Organic Carbon Concentrations and Transport in Small Mountain Rivers, Panama

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Abstract

Tropical small mountainous rivers (SMRs) are increasingly recognized for their role in the global export of dissolved organic carbon (DOC) to the oceans. Here we utilize the Isthmus of Panama as an ideal place to provide first-order estimates of DOC yields across a wide assemblage of bedrock lithologies and land cover practices. Samples for dissolved organic carbon (DOC) analysis were collected across Panama along an E-W transect from the central Panama area to the Costa Rican border for 24 mainstem rivers, 3 large tributary rivers, and one headwater stream. Sampling occurred during both the wet and the dry seasons. DOC concentrations during the wet season are higher than during the dry season in all but three of the rivers. Concentrations vary greatly from river to river and from season to season, with values as low as 0.64 mg l⁻¹ to greater than >25 mg l⁻¹ with the highest concentrations observed for the rivers draining Tertiary marine sedimentary rocks in the Burica and Azuero peninsulas. DOC yields from Panamanian rivers (2.29 to 7.97 tons/km²/y) are similar to or slightly lower than those determined for other tropical SMR systems. Areas underlain by Tertiary aged sediments exhibited significantly higher mean DOC yields compared to their igneous counterparts, despite maintaining substantially lower aboveground carbon densities, suggesting the important influence of lithology. Finally, regression analyses between DOC yields and select watershed parameters revealed a negative and statistically significant relationship with maximum and mean gradient suggesting lower soil retention times may be linked to lower DOC yields.

Key words: Organic carbon, riverine yields, watershed, Panama

1. Introduction

The transport of organic carbon from the terrestrial landscape to the ocean is a major process in the global carbon cycle (Ludwig et al., 1996; Aitkenhead and McDowell, 2000; Raymond and Bauer, 2001; Lyons et al., 2002; Cole et al., 2007). The amount of organic matter transported and buried in marine sediments and terrestrial deposits, compared to the amount of carbon that is recycled in both the terrestrial landscape and the aquatic system, has real importance with regard to global carbon sequestration (Cole et al., 2007). Recently, tropical and subtropical mountainous regions of the world have been shown to play an important role in the transport of particulate organic carbon (POC) and dissolved organic carbon (DOC) to the global ocean (Kao and Liu, 1997; Blair et al., 2003; Gomez et al., 2003; Komada et al., 2004; Carey et al., 2005; Hilton et al., 2012; Lloret et al. 2011, 2013). However, there is still a need to substantiate these suggestions as datasets acquired to date are generally from isolated localities that are of limited spatial extent. This lack of organic carbon flux data is particularly true for the humid tropics which contain as much as 30% of the world's total soil organic carbon (Batjes, 1996). In addition, these studies often overlook how factors such as lithology, stream geomorphology and ecosystem modification can ultimately modify these rates of DOC export.

This paucity of data has also complicated the search for controls on organic matter export from SMR locales. In fact in many regions of the world fluxes and yields have been determined by extrapolation and by modeling (Ludwig et al., 1996, Lloret et al., 2013). Steep slopes and high rainfall have been attributed to elevated POC yields (Hilton et al., 2012), much of which is transported to the ocean during periodic to aperiodic intense precipitation events (Goldsmith et al., 2008; Hilton et al., 2008; Wohl et al., 2012). However, these same factors have been shown to have a varying relationship with DOC yields (Guyot and Wasson, 1994; Townsend-Small et al., 2005; Lloret et al., 2013) as thin soils prevent the building up of organic material in shallow soils. To discern elevation effects on DOC concentrations in SMRs is often further complicated by the influence of anthropogenic activities associated with higher population densities at lower altitudes (Yang et al., 2013). Furthermore, studies on DOC export from subtropical and tropical SMRs tend to focus on monolithic settings consisting of either uplifted sedimentary/lightly metamorphosed terrains (Kao and Liu, 1997; Carey et al., 2005; Alin et al., 2008) or volcanic islands (Lloret et al. 2011; 2013) with limited inter-basin climate variability. Thus, an understanding of the role of these constraining factors is crucial before extrapolating values to other settings for modeling purposes.

This paper addresses existing knowledge gaps by presenting both wet and dry seasons DOC concentrations for 24 mainstem rivers, 3 tributary rivers, and a headwater stream from central

and western Panama. In addition, DOC yields have been calculated from watersheds where river discharge measurements exist. DOC yields are subsequently compared to a series of hydrologic, lithologic, geomorphologic, and land cover parameters in a search for controls. These data substantially improve our overall knowledge of carbon yields from tropical watersheds.

2. The West-Central Panama Study Area

Panama is located in the humid seasonal tropics and has a tropical climate that is characterized by constant high temperature at sea level and low elevation, distinct wet and dry seasons, and annual rainfall exceeding evapotranspiration across most of the country (Kotteck et al., 2006; Peel et al., 2007). Temperatures are uniformly high across the country, with each month of the year having an average temperature of 18 °C or higher and seldom exceeding 32 °C, except in the higher parts of the mountain ranges where frosts can occur during winter months.

