) and estuarine (panels **d**–**f**) samples. *Boxes* represent typical ranges of δ^{13}C and Δ^{14}C for potential sources of DIC, DOC, and POC to each system (see Sect. 4 in text). Rio Loco and its estuary: *filled circle* September/October, *open circle* March, Rio Fajardo and its estuary: *filled triangle* September/October, *open triangle* March. *FW Equil. Atmos. CO_2* predicted values for freshwater equilibrated with atmospheric CO_2, *PP* primary production, *Ag. soil* modern C_4-dominated agricultural soil, *Pre-ag. soil* pre-agricultural period C_3-dominated soil, *C_3 and C_4 plants* terrestrial plants

from organic-rich bedrock (Kao and Liu 1996; Leithold and Blair 2001; Masiello and Druffel 2001; Leithold et al. 2006). The δ^{13}C signature of riverine DOC and POC are typically reflective of these sources, with riverine δ^{13}C-DOC and -POC values being most similar to those of the plant biomass and soil OM within a given catchment. Plant-derived OM (e.g., leaf litter) in catchments dominated by terrestrial C_3 plants (including most tropical trees and shrubs) in Puerto Rico has an average δ^{13}C of ~ -30 ‰ (von Fischer and Tieszen 1995), while bulk soil OM averages ~ -27 ‰ (Marín-Spiotta et al. 2009). Catchments dominated by terrestrial C_4 plants (e.g., sugarcane, corn, most pasture grasses) contain biomass and soil OM with average δ^{13}C values of ~ -13 and ~ -19 ‰, respectively (Smith and Epstein 1971; Marín-Spiotta et al. 2009). The isotopic distinction between terrestrial C_3 and C_4 plants is important in Puerto Rico, where much of the island was once deforested and sugarcane was the dominant crop from the early nineteenth century to the mid-twentieth century. Within the rivers themselves, the δ^{13}C values of autochthonous OM can be predicted from measured riverine δ^{13}C-DIC values (Table 1), assuming a kinetic fractionation of ~ -20 ‰ for freshwater primary production by aquatic C_3 plants and algae (e.g., Chanton and Lewis 1999). Therefore in Puerto Rico, the δ^{13}C values for freshwater primary production of autochthonous riverine OM would be expected to range from -35 to -26 ‰ in both rivers (Fig. 6a, b). In terms of age of the OM, samples with low Δ^{14}C values indicate that the source of DOC and POC is aged terrestrial C_3 plant-derived OM (i.e., pre-agricultural soils). Conversely, DOC and POC samples with high Δ^{14}C values are derived from modern C_3 plant OM.

Despite a history of island-wide sugarcane production dating to the 1500s, the DOC and POC in both study areas had δ^{13}C values reflective of significant inputs from terrestrial C_3 plant material, with corresponding Δ^{14}C values indicative of OM that ranges from modern to highly aged (Fig. 6a, b; Table 1). Dual isotope ratio (δ^{13}C and Δ^{14}C) mass balance calculations (Supplementary Text S1; Supplementary Table S4) indicate that as much as 52 % of the riverine DOC and 65 % of the POC may be derived from modern terrestrial C_3 plants, while only 24 % of the DOC and 21 % of POC originate from pre-agricultural soils that consist of aged terrestrial C_3 plant-derived soil OM (Fig. 6a, b; Table 2). Agricultural soils, representing a mixture of modern and aged C_3 and C_4 plant materials, account for 24 % of the riverine DOC, and 14 % of riverine POC (Fig. 6a, b; Table 2). Interestingly, the mean estimated contribution of agricultural soils to the DOC pool was nearly equal for the Rio Loco and Rio Fajardo (21 and 28 % respectively; Table 2). This result was unexpected given the modern land-use within each catchment, and may be explained by the geomorphological differences between the two catchments.

The Rio Loco study area has a large, low-elevation valley, while the Rio Fajardo study area largely encompasses the steep slopes of the Luquillo Mountains and has a very narrow coastal plain (Fig. 1; Supplementary Table S1). In the Rio Loco, pre-agricultural soils contribute to the DOC pool in relatively greater amounts than in the Rio Fajardo (Table 2). It is likely that this is due to higher rates of aged soil accumulation within the Lajas Valley and larger role of groundwater transport into the irrigation canals or main stem of the Rico Loco (Fig. 1). Indeed, the old Δ^{14}C-DOC values obtained from the drainage canal within the valley support this contention (Table 1). In the Rio Fajardo, modern C_3 plant material contributed to the DOC pool to a greater extent than in the Rio Loco, and this can likely be explained by the high abundance of modern plant material and rapid erosion rates associated with tropical rain forest headwaters (Scatena and Larsen 1991; Scatena et al. 2005; Larsen and Webb 2009). It should additionally be noted that a regional wastewater treatment plant began operating on the Rio Fajardo in 2006. While comparison of downstream Rio Fajardo data (Rio Fajardo Mouth FW; Table 1) between 2004/2005 and 2007/2008 show that neither DOC or POC increased in abundance after the plant went into operation, there was a shift in δ^{13}C signature of the two OM pools. Riverine δ^{13}C-DOC and -POC each decreased by an average of $\sim$3 ‰ in 2007/2008 compared to 2004/2005. In addition, a source of aged DOC was also present below the wastewater plant in 2008 (Table 1). These findings are consistent with isotopic studies of wastewater effluent (Griffith et al. 2009), and indicate that anthropogenic factors may also partially explain the isotopic character of the OM currently being exported on the Rio Fajardo.

The oldest DOC in the Rio Loco catchment was measured in an agricultural irrigation effluent drain (Lajas Canal Drainage Ditch, Fig. 1) during March 2008 when irrigation rates are highest (Fig. 7; Table 1). Relatively lower rainfall in this region is likely to increase the residence time of soil OM due to a low degree of mobilization, and this should be most pronounced during March, which has the lowest average rainfall of any month in Puerto Rico. Previous studies have demonstrated that Δ^{14}C-depleted riverine DOC may arise from increased inputs from deeper soil profiles containing older sedimentary OM (Trumbore 1993, 2009; Evans et al. 2006; Neff et al. 2006). However, agricultural practices, such as tilling and use of petrochemicals, also increase the export of aged soil OM (Fontaine et al. 2007; Sickman et al. 2010). Thus, when the agricultural soil OM is mobilized within the Rio Loco catchment (either by rainfall or irrigation) it is likely the major source of the aged DOC measured in the Rio Loco. However, since irrigation effluent is not the only source of DOC to the Rio Loco, and indeed modern DOC was also measured in the Rio Loco, some of the observed variability is likely explained by the mixing of modern DOC originating from Presado Loco reservoir and the smaller headwater tributaries (Fig. 1; Table 1).

In contrast to the Rio Loco, the riverine DOC pool in the Rio Fajardo study area, which is non-agricultural and originates in a tropical rainforest, was younger and less variable (Fig. 6; Table 1). Rapid mobilization of OM caused by abundant rainfall and steep slopes likely account for the modern DOC ^{14}C ages measured in the headwaters of the Rio Fajardo. The moderately aged DOC measured in samples taken from the lower Rio Fajardo (Figs. 1 and 6) is likely a result of increased storage and reduced mobilization of soil OM in the floodplain (Clark and Wilcock 2000). However, some aged DOC may also originate from urban petrochemical or wastewater runoff (both ^{14}C-dead) in the Rio Fajardo catchment, since the town of Fajardo and a regional wastewater treatment facility are located directly on the northern banks of the lower Rio Fajardo (Griffith et al. 2009).

Potential sources of DIC to tropical SMRs

Primary sources of DIC to most rivers include the oxidation of OM via both abiotic (e.g., photo-oxidation; Miller and Zepp 1995; Opsahl and Zepp 2001; Obernoster and Benner 2004) and microbial processes (e.g., soil and aquatic respiration; Raymond and Bauer 2000; Raymond and Bauer 2001a; Obernoster and

Benner 2004), weathering of carbonate and siliciclastic rocks (Telmer and Veizer 1999), and direct exchanges with atmospheric CO_2 (Mook et al. 1974; Mook and Koene 1975). Dual isotope ratio mass-balance calculations indicate a larger contribution of atmospheric CO_2 equilibrated with river waters (~57 %) to the Rio Loco and Rio Fajardo DIC pools than from respired riverine DOC and POC (~30 %) sources (Fig. 6c; Table 2). Respired soil CO_2 was estimated to be only a minor source (~13 %; Table 2) of riverine DIC. This is in direct contrast to large tropical river systems such as the Amazon, where CO_2 respired from riverine DOC and POC or DIC produced as a weathering product of carbonate and siliciclastic rocks may contribute significantly to riverine DIC (Das et al. 2005; Mayorga et al. 2005). As a result, δ^{13}C-DIC in these larger tropical systems is not reflective of atmospheric CO_2 inputs (Das et al. 2005; Mayorga et al. 2005).