Rainfall across Panama is strongly seasonal, with pronounced wet and dry seasons, and varies regionally from less than 1.3 m to nearly 7 m per year (Rand and Rand, 1982; Cavelier et al., 1996). Because the primary source of moisture to Panama's precipitation comes from the Atlantic Ocean, the Atlantic coastal region receives greater rainfall than the Pacific coastal region on the leeward side of the continental divide. Rain falls throughout the year along the Caribbean coast, so that annual accumulations on the north slopes of the Cordillera Central can range 3000–7000 mm, whereas the Pacific coast of central Panama and the Azuero peninsula have a tropical dry and wet climate with annual rainfall of <2000 mm. The Cordillera Central creates an elevation barrier and, therefore, a strong climate gradient from north to south across Panama that generates higher precipitation and consequent greater runoff, erosion, and river incision on the Caribbean side of Panama compared to the Pacific side. About 90% of the annual precipitation falls during the rainy season between May and December. This wet period is followed by a marked dry season from January to April. River discharge correlates well with precipitation. Since wet season storms approach Panama from the north, the Caribbean slope of the Cordillera Central is moist and heavily forested by comparison to the Atlantic side, which has a longer dry season, receives less precipitation, and therefore is comparatively drier and much more developed (Condit et al., 2001). The H- and O- isotopic composition of surface waters in Panama becomes more depleted with distance from the Caribbean coast, documenting progressive rainout as the moisture-rich air masses move southward across the country (Lachniet and Patterson, 2006; Harmon et al., 2009).

The land that today composes Panama formed over the past 140 million years as a consequence of Caribbean, South American, Cocos, and Nazca plate interactions as an island arc

archipelago developed on Mesozoic oceanic crust of the Caribbean plate and interacted with associated marine sedimentary basins (Molnar and Sykes, 1969). Geologically, Panama consists of a mosaic of bedrock lithologies that range from hydrothermally altered marine oceanic crust, intrusive mafic to intermediate composition, igneous rocks, a broad array of volcanic rock compositions, and uplifted loosely consolidated marine and clastic sedimentary rocks deposited unconformably upon the igneous rocks of the volcanic arcs during Tertiary time in the Bocas del Toro region, the Burica and Azuero peninsulas, and in portions of the Trans-Isthmus, Colon, and East Panama regions (Coates et al., 2004; Wegner et al., 2011). Silicate rocks across Panama comprise a broad range of volcanic and intrusive lithologies. Tholeiitic to low-K calc-alkaline basalts and andesites dominate the extrusive suite, whereas gabbros to granodiorites are the most common intrusive rocks. As a consequence, the solute signature of Panamanian rivers, which is largely acquired in watershed headwater areas (Harmon et al., 2013), is broadly similar in terms of major elements, except where rivers are developed predominantly on rhyolite and granite or on associated Tertiary shallow marine sediments. The Panama land bridge, which presently forms the terrestrial connection between North and South America, formed during the past few million years by tectonic amalgamation and transpressive faulting of these igneous rocks at this active plate margin (Coates and Obando, 1996).

Across the tropics, oxide and clay minerals accumulate as a thick mantle of residual soil develops above active bedrock weathering in the critical zone. The geomorphic situation in Panama is characteristic of the mountainous tropics, where (i) thick, cation-depleted soils are present on ridges and topographic high ground, (ii) soils on mountain slopes are thin and cation depleted, and (iii) lowland soils are highly variable in both thickness and composition. The dominant soil type in much of Panama can be described as broadly saprolitic, although some minor surficial soil deposits derived from marine sediments are important locally. Like saprolitic soils across the humid tropics, these soils generally consist of clay- and silt-size particles that have been depleted of most alkali and alkaline earth cations, leaving a matrix consisting primarily of oxides of iron and aluminum (e.g. Stallard, 1985). Where quartz-bearing lithologies are present, soils will tend toward a sandy texture having a high permeability, whereas soils on mafic and intermediate volcanic terrains where quartz is absent tend to be fine-grained and are characterized by a decreased porosity and low hydraulic conductivity. It is not uncommon to find multiple soil types in close geographic proximity.

Because of its diverse tropical climate, Panama has one of the world's most varied ecosystems and is noted for its species richness (Myers et al., 2000). Forests dominate across mountain and upland areas, with secondary scrub forest, grasslands, and crops present to varying extents across the lowlands areas and coastal plains. Although nearly 40% of Panama is still

wooded, deforestation is a continuing threat to the rain-drenched woodlands. Tree cover has been reduced by more than half over the past fifty years and there is concern that this deforestation is causing soil erosion and affecting the river chemical quality. Subsistence farming is practiced widely across the country and secondary forests arise when low-productivity agricultural land and pastures are abandoned.

Almost 500 rivers drain the mountainous areas of Panama, most of which are small mountain rivers that originate as swift highland streams. In general, rivers in Panama are short, having an average length of 106 km, although an average of only 56 km for rivers flowing north to the Caribbean Sea, with their overall flow direction tending to be oriented perpendicular to the coast. The largest rivers have produced well-developed valleys and in their lower reaches comprise meandering coastal plain rivers and associated deltas. About one-third of Panamanian rivers flow northward into the Caribbean Sea and drain about 30% Panama's land area. The remaining two-thirds, including 22 of the 24 rivers sampled in this study flow southward into the Pacific Ocean, draining the remaining 70% of the country. The Rio Pequini and Rio Piedras tributary to the Upper Rio Chagres in the Trans-Isthmus region flow into Lago Alajuela, which is a storage reservoir for Panama Canal operations. The hydrology of Panama is driven by the seasonality of precipitation and the character of the landscape upon which rain falls. Local soil character and hydraulic processes control how incident rainfall is apportioned into surface runoff, infiltration, transmission, evapotranspiration, and ground water recharge. The major factors that determine the extent of runoff production in the mountainous landscape of tropical Panama watersheds are their steep slopes, extensive soil macropore networks, and soils with high water retention capacity.

The rivers of central-western Panama sampled in this study (Fig. 1) have watersheds that range in size about 2–1400 km² and can be divided into six groups (Table 1) on the basis of their local geology, geomorphology, and land cover as described below. The largest rivers samples, i.e. Rio Chiriqui Viejo, Rio Chiriqui, Rio Fonseca, Rio San Juan, Rio Santa Maria and Rio Pacora, run across the southern coastal plain developed on Tertiary sediments, but were sampled in their middle reaches north of the Pan American highway where the river channels were developed on Tertiary igneous bedrock.