The greater contribution of atmospheric CO_2 to tropical SMR DIC compared to large tropical rivers may be due to their small catchment sizes, steep slopes, poorly developed soils, and rapid flushing rates, all of which may prevent the accumulation of respired soil CO_2 during baseflow conditions. However, the seemingly large contribution of atmospheric CO_2 to riverine DIC may still be a product of direct physical and chemical weathering of silicates in Puerto Rico. Recent studies have shown Puerto Rico to have very high chemical weathering rates, which contributes significantly to the DIC pool (Riebe et al. 2003) and produce waters with high pCO_2 values (Bhatt and McDowell 2007). Studies from other SMR catchments in Puerto Rico have suggested that a high frequency of landslides serves to increase the atmospheric CO_2 content of soils, and also provide fresh exposures of bedrock to enhance chemical weathering (Bhatt and McDowell 2007). Hence, such processes would enable atmospheric CO_2, rather than respired soil CO_2 to be the dominant source of DIC to the SMRs of Puerto Rico. Unfortunately, it is difficult to isotopically differentiate DIC that is produced by silicate weathering from that which is produced by direct invasion of atmospheric CO_2, unless aged respired soil CO_2 is responsible for the weathering, or significant carbonate weathering is involved. However, given the fast soil turnover times (Marín-Spiotta et al. 2008), the lack of carbonates in the Luquillo Mountains and Cordillera Central, and the high rates of physical and chemical weathering that are known to occur in Puerto Rico (McDowell and Asbury 1994; Riebe et al. 2003; Bhatt and McDowell 2007), it is most likely that the dominant DIC isotopic signature results from atmospheric CO_2 that is equilibrated with meteoric and surface waters.

Potential sources of C and OM to tropical SMR estuaries and adjacent coastal waters

The large variability observed in the Rio Loco and the Rio Fajardo estuarine DOC and POC concentrations (Figs. 3a–d and 4a–d; Table 1) and δ^{13}C and Δ^{14}C signatures (Figs. 3e–l and 4 e–l; Table 1) indicates that estuarine OM in these systems is derived from a combination of terrestrial and marine sources with variable ages. The mesohaline sites with δ^{13}C-DOC values closest to those expected from a marine primary productivity source had higher Δ^{14}C-DOC values, while those sites having δ^{13}C-DOC values predominantly reflective of DOC derived from terrestrial OM also had lower Δ^{14}C-DOC values (Fig. 5d; Table 1). These findings contrast with those from a number of other studies showing that river and estuarine DOC is usually much younger (typically modern or near-modern) than marine DOC (up to 1–2 thousand years, reviewed by Bauer 2002). The presence of aged DOC in estuarine and coastal waters in this study, coupled with similar findings in the POC fractions of other temperate and tropical SMRs (Masiello and Druffel 2001; Komada et al. 2004) indicates that tropical SMRs may be a direct source of aged OM to the coastal ocean (Fig. 6d).

The potential for tropical SMRs to provide a direct source of unaltered DOC to the coastal ocean may be explained in part by the hydrological characteristics typically associated with them. In general, DOC sampled at the mouth of the Rio Fajardo had terrestrial δ^{13}C-DOC signatures (Figs. 3g, h; Table 1). The headwaters of the Rio Fajardo receive some of the largest amounts of annual rainfall in all of Puerto Rico, and the associated higher river discharges in the Rio Fajardo (Table S1) may enable rapid transport of DOC to the coastal ocean before it becomes oxidized, degraded, or otherwise altered isotopically (Wiegner et al. 2009). Similar findings and interpretations have been reported from other tropical SMRs (Goñi et al. 2008) and in the POC fraction of temperate SMRs