Figure 1. Map of Panama showing rivers and sample collection locations.

Group 1 (Burica Peninsula): Rivers of the Burica Peninsula in far western Panama (Rio Corotu, Rio San Bartolo, and Rio Palo Blanco) drain a surface geology comprising sequences of shallow marine and terrestrial forearc sediments that include limestones, marine siliceous deposits, and detrital volcano-sedimentary units deposited unconformably upon the igneous rocks of the volcanic arcs during Tertiary time (Escalante, 1990). Watersheds in the Burica Peninsula are comparatively small, with areas ranging from just 2–52 km² and have 22 to 65% forest cover.

Group 2 (Chiriqui Region): Rivers of the western Chiriqui province (Rio Chiriqui Viejo and one of its low-order tributary streams, Rio Platanal, and Rio Chico Concepción) drain the Holocene adakitic basalts and andesites of the Pleistocene-age Volcán Barú (Drummond et al., 1995), whereas those located in the eastern portion of Chiriqui province (Rio Fonseca, Rio San Juan, and Rio San Felix) drain igneous rocks of the ‘Older’ volcanic arc (Wegner et al., 2011). These watersheds range from 19–606 km² in size and have 13 to 79% forest cover.

Group 3 (Veraguas-Cocle Region): Rivers of Veraguas, and western Cocle provinces (Rio Santiago, Rio Grande, Rio Santa Maria, Rio Conaca, Rio Chico, and Rio Cocle) drain igneous rocks of the ‘older’ and ‘younger’ volcanic arcs (Wegner et al., 2011), which largely consist of intrusive and extrusive submarine and subaerial volcanic arc suites (Wörner et al., 2005; 2009).

Table 1: Dissolved organic carbon content during wet and dry season sampling for 27 rivers in Panama

Map ID*	River	Sampling UTM E	Sampling UTM W	19-25 Aug 2006 (wet season) mg l ⁻¹	20 Feb – 1 Mar 2007 (dry season) mg l ⁻¹
<i>Group 1. Burica Peninsula</i>					
1	Rio Corotu	293804	913110	>25	2.87
2	Rio Bartolo	296301	916566	>25	1.73
3	Rio Palo Blanco	298894	920017	24.55	1.67
<i>Group 2. Chiriqui Region</i>					
4	Rio Chiriqui Viejo (n=5)	298266	943179	1.52	1.21
	Rio Chiriqui Viejo at volcan (headwater reach)			6.19	ND
5	Rio Chico Concepcion	324385	939597	1.26	ND
6	Rio Platanal	332644	935712	1.05	0.83
7	Rio Chiriqui	351523	929671	1.55	1.01
8	Rio Fonseca	384303	915166	1.91	0.94
9	Rio San Juan	393359	913962	2.88	1.13
10	Rio San Felix	405028	914518	0.76	0.67
<i>Group 3. Veraguas-Cocle Region</i>					
11	Rio Santiago	419769	908175	0.87	1.96
12	Rio Santa Maria	534705	899336	3.41	1.18
13	Rio Conaca	526169	896401	4.43	2.53
14	Rio Chico at Nata (tributary to Rio Grande)	553005	919929	1.99	1.06
15	Rio Grande	554841	931243	2.01	1.84
19	Rio Cocle del Sur (tributary to Rio Grande)	562156	934710	2.97	1.41
<i>Group 4. Azuero Peninsula</i>					
16	Rio Escota	541829	894670	8.85	4.15
17	Rio Parita	555561	882141	9.21	2.29
18	Rio La Villa	563756	877880	6.46	1.29
<i>Group 5. El Valle Region</i>					
20	Rio Anton	581615	928571	1.92	1.08
21	Rio Hato	591099	926735	1.59	1.15
22	Rio Las Lajas	619042	943994	4.65	2.82
<i>Group 6. Trans-Panama Region</i>					
23	Rio Nombre de Dios	666296	1058502	7.3	0.64
24	Rio Cuango	686100	1055100	2.35	6.27
25	Rio Pequini	660976	1035763	1	1.14
26	Rio Piedras (tributary to Upper Rio Chagres)	675710	1026445	ND	1.25
27	Rio Pacora	688094	1003560	8.04	1.15

Rivers here are some of the longest in Panama and watersheds in this region are large, ranging 166–1797 km² in size. These rivers have their headwater reaches in the fully forested highest

elevations of the Cordillera Central but overall are characterized by 31–81% forest cover as a consequence of deforestation in their lower reaches.

Group 4 (Azuelo Peninsula): Rivers of Azuelo Peninsula of south-central Panama (Rio Escota, Rio Parita, and Rio La Villa) that drain a geologically complex upland terrain consisting of Late-Cretaceous-Early Tertiary intrusive and volcanic rocks that underlie the mid-Tertiary sediments to the nearby Pacific Ocean. These watersheds vary from 24–919 km² in size and have a forest cover varying only 3–38%.

Group 5 (El Valle Region): Rivers of the El Valle region of west-central Panama (Rio Anton, Rio Hato, and Rio Las Lajas) are largely formed on the silicic dacites and rhyolitic ignimbrites of the Late-Pleistocene age El Valle caldera volcanic complex (Defant et al., 1991) and run only short distances to the Gulf of Panama. Their watersheds vary only 12–435 km² in size and have a diminished forest cover that varies 7–72%.

Group 6 (Trans-Isthmus Region). This region of central Panama contains rivers (Rio Nombre de Dios, Rio Cuango, Rio Pequini, Rio Piedras, Rio Pacora) that largely drain the Chagres-Bayano Arc Complex that extends across the Chagres Uplands into east-central Panama. The geology of this area has been described by Wörner et al. (2005; 2009) and Wegner et al. (2011), with exposed igneous rocks here of ages between 65 to 45 Ma for intrusive suites that range from gabbro and diorite to granodiorite and low-K granite. The Rio Pacora is formed on mafic igneous rock in its headwater region and flows across Tertiary marine sediments in its lower downstream reaches (Harmon et al., 2009) These watersheds vary from 12–414 km² in size and have forest covers that vary 38–99%. This region contains the two most pristine rivers in our study, the Rio Pequini and Rio Piedras, both largely-forested tributaries of the Upper Rio Chagres that have their headwaters in pristine triple canopy tropical rainforest. As noted by Condit et al. (2000), the forest of the Upper Rio Chagres drainage has been preserved as the Chagres National Park and therefore is largely undisturbed compared to most other areas of the Pacific slope of the Cordillera Central where forests have been largely cleared except in the highest, headwater areas. The Rio Nombre de Dios, Rio Cuango, and Rio Pacora also originate in this same headwater area but land uses in their lower reaches include various types of agriculture and suburban to urban impacts, with the Rio Pacora most significantly modified.

In general, the sedimentary rock-dominated landscapes of the Burica and Azuelo peninsulas (Fig. 1) receive less rainfall and are characterized by higher mean annual temperature than the other regions of this study. The rivers draining these regions generally have higher total dissolved solids than rivers developed on the igneous terrains of the other four regions sampled (Harmon et al., 2013). All river systems, with the exceptions noted above, are directly affected by anthropogenic activities, with farming, grazing, low-density urbanization, and residential land use widespread across the Pan American Highway region of Chiriqui, Veraguas, Cocle, and

Panama provinces where rivers were sampled. Truck farm agriculture, grazing, and urbanization form the prevailing land use in the northern headwater area of the Chiriqui province. Livestock grazing is the predominant land use in the semi-arid Azuero region and in the Burica Peninsula away from the urbanized coastal areas.

3. Sampling and Analytical Procedures

Water samples for DOC analysis were collected in one headwater stream of the Rio Chiriqui Viejo in the Volcán Barú area of western Panama and from the middle or lower reaches of 27 rivers across western and central Panama (Fig. 1; Table 1). This DOC study was undertaken as part of a larger, more comprehensive examination of the geochemistry of streams and rivers in west-central Panama (Harmon et al., 2013). Except in the Burica and Azuero peninsulas, all rivers sampled have their headwater reaches at the high elevation in the forested portion of the Cordillera Central and then flow either northwards in to Atlantic Ocean or southwards into the Pacific Ocean (Fig.1). The Rio Pequini and Upper Rio Chagres, which has the Rio Piedras as a major tributary, presently flow into the Lake Alajuela reservoir for Panama Canal operations.

Samples were collected by using the techniques outlined in Carey et al. (2005). Samples were collected at most locations during both the wet season (19–23 August 2006) and dry season (20 February to 1 March 2007). Samples were stored in the dark on ice immediately upon collection and shipped back to The Ohio State University within five days, where they were vacuum filtered directly into 20 ml amber glass vials through Millipore™ 0.7 µm nominal pore-size glass fiber filters. Filters, vials, and the filtration units had previously been combusted at 450 °C for 3 hours and later rinsed with 10% (v/v) HCl in deionized water. After filtration, samples and blanks were acidified with HCl to pH 2 and stored at 4 °C. Analyses were performed using a Shimadzu 5050A Total Organic Carbon analyzer. The high sensitivity catalyst was used to quantify to ~0.1 mg l⁻¹ DOC. The normal sensitivity catalyst was used for concentrations in excess of 3.0 mg l⁻¹ DOC. Samples were sparged with hydrocarbon-free air for up to 7 minutes prior to analysis to remove CO₂. Each sample was injected 3–4 times. The relative standard deviation (RSD) of the multiple analyses of individual samples ranged 0.6–3.8%. Filtration blanks and field blanks were also analyzed as samples. All blanks were below the limit of detection of 0.03 mg l⁻¹ DOC. Accuracy of the measurement of the 1.0 mg l⁻¹ concentration was 2.3–2.9%.

In addition to the DOC samples, samples of the top 1 cm of surface streambed sediment were collected from mud deposits (sand-size grains and below) on the flood banks (13 samples in August 2006 and 2 in February 2007) using a nylon spoon. Samples were placed into clean,

plastic ziplock bags and stored in the dark. After shipment back to Ohio State, samples were air dried and then analyzed for percent organic carbon using the dry combustion method and thermal conductivity detection with a Perkin-Elmer CHN2400 High Temperature Induction Furnace (Nelson & Sommers, 1996) at the Ohio State University School of Environment and Natural Resources.

Estimates of the annual DOC yields were computed where stream discharge data were available. For the 2-year period covering our DOC measurements, the yields were determined using the mean daily discharge values for the wet and the dry seasons for 14 rivers with data provided by the Empresa Territorial para la Salud (ETESA). The Rio Pequini yields were calculated using discharge data from Harmon et al. (2009). Wet and dry seasonal discharge values were determined using the average monthly discharge values for the respective seasons. For both periods of record, the subsequent wet and dry seasonal yields were summed to determine the annual DOC yield. The ETESA discharge records range in length from 17 to 42 years in duration (mean = 41 years) and are considered of high quality. As noted above, not all the rivers with samples analyzed for DOC had associated river discharge data and only 15 yields could be determined.