Table 2 Estimates of the relative contributions (%) of various sources of carbon to the dissolved and particulate organic carbon, and dissolved inorganic carbon pools of the Rios Loco and Fajardo stiudy areas

	Relative contribution of sources									
	Equil. atmos. CO_2 (%)	Riverine DOC and/or POC (%)	Oceanic surface DOC or POC (%)	Soil CO_2 and silicate weathering (%)	Riverine DIC (%)	Carbonate sediments (%)	Terrestrial C_3 plants (%)	Agricultural soils (%)	Pre-agricultural soils (%)	Marine primary productivity (%)
Rivers										
Rio Loco DOC	–	–	–	–	–	–	48 (0–88)	21 (0–48)	31 (0–74)	–
Rio Fajardo DOC	–	–	–	–	–	–	58 (11–82)	28 (0–89)	14 (0–28)	–
All riverine DOC	–	–	–	–	–	–	52 (0–88)	24 (0–89)	24 (0–74)	–
Rio Loco POC	–	–	–	–	–	–	60 (44–76)	12 (0–27)	28 (12–39)	–
Rio Fajardo POC	–	–	–	–	–	–	70 (52–84)	17 (0–33)	13 (8–16)	–
All riverine POC	–	–	–	–	–	–	65 (44–84)	14 (0–33)	21 (8–39)	–
Rio Loco DIC	51 (44–57)	31 (22–39)	–	18 (4–28)	–	–	–	–	–	–
Rio Fajardo DIC	66 (59–78)	28 (20–36)	–	6 (0–19)	–	–	–	–	–	–
All riverine DIC	57 (44–78)	30 (20–39)	–	13 (0–28)	–	–	–	–	–	–
Estuarine and marine sites										
Loco DOC	–	28 (7–58)	47 (0–78)	–	–	–	–	–	–	25 (0–45)
Fajardo DOC	–	31 (17 –80)	45 (0–74)	–	–	–	–	–	–	24 (8–73)
All est and mar. DOC	–	29 (7–80)	46 (0–78)	–	–	–	–	–	–	24 (0–73)
Loco POC	–	9 (0–27)	28 (0–95)	–	–	–	–	–	–	63 (0–100)
Fajardo POC	–	22 (0–39)	20 (11–40)	–	–	–	–	–	–	58 (37–89)
All est. and mar. POC	–	15 (0–39)	24 (0–95)	–	–	–	–	–	–	60 (0–100)
Loco DIC	89 (60–100)	–	–	–	10 (0–39)	1 (1–2)	–	–	–	–
Fajardo DIC	82 (20–100)	–	–	–	17 (0–79)	1 (1–3)	–	–	–	–
All est. and mar. DIC	85 (20–100)	–	–	–	14 (0–79)	1 (1–3)	–	–	–	–

Estimates are based on calculations from three source isotope mixing models (see Supplementary Text S1). The average percent contribution is given for each source, along with the range (in parentheses)

Equil. atmos. CO_2 waters equilibrated with atmospheric CO_2, *Est. and mar.* estuarine and marine, – not applicable

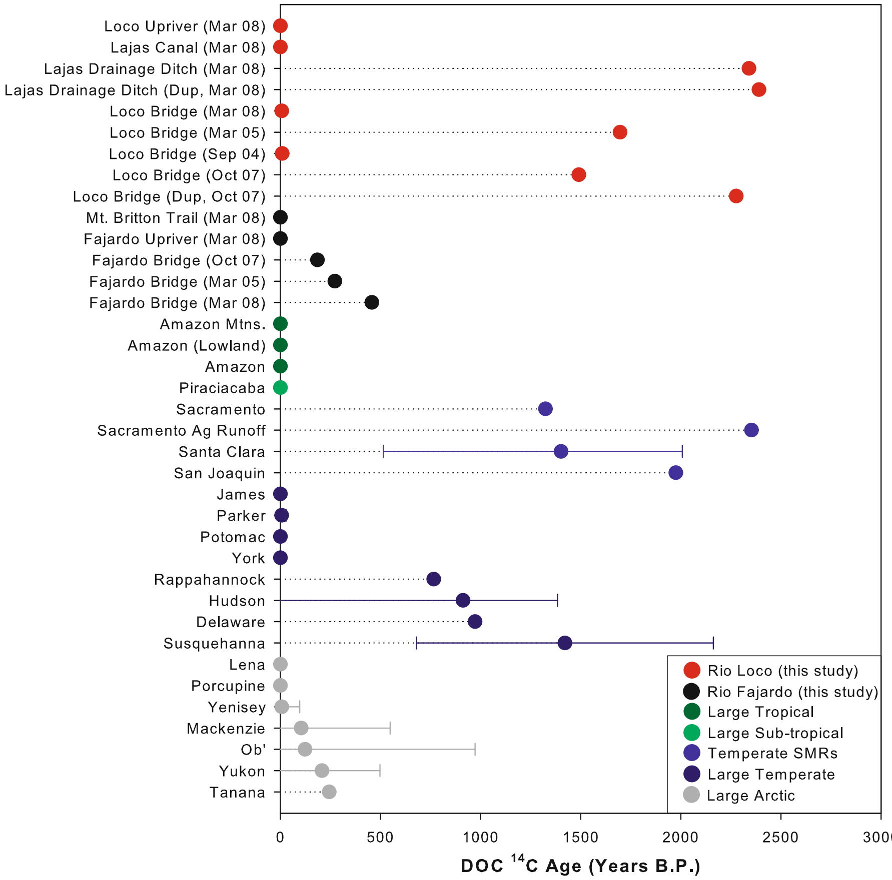

Fig. 7 Radiocarbon ages of riverine DOC reported for the Rio Loco and its tributaries (*red*) and the Rio Fajardo and its tributaries (*black*) in this study and from other tropical (*dark green*), sub-tropical (*light green*), small and large temperate (*light and dark blue*, respectively), and arctic (*grey*) rivers. *Circles* represent average values reported from all published studies of radiocarbon ages for a given river. *Horizontal error bars* represent the total range (max. and min.) of all published radiocarbon ages for a given river. *ybp* years before present, *SMR* small mountainous river. Sources other than this study: Krushe et al. (2002) = Piraciacaba; Masiello and Druffel (2001) = Santa Clara; Mayorga et al. (2005) = Amazon; Raymond and Bauer (2001a) = Amazon, Hudson, Susquehanna, Rappahannock, James, Parker, Potomac, York; Raymond et al. (2007) = Ob', Mackenzie, Yukon, Yenisey; Sickman et al. (2010) = Sacramento, San Joaquin; Striegl et al. (2007) = Lena, Porcupine, Tanana. (Color figure online)

(Masiello and Druffel 2001). Therefore, the transport of minimally altered terrestrially derived riverine OM to the coastal ocean is a process that may be unique to SMRs. This contrasts with larger river systems where OM is typically modified considerably during transport, and prior to discharge to the coastal ocean (Raymond and Bauer 2000, 2001a, c; Raymond et al. 2004), The agreement between the findings of this study (Fig. 6d; Table 1) and those from a temperate SMR (Masiello and Druffel 2001), give good indication that these tropical SMRs could be a source of ^{14}C-depleted continental OM to the Caribbean Sea, which are in turn sources of aged DOC to the deep ocean (Bauer and Druffel 1998).

In terms of its δ^{13}C and Δ^{14}C signatures, estuarine POC in general was isotopically indistinguishable from that of marine sites in both study areas (Fig. 6e; Table 1). While two notable outliers (Bahia Noroeste and Rio Loco Mouth, Oct. 2007; Table 1; Fig. 6e) had isotopic values that were consistent with present-day agricultural practices within the lower Rio Loco catchment, we can also not rule out the possibility that some fraction of this POC is derived from mangroves (C_3) and seagrass (δ^{13}C signature similar to C_4 plants) within the Rio Loco estuary. Both mangroves and seagrass have been shown to be major sources of particulate OM in other tropical estuaries (Kuramoto and Minagawa 2001).