In an effort to place the data in context, we have provided average daily discharge values on the date of sample collection for 9 of the 13 rivers for which we calculated seasonal/annual DOC fluxes (Table 2; Fig. 2). Average daily discharge values for the day of sampling represent a decrease between 1% and 56% of their seasonal average values. This reduction in discharge is likely the result of 2006–07 being an El Niño period. Previous work has demonstrated clearly that during El Niño periods there is reduced rainfall and stream discharge in the Pacific slope areas of Central America (Waylen and Laporte, 1999). Furthermore, we observed an increase in wet season DOC concentrations for 24 out of 28 of our rivers. Others have identified increasing DOC concentrations and yields with increasing rainfall in tropical SMRs (Jeong et al., 2012; Lloret et al., 2013), particularly during intense precipitation events. Therefore, given the reduced discharge values at the time of sampling due to ENSO conditions, coupled with an expected increase in DOC concentrations with increased discharge, it is likely our yields are highly conservative.

Table 2

Average daily and seasonal discharge values for select Panama rivers

River	Dry Season Sample Date	Average Daily Discharge/ Season	Long- Term Wet Season	% difference	Wet Season Sample	Average Daily Discharge/ Season	Long- Term Dry Season	% difference
<i>Chiriqui Region</i>								
Rio Chiriqui Viejo	8/20/2006	70.9	80	-11%	2/24/2007	16.8	23.3	-28%
Rio Chiriqui	8/19/2006	153	176	-13%	2/24/2007	29.4	47.7	-38%
Rio Fonseca	8/21/2006	32.4	48.4	-33%	2/24/2007	N/A	16.9	
Rio San Juan	8/21/2006	N/A	18.0		2/24/2007	0.65	2.74	-76%
Rio San Felix	8/21/2006	14.3	27.1	-47%	2/24/2007	1.34	3.05	-56%
<i>Veraguas-Cocle Region</i>								
Rio Santa Maria	8/19/2006	103	104	-1%	2/26/2007	16.4	33.1	-50%
Rio Chico at Nata (tributary to Rio Grande)	8/19/2006	19.9	22.1	-10%	2/26/2007	3.25	4.00	-19%
Rio Grande	8/19/2006	19.2	23.3	-18%	2/26/2007	2.55	9.35	-73%
<i>Azuero Peninsula</i>								
Rio La Villa	8/21/2006	13.3	41.5	-68%	2/22/2007	4.90	7.50	-35%

^aLong-term discharge data from Empresa de Transmisión Eléctrica (ETESA)^bData not available for the date of sampling

Figure 2. Average daily discharge values for the Rio Chiriqui Viejo for the 2006-2007 water year. Average daily discharge values for the day of sampling are denoted with triangles.

Finally, a digital elevation model (DEM) for the Panama watersheds was subsequently prepared to evaluate the control of landscape geomorphology, land cover and climate on DOC fluxes. The DEM is based on NASA Jet Propulsion Laboratory's Shuttle Radar Topography Mission (SRTM) 90m data (<http://www2.jpl.nasa.gov/srtm/>) and was generated using Global mapper (8.0 version). The DEM was used to determine watershed area and stream gradient for each of the watersheds. Land use cover was also incorporated into the DEM using data provided by the European Space Agency's Global Land Cover Map (<http://due.esrin.esa.int/globcover/>). Finally, average annual low/high temperature, annual minimum/maximum precipitation values were determined for each of the watersheds using data obtained from Esri's ArcAtlas (http://gcmd.nasa.gov/records/GCMD_ESRI_Arc_Atlas.html).

4. Results and Discussion

4.1 The DOC and POC Dataset

The DOC concentrations ranged 0.67 mg l^{-1} to 2.87 mg l^{-1} in the dry season and 0.76 mg l^{-1} to $>25 \text{ mg l}^{-1}$ in the wet season (Table 1). Results of a two tailed t-test show ($\alpha = 0.05$) that the average wet season DOC concentration of all rivers is greater than in the dry ($t=2.54 > t_{\text{crit}}=2.05$;

$p=0.02$). Where samples for both the wet and dry seasons exist for an individual river, there are only three locations where the dry season concentrations are higher. These are Rio Santiago, Rio Pequini and Rio Cuango (Table 1). Recent work on other tropical mountainous watersheds has also demonstrated higher DOC concentrations during the wet portions of the year (Zhang et al., 2009) and higher DOC concentrations with higher discharges (Lloret et al., 2013). DOC values from this study are in line with those previously measured for the SMRs of Puerto Rico (1.32 to 2.16 mg l⁻¹; McDowell and Asbury, 1994), Guadeloupe (0.52 to 7.22 mg l⁻¹; Lloret et al., 2011) and New Zealand (1 to 7.6 mg l⁻¹; Carey et al., 2005).

Spatial effects in DOC concentrations can be elucidated from the grouping the rivers into the geographic regions, as discussed above. For example, during the wet season, the Burica and Azuero Peninsula rivers and the Eastern Panama rivers have higher mean DOC concentrations than the Colon and Veraguas region rivers, which in turn have higher mean concentration than the El Valle and trans-Isthmus region rivers, which are higher than the mean values for Chiriqui region rivers (Table 1). The dry season regional means are much less variable, but the Azuero Peninsula rivers still have the highest means, followed by the Colon and Burica Peninsula region rivers, while the trans-Isthmus and Chiriqui region rivers have the lowest mean concentrations (Table 1). Groups 1 and 4 rivers (Burica and Azuero peninsula rivers) drain mid-Tertiary marine sedimentary rocks and sediments. These data suggest that land use and perhaps watershed lithology have some control on the DOC concentrations in these rivers.