The Rio Loco and Rio Fajardo estuaries both had δ^{13}C-DIC values that were higher than riverine δ^{13}C-DIC, but lower than marine δ^{13}C-DIC (Figs. 5e–h and 6f). Estuarine Δ^{14}C-DIC was reflective of modern sources in both study areas (Figs. 5 and 6f), indicating a larger component ($\sim$85 %; Table 2) of atmospherically derived CO_2 in estuarine waters (including from surface marine waters), with a smaller contribution ($\sim$14 %; Table 2) of DIC produced from the oxidation of terrestrial OM (e.g., Cai and Wang 1998; Cai 2003). The δ^{13}C-DIC and Δ^{14}C-DIC values at the marine end-member sites in both study areas are reflective of modern atmospheric CO_2 as the major source of marine surface water DIC (Fig. 6f), and the influx of marine waters to tropical SMR estuaries may result in estuarine DIC also being dominated by this source.

Comparison of C ages in tropical SMRs to other river systems

The radiocarbon ages of DOC from the freshwater sites in the Rio Loco and Rio Fajardo study areas were, in many cases, distinct relative to other large tropical, sub-tropical, and temperate river systems (Fig. 7). Several of the freshwater samples collected from the Rio Loco study area (i.e., Rio Loco Bridge and Lajas Drainage Ditch sites; Fig. 1) are among the most highly aged DOC samples observed in any global river system (Fig. 7; Masiello and Druffel 2001; Raymond and Bauer 2001a; Krushe et al. 2002; Mayorga et al. 2005; Raymond et al. 2007; Sickman et al. 2010). However, the age of freshwater DOC in the Rio Loco system was also highly variable with respect to sampling location and season. Differences in the amount of rainfall, relief of the landscape, and land-use practices (agricultural vs. non-agricultural) may help explain the high variability in both the concentrations and ages of freshwater DOC observed in Puerto Rico (Fig. 7; Table 1).

The ages of POC measured in both study areas (modern to a few centuries old) were relatively young compared to other tropical and temperate SMRs (Fig. 8). On average, riverine POC in the Rio Loco was younger than its corresponding DOC (Figs. 7 and 8; Table 1). This differs from temperate and large tropical rivers where POC is often older than the corresponding DOC pool (Figs. 7 and 8 and references therein). Catchment size and climate dynamics, which combine to influence the mobilization of soil OM to a river (Goldsmith et al. 2008; Hilton et al. 2008; Townsend-Small et al. 2008; Wheatcroft et al. 2010), are likely the dominant factors underlying the difference in POC ages between SMR and large continental river systems. For instance, the frequent rainfall and rapid flushing rates coupled with higher recurrence of natural disturbances (i.e., tropical cyclones and landslides) associated with most tropical SMRs (Scatena et al. 2005; Goldsmith et al. 2008; Hatten et al. 2010; Wheatcroft et al. 2010) are more likely to mobilize modern POC from steep, tectonically active slopes when compared to larger, lower-relief, tectonically stable temperate river systems where catchments are extensive and POC may become much more highly aged (Raymond and Bauer 2001a; Nagao et al. 2005). Other major factors that may account for the observed differences between SMRs and larger rivers include total catchment area, floodplain area and storage potential, and composition and erodibility of the underlying bedrock of each catchment type (see Meade 1988; Hatten et al. 2010). In large tropical systems (i.e., the Amazon), where most POC is relatively young compared to large temperate rivers (Fig. 7 and references therein), headwater streams tend to have POC that is similar in age to that of the two SMRs in this study, and also have POC younger than that in the lowland portion of the river (Mayorga et al. 2005; Townsend-Small et al. 2007). This observed difference between the age of OM in tropical SMRs and a large tropical river has been attributed to preferential respiration of young OM and mixing with older material stored on the lowland floodplains (Townsend-Small et al. 2007). In contrast to other tropical river systems such as the Amazon (Mayorga et al. 2005) or Lanyang Hsi (Kao and Liu 1996), the underlying lithology in the two study areas is not thought to be a major source of organic or inorganic C. The oldest reported POC ages have come from rivers directly eroding organic-rich sedimentary bedrock (i.e., shales; Kao and Liu 1996; Leithold et al. 2006). Although storm-driven erosion of organic-rich bedrock results in the export of highly aged POC in some tropical SMRs (e.g., Kao and Liu 1996; Leithold et al. 2006; Hilton et al., 2008), other studies have shown that soil turnover rates are fast in tropical forests, including those of Puerto Rico (Marín-Spiotta et al. 2008). Such fast turnover of soil OM may limit the age of POC exported by tropical SMRs where organic-