It has been suggested that with respect to organic carbon transport, smaller headwater streams often have very different biogeochemical characteristics. These differences are thought to be due in part to differences in catchment geomorphology and ecology (Townsend-Small et al., 2005). This is particularly true of mountainous rivers, due to changes in terrestrial vegetation with respect to elevation (Townsend-Small et al., 2005).

The concentrations of DOC in the rivers of western-central Panama sampled in this study, for the most part, are similar to what has been observed in other tropical and mountainous regions. The exceptions are the very high wet season values observed in the marine sedimentary terrains of the Azuero and Burica Peninsulas (Table 1). A portion of the DOC in the sedimentary rock-dominated watersheds could come from the weathering of the rocks themselves (Schillawski and Petsch, 2008) but currently there are no carbon characterization data (including ¹⁴C ages) to confirm or disprove this idea.

The sediment organic carbon concentrations range 0.2–5.2% and show no relationship to DOC concentration (Table 3). Furthermore, a relative lack of geographic distribution for the POC samples prevented a regional comparison.

Table 3

Paticulate organic carbon concentrations for 15 Panama rivers

River	Sampling UTM E	Sampling UTM N	Sample Date	% OC
<i>Group 6. Trans-Panama Region</i>				
Rio Piragua	764201	1019310	2/22/2007	0.85
Rio Nombre De Dios	666354	1058540	8/23/2006	0.71
Rio Diablo	777830	1019110	8/23/2006	0.19
Rio Limpio	670170	1029140	8/24/2006	0.47
Rio Pequini	666327	1038560	8/23/2006	0.55
Rio Chepo	787121	1017840	8/24/2006	0.92
Rio Piedras	675721	1026460	8/24/2006	0.57
Rio Chico	664040	1025010	8/24/2006	5.23
Rio Pacora	689317	1006920	8/22/2006	1.04
Upper Rio Chagres	689117	1035230	8/24/2006	0.68
Rio Cuango	686168	1055140	8/23/2006	0.84
Rio Pacora	689317	1006920	8/22/2006	0.54
Rio Esperanza	680312	1036820	8/23/2006	0.79
Rio Espave	755181	1024860	8/24/2006	1.07
Rio Carti Grande	722329	1041960	2/22/2007	1.88

4.3. DOC and POC yields and search for controlling variables

With the annual runoff data where they exist, DOC yields have been calculated (Table 4 & 5). The annual yields range 2.3–8.0 tons/km²/y. The Azuero Peninsula rivers exhibited the highest average DOC yields (7.2 tons/km²/y) followed by those of the Chiriqui region (4.5 tons/km²/y). The Veraguas-Cocle and trans-Isthmus province rivers exhibited the next highest average DOC yields (3.7 and 3.5 tons/km²/y, respectively) followed by those of the El Valle region (3.2 tons/km²/y). The Panama DOC yields are equal to or lower than those from other tropical mountainous watersheds in Guadeloupe and Puerto Rico of 1.9–9.4 tons/km²/y (Lloret et al., 2013; McDowell and Asbury, 1994; Stallard et al., 2012) and are equal to or slightly higher than those from mountainous rivers in New Zealand, Papua New Guinea, and Taiwan of 0.4–5.2 tons/km²/y (Carey et al., 2005; Alin et al., 2008; Burns et al., 2008; Kao and Liu, 1997). However, our mean yield from these Panama rivers (4.5 tons/km²/y) is slightly lower than the

mean determined previously for tropical river systems (6.0 tons/km²/y) by Aitkenhead and McDowell (2000). It has also been demonstrated that, in general, DOC export from tropical rivers is not greater than from rivers and streams from other climatic types (McDowell and Asbury, 1994). In general, these yields from the Panama rivers are higher than yields from much larger rivers such as the Niger (0.5 tons/km²/y), Yukon (1.5 tons/km²/y), St. Lawrence (1.35 tons/km²/y), and Mississippi (0.9 tons/km²/y) Rivers (Martin and Probst, 1991; Telang et al., 1991; Bianchi et al., 2004, respectively).

Table 4: Dissolved organic carbon yields from Panama Rivers

River	Watershed Area Upstream of Sampling Site (km ²)	Annual Average Discharge (m ³ /s) ^a	Wet Season Discharge (m ³ /s)	Dry Season Discharge (m ³ /s)	Years of Record	DOC Yields (t km ⁻² yr ⁻¹)			Geologic Domain
						Wet Season	Dry Season	Annual	
<i>Chiriqui Region</i>									
Rio Chiriqui Viejo	788	61	80.0	23.3	40	4.86	1.13	3.97	QV
Rio Chiriqui Viejo (headwater reach)	108	6.43	7.17	5.19	39	12.96	---	---	QV
Rio Chiriqui	1337	132	176	47.7	42	6.44	1.14	5.17	QV
Rio Fonseca	406	36.4	48.4	16.9	21	7.18	1.23	5.75	ARC
Rio San Juan	254	12.9	18.0	2.74	38	6.43	0.38	4.98	ARC
Rio San Felix	198	19.2	27.1	3.05	14	3.28	0.33	2.57	ARC
<i>Veraguas-Cocle Region</i>									
Rio Santa Maria	1370	80.6	104	33.1	42	8.19	0.90	6.44	ARC
Rio Chico at Nata (tributary to Rio Grande)	316	15.9	22.1	4.00	41	4.39	0.42	3.43	ARC
Rio Grande	471	18.1	23.3	9.35	41	3.13	1.15	2.66	ARC
Rio Cocle del Sur (tributary to Rio Grande)	310	6.92	9.78	1.39	28	2.95	0.20	2.29	ARC
<i>Azuero Peninsula</i>									
Rio Parita	451	10.9	16.2	1.25	23	10.42	0.20	7.97	TS
Rio La Villa	1000	29.5	41.5	7.50	32	8.45	0.31	6.50	TS
<i>El Valle Region</i>									
Rio Anton	90	4.35	6.06	1.33	17	4.08	0.50	3.22	QV
<i>Trans-Isthmus Region</i>									
Rio Pequini	135	13.9	17.4	6.99	135	4.06	1.86	3.53	ETT ARC
Rio Piedras (tributary to Upper Rio Chagres)	93	5.74			65	---	---	---	ETT ARC

Table 5: Comparison of Panama DOC to other high yielding locales

Geographic Region	DOC Yields (t km ⁻² yr ⁻¹)
<i>THIS STUDY</i>	
Chiriqui Region	2.57 – 5.75
Veraguas-Cocle Region	2.29 – 6.44
Azuero Region	6.50 – 7.97
El Valle Region	3.22
Trans-Isthmus Region	3.53
<i>OTHER REGIONS</i>	
Guadeloupe ^a	1.9 – 8.6
New Zealand ^b	0.6 – 5.2
Papua New Guinea ^{c,d}	0.4 – 5.0
Puerto Rico ^{e,f}	3.3 – 9.4
Taiwan ^g	4.1
Tropical river system mean value ^h	6

^aLloret et al. (2013), ^bCarey et al. (2005), ^cAlin et al. (2008), ^dBurns et al. (2008), ^eMcDowell and Asbury (1994), ^fStallard (2012), ^gKao and Liu (1997), ^hAlin et al. (2000)

In an effort to evaluate potential controls on DOC yields in Panama, calculated values were compared to a variety of parameters including lithology (geologic domain), climate (annual low/high temperature, annual minimum/maximum precipitation), river geomorphologic character (minimum/maximum gradient, mean gradient, minimum/maximum elevation, mean elevation, watershed perimeter, channel length), land cover and extent (forest, agricultural, and grassland/shrubland), and previously determined long term physical erosion rates for Panama rivers from Sosa-Gonzalez (2011) (Table 6).

A comparison of DOC yields by lithological domain exhibited the following order: Tertiary Sediments>>Quaternary Volcanics≈Volcanic Arc>Early Tertiary Theolitic Island Arc. Results of a two tailed t-test ($\alpha = 0.05$) show that the average annual DOC yields for the TS terrain were significantly greater than that for the ARC terrain ($t=3.31 > t_{crit}=3.18$; $p=0.05$). A paucity of samples for the Early Tertiary Theolitic Island Arc terrain prevented a statistical comparison

with that dataset. This finding was not unexpected as others have identified elevated yields in subtropical SMRs draining sedimentary and metamorphic regions of New Zealand and Taiwan (Carey et al., 2005; Kao and Liu, 1997), which possibly can be elevated due to a portion of the DOC originating from the weathering of the rocks themselves (Schillawski and Petsch, 2008). This idea is also supported by remote sensing obtained aboveground carbon density data for the Isthmus of Panama, which identified carbon stocks in the Chiriquí region (underlain by Quaternary volcanics) more than an order of magnitude greater than those for the Azuero Peninsula (underlain by Tertiary sediments) (Asner et al., 2013).

Table 6: Regression statistics for Panama DOC Yields and select hydrogeological, geomorphological and land cover parameters

	Annual DOC yield			Dry season DOC yield			Wet season DOC yield		
	n	r ²	p value	n	r ²	p value	n	r ²	p value
Runoff	13	0.25*	0.42	13	0.58	0.04	13	0.21*	0.48
Physical Erosion Rates (m/myr)	4	0.64*	0.36	4	0.12	0.88	4	0.30*	0.63
Landcover (% forest)	13	0.35*	0.24	13	0.49	0.09	13	0.38*	0.20
Landcover (% agricultural)	13	0.26	0.40	13	0.50*	0.08	13	0.29	0.34
Landcover (% grassland/shrubland)	13	0.23	0.46	13	0.27*	0.38	13	0.24	0.42
Elevation Maximum (m)	13	0.37*	0.21	13	0.01*	0.71	13	0.38*	0.21
Maximum Gradient	13	0.57*	0.04	13	0.01*	0.97	13	0.56*	0.05
Mean Gradient	13	0.55*	0.05	13	0.07*	0.82	13	0.54*	0.05
Annual Low Temperature (°C)	13	0.17*	0.58	13	0.19*	0.54	13	0.16	0.61
Annual High Temperature (°C)	13	0.17*	0.58	13	0.19*	0.54	13	0.16	0.61
Annual minimum mean Precipitation (mm)	13	0.35*	0.24	13	0.52	0.07	13	0.39*	0.19
Annual maximum mean Precipitation (mm)	13	0.35*	0.25	13	0.52	0.07	13	0.38*	0.20

*Indicates negative correlation

†Values in italics indicate statistical significance

Previous work in tropical mountainous systems has demonstrated higher DOC concentrations or yields of DOC associated with land use type (Guyot and Wasson, 1994; Yang et al., 2013). However, no statistically significant relationship was observed between our annual DOC yields and percent forest area for the long term data set ($r = -0.35$, $p=0.24$) (Table 6). Interestingly, this relationship improved from negative to positive when considering dry season fluxes only ($r = 0.49$, $p=0.09$, respectively) suggesting percent of forest land cover may play a more active role in DOC export during baseflow conditions. This idea is supported by a statistically significant relationship between mean annual runoff with dry season DOC yields ($r = 0.58$, $p=0.04$).

These relationships correspond with recent findings from the Aqua Salud experimental watersheds in Panama, suggesting that forest areas maintain relatively higher flow in these systems during the dry season (Ogden et al., 2013). Alternatively, this lack of a significant relationship may indicate that a general landuse category such as lumped forest types is not adequate to determine the importance of any one landscape component in influencing DOC flux.