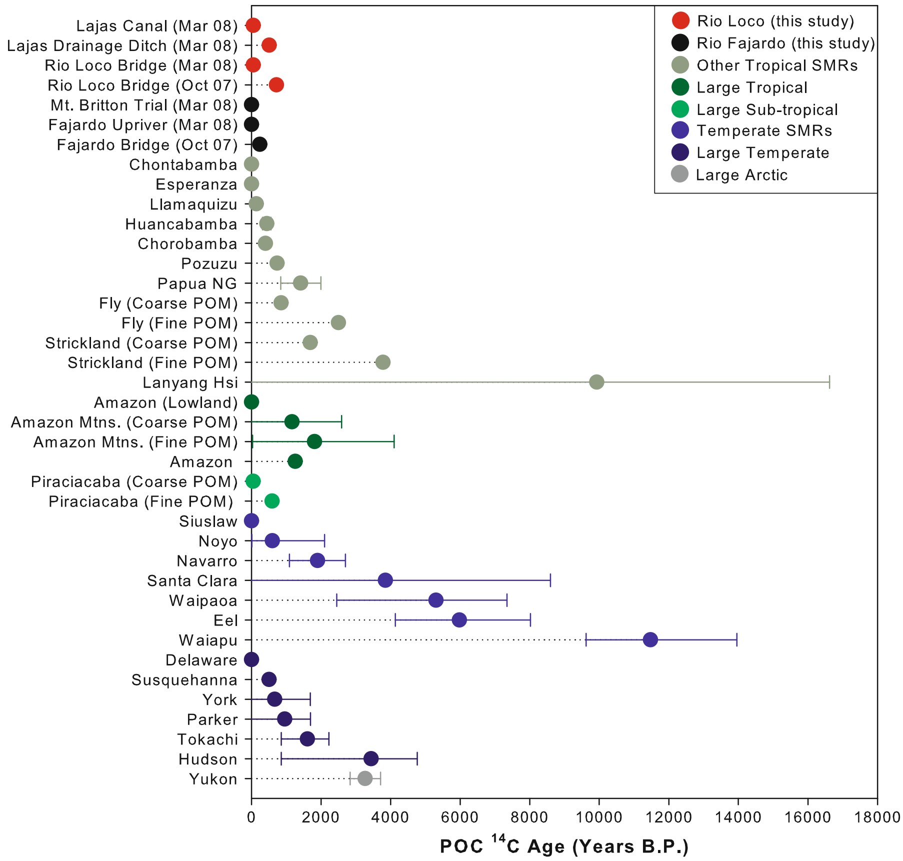

Fig. 8 Radiocarbon ages of riverine POC reported in this study for the Rio Loco and its tributaries (*red*) and the Rio Fajardo and its tributaries (*black*) and for other small (*olive*) and large tropical (*dark green*), sub-tropical (*light green*), small (*light blue*) and large temperate (*dark blue*) and arctic (*grey*) rivers. *Circles* represent average values reported from all published studies of radiocarbon ages for a given river. *Horizontal error bars* represent the total range (max. and min.) of all published radiocarbon ages for a given river. *ybp* years before present, *SMR* small mountainous river. Sources other than this study: Alin et al. (2008) = Fly, Strickland; Kao and Liu (1996) = Lanyang Hsi; Masiello and Druffel (2001) = Santa Clara; Raymond and Bauer (2001a) = Amazon, Hudson, Parker, York; Krushe et al. (2002) = Piraciacaba; Komada et al. (2004) = Papua New Guinea; Raymond et al. (2004) = Deleware, Susquehanna; Mayorga et al. (2005) = Amazon; Nagao et al. (2005) = Tokachi; Leithold et al. (2006) = Eel, Noyo, Navarro, Siuslaw, Waiapu, Waipaoa; Townsend-Small et al. (2007) = Chontabamba, Llamaquizu, Esperanza, Chorobamba, Huancabamba, Pozuzu; Striegl et al. (2007) = Yukon. (Color figure online)

rich bedrock is not present. The lithology of most of Puerto Rico is andesitic basalts in the central mountain ranges flanked by sedimentary deposits of consolidated alluvium and carbonates on the coastal plains (Bawiec 1999). No major outcrops of organic-rich sedimentary rocks have been described on the island, and hence there is limited potential for underlying lithology to be a primary source of aged POC in this study.