Some previous work in tropical SMRs has demonstrated higher DOC concentrations or yields of DOC associated with elevation changes (Guyot and Wasson, 1994), whereas other research has not (Townsend-Small et al., 2005). Our analysis revealed statistically significant negative relationships were also observed between annual DOC yields and mean channel gradient ($r = 0.55$, $p=0.05$) and maximum channel gradient ($r = 0.57$, $p=0.04$). A previous study examining DOC yields from three tropical SMRs in Guadeloupe attributed relatively lower DOC yields in the Vieux-Habitants watershed to a relatively lower residence time of water in the system, as a result of its high overall percentage of steep slopes and highest mean annual rainfall in its headwater regions (Lloret et al., 2013). This influence of decreased residence time might explain our results that annual DOC yields ($r = -0.64$, $p=0.36$) are negatively, albeit statistically insignificantly, related to previously determined physical erosion rates of Sosa-Gonzalez (2011). Alternatively, relatively lower DOC concentrations observed at higher elevation from subtropical SMRs in Taiwan and southern China were attributed both to increased dilution from rainfall and to relatively lower population densities compared to their downstream counterparts (Yang et al., 2013). The majority of our samples were collected at the lower reaches of the watersheds and so we are unable to tease out relative anthropogenic impacts at different elevations within the same systems or within stream changes associated with elevation.

A comparison of annual DOC yields with climate parameters identified a negative correlation with minimum and maximum mean annual precipitation ($r = -0.35$, $p=0.24$). While this relationship held for both the annual and wet season values, the dry season values exhibited a positive correlation with these parameters ($r = 0.52$, $p=0.07$). While much of Panama

experiences distinct wet and dry seasons, precipitation across the Panamanian Isthmus is highly variable and convective rainfall is still generated year round in elevated areas of the Cordillera Central, which forms the headwaters for several streams in our study. While we cannot tease out the effects of headwater elevation on maintaining year round precipitation this varying relationship between seasonal DOC yields and minimum and maximum mean annual precipitation suggests a seasonal distribution of rainfall may minimize dilution effects.

Another important factor to consider is that 2006–07 was an El Niño period. Previous work has demonstrated clearly that during El Niño periods there is reduced rainfall and stream discharge in the Pacific slope areas of Central America (Waylen and Laporte, 1999). This suggests that our yields may be lower than what would be expected during average discharges due to ENSO conditions during our sampling period. No other statistically significant relationships were observed between DOC yields and any of the remaining parameters.

As observed in other SMRs (Guyot and Wasson, 1994, Jeong et al., 2012; Lloret et al., 2013), DOC yields can increase with specific discharge (Fig. 3). Karmalkar et al. (2008) have used the IPCC A2 scenario climate model for montane forests in Costa Rica and project an increase in temperature for this region, especially at higher elevations, and a decrease in precipitation of as much as 30%. Their modeling also suggests a decrease in the frequency of high precipitation events with greater changes on the Pacific side. If this were also the case for the montane regions of Panama, one might expect that in the increased CO₂ atmospheric environment of the future, DOC yields from these rivers might reflect this decreased discharge (assuming no major changes to present day land cover or land use patterns). Another important consequence of this decrease in discharge would be lower fluxes of total organic matter to the coastal zones.

Figure 3. Dissolved organic carbon yield plotted versus river specific annual average discharge (excluding rivers from the Azuero Peninsula underlain by sedimentary lithology).

Long-term suspended load data exist only for the Rio Chagres (Nichols et al., 2005); so with those data and the Rio Pequini POC value, a POC yield of $1.9 \text{ tons km}^{-2} \text{ a}^{-1}$, or 60% of the total (POC+DOC) yield was calculated for the Upper Chagres Basin. The Chagres POC yield is within the range of those previously determined for the small mountainous rivers draining of New Zealand ($2.6\text{--}3.8 \text{ tons km}^{-2} \text{ a}^{-1}$) by Carey et al. (2005). Surface (0–8 cm) soil organic carbon in the Upper Chagres Basin is 2.6–4.2% by weight (Hannah, 2009), suggesting that much of the organic matter produced in the forest is recycled in place on the landscape or during rapid transit through the aquatic system, as these soil OC concentrations are considerably higher than most of our stream POC values. Even though landslides mobilize large volumes of material in the Upper Chagres Basin, large woody debris in the Upper Rio Chagres watershed has a short residence time in the channels because of the flashy hydrographs with large peaks, and the resultant rapid transport times (Wohl et al., 2009). All these data and observations suggest that organic carbon is rapidly lost from the pristine, forested watersheds, either through rapid transport to the ocean or rapid decay and mineralization.

5. Conclusions

DOC data have been presented for water samples collected during both the dry and the wet seasons for a selection of small to large rivers in Panama. Most of the headwaters of these rivers originate in high elevation regions of the country. DOC concentrations are higher in the wet season and DOC yields correlate strongly to the specific discharge in the watersheds. Both findings suggest that rainfall and runoff control the flux of DOC in these tropical environments. The POC concentrations are generally low, reflecting rapid transport and recycling of organic matter in these watersheds.

Yields of DOC are similar to or slightly lower than those determined from other tropical, SMR regions. Significantly higher mean DOC yields for regions underlain by Tertiary sediments compared to those underlain by igneous rocks suggests the important influence of lithology to DOC yields despite substantially lower aboveground carbon densities. Subsequent regression analyses between DOC yields and select watershed parameters revealed a negative and statistically significant relationship with mean elevation, maximum gradient and mean gradient suggesting lower soil retention times may be linked to lower DOC yields.

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