Based on the isotopic evidence presented here and other studies of tropical SMRs (Townsend-Small et al. 2007; Alin et al. 2008), the abundance and age of the OM in these tropical SMRs appears to be controlled primarily by the residence time of soluble soil OM prior to mobilization by rivers. Relatively warm, wet climates (Raich and Schlesinger 1992) and the large range in discharge dynamics (Goldsmith et al. 2008; Hatten et al. 2010) associated with tropical SMRs are likely key factors in determining such residence times. However, recent studies in other temperate and tropical SMRs have demonstrated the importance of physiographic characteristics of catchments in controlling OM abundance and age. Therefore, other factors such as lithology (Kao and Liu 1996; Leithold et al. 2006), tectonic stability (Hatten et al. 2010), and stream channel morphology (Clark and Wilcock 2000) must also be considered important drivers of OM abundance and age in tropical SMRs. Finally, as demonstrated in this study and others (e.g., Sickman et al. 2010), anthropogenic influences such as agriculture and urban runoff must also be considered key contributors of aged OM to tropical SMRs.

The ^{14}C ages of DIC measured in both study areas were all modern (Table 1) and comparable to ^{14}C ages reported in some continental rivers of the northeast United States (Raymond et al. 2004), the lowlands of the Amazon (Mayorga et al. 2005), and several SMRs in New Zealand (Taylor and Fox 1996). Aged DIC has been reported from SMRs in Papua New Guinea (Fly and Strickland Rivers; Alin et al. 2008) as well as larger rivers in the Amazon highlands (Mayorga et al. 2005) and the Hudson River and tributary system (Raymond et al., 2004). In all cases, weathering of aged carbonate or shale bedrock was thought to be a major source of the aged riverine DIC (Raymond et al. 2004; Mayorga et al. 2005). Organic-rich lithologies such as shale are rare in Puerto Rico, and while carbonate does exist and can be quite extensive, it did not return viable results as a potential end-member source in the three end-member mixing model analysis (see Section Potential sources of DIC to tropical SMRs above). In those rivers with modern DIC, net heterotrophy has been identified as a major source of young DIC (Raymond et al. 2000, 2004; Mayorga et al. 2005). The relatively warm climates common to tropical SMRs would favor enhance biological respiration, and when combined with DIC produced by high rates of chemical weathering in tropical islands (e.g., Riebe et al. 2003; Goldsmith et al. 2010; Lloret et al. 2011) likely serve as the main source of apparently young DIC in these tropical SMRs.

Summary

This study represents a comprehensive dual isotope ($\delta^{13}C$ and $\Delta^{14}C$) characterization of the three major carbon pools (DOC, POC, and DIC) at base flow conditions in tropical SMRs and their associated estuaries and coasts. Such information is critical for quantitatively constraining the importance of tropical SMRs in local-to-regional scale ocean C budgets, as well as the role of past, present, and future land use and other environmental change in tropical island settings. The results clearly show that abundance and isotopic character of OM can be highly variable among and between individual SMRs (Figs. 3–5; Table 1). Thus, caution must be exercised when extrapolating limited data sets from a few SMRs to SMRs globally.

The isotopic character of each carbon pool in the two tropical SMR systems studied here was highly dependent upon the sources of carbon to the river or estuary (Fig. 6; Table 2), and the natural or anthropogenic processes which influence the abundance and lability of that source material. For instance, the agricultural study area (Rio Loco) was characterized by highly aged riverine DOC, and this is likely a direct product of the agricultural practices within the catchment. The isotopic character of OM in estuarine and marine waters in these systems suggested that during times of greater discharge, terrestrial carbon may be transported to the coastal ocean without experiencing biogeochemical turnover and alteration in estuarine waters. Such a finding is supported by studies in other temperate and tropical SMRs (Masiello and Druffel 2001; Komada et al. 2004), but rare in comparison to most large tropical (Mayorga et al. 2005) and temperate (Raymond and Bauer 2000, 2001a, c; Raymond et al. 2004) river systems.

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