Examining organic carbon transport by the Orinoco River using SeaWiFS imagery

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[1] The Orinoco River is the fourth largest in the world in terms of water discharge and organic carbon export to the ocean. River export of organic carbon is a key component of the carbon cycle and the global carbon budget. Here, we examined the seasonal transport of organic carbon by the Orinoco River into the eastern Caribbean using the conservative relationship of colored dissolved organic matter (CDOM) and dissolved organic carbon (DOC) in low salinity coastal waters influenced by river plumes. In situ measurements of CDOM absorption, DOC, and salinity were used to develop an empirical model for DOC concentration at the Orinoco River Plume. Satellite remote sensing reflectances were used with empirical models to determine DOC and Particulate organic carbon (POC) river transport. Our estimates of CDOM and DOC significantly correlated with in situ measurements and were within the expected ranges for the river. Total organic carbon transport by the Orinoco River during the period of 1998 to 2010 was 7.10 × 10^{12} g C y^{-1}, from 5.29 × 10^{12} g C y^{-1} of DOC and 1.81 × 10^{12} g C y^{-1} of POC, representing ~6% increase to previous published estimates. The variability in organic carbon transport responded to the seasonality in river flow more than to changes in organic carbon concentration in the river. Our results corroborate that it is possible to estimate organic carbon transport using ocean color data at global scales. This is needed to reduce the uncertainties of land–ocean carbon fluxes.


1. Introduction

[2] The export of terrestrial carbon to the ocean is a key component of the global carbon cycle. Rivers discharge about 73% of global runoff to the ocean [Dai et al., 2009] along with an estimated 4.0 × 10^{14} g y^{-1} of terrestrial organic carbon [Schlesinger and Melack, 1981; Schlinz and Schneider, 2000; Romankevich et al., 2009]. Dissolved organic carbon (DOC) is a major component of terrestrial carbon transported by rivers, comprises most of the organic carbon found in the coastal ocean, and is one of the largest global carbon pools [Hedges, 2002]. The concentration of particulate organic carbon (POC) varies from 0.5 to 40 percent of the concentration of total suspended solids transported by rivers [Meybeck, 1982; Smith and Hollibaugh, 1993].

[3] The Orinoco River ranks third by global river discharge with an average annual discharge of 3.5 × 10^{6} m^{3} s^{-1} [Spitzy and Leenheer, 1988]. This flow delivers approximately 6.4 × 10^{12} g y^{-1} of organic carbon into the western tropical Atlantic or about 1.6% of global carbon transported by rivers [Lewis and Saunders, 1989]. DOC comprises about 75% of the total organic carbon transported by the Orinoco River or about 4.98 × 10^{12} g y^{-1} [Paolini et al., 1987; Spitzy and Leenheer, 1988; Lewis and Saunders, 1989], while the flux of POC is a maximum of 9.1% of the total particulate load or 1.6 × 10^{12} g y^{-1} POC [Lewis and Saunders, 1989].

[4] Accurate assessments of the global ocean carbon concentration and understanding of ocean carbon cycle dynamics is limited in large-part by the availability of in situ data particularly in dynamic coastal environments where physical constraints and political and geographical borders frequently limit efforts to acquire field data. In contrast, the easily accessible, large sets of ocean color data obtained from satellite instruments such as the Sea-Viewing Wide Field-of-View Sensor (SeaWiFS) and the Moderate Resolution Imaging Spectroradiometer (MODIS) may provide a means to obtain global estimates of land-ocean carbon fluxes of DOC and POC.
[5] DOC concentration cannot be measured directly using ocean color sensors because not all the organic carbon is colored. However, colored dissolved organic matter (CDOM) is a major component of the total dissolved organic carbon pool in coastal waters influenced by rivers. CDOM, in contrast to non-chromophoric DOC, absorbs light over a broad spectral range [Brucaud et al., 1981]. In river plumes, CDOM dominates the absorption of ultraviolet and blue light accounting for 20 to 70% of light absorption at 440 nm [Del Vecchio and Subramaniam, 2004]. Although phytoplankton and detrital substances also absorb in this spectral region, CDOM is often the major absorber and provides a direct approach to determining DOC concentration in coastal waters particularly those environments influenced by rivers.

Several investigators have reported that in low salinity coastal waters CDOM and DOC behave conservatively and correlate such that CDOM can be used as a proxy for total DOC concentration [e.g., Del Castillo et al., 1999, 2001; Blough and Del Vecchio, 2002; Coble, 2007; Del Castillo and Miller, 2008; Mannino et al., 2008]. Using SeaWiFS and MODIS Aqua images Mannino et al. [2008] developed algorithms to retrieve CDOM and DOC concentrations in the U.S. Middle Atlantic Bight to examine DOC dynamics. Del Castillo and Miller [2008] used SeaWiFS data to model DOC concentrations associated with the Mississippi River Plume to examine DOC seasonal export. The success of these investigations provided the motivation for examining DOC dynamics of the Orinoco River Plume (ORP) using CDOM concentration derived from ocean color images.

[6] Mannino et al. [2008] and Del Castillo and Miller [2008] used empirical models to successfully retrieve CDOM and DOC concentrations using SeaWiFS and MODIS images in the U.S. Middle Atlantic Bight and the Mississippi River Plume region. However, semi-analytical algorithms are better suited for a more general approach to optically complex waters. A semi-analytical approach is based on approximations of the remote sensing reflectance to the inherent optical properties that allows for a flexible, general algorithm that can be applied to different water types to retrieve estimates of the optically significant components, such as phytoplankton, CDOM and non-algal particles. The Quasi-Analytical Algorithm (QAA) developed by Lee et al. [2002] derives the absorption and backscattering coefficients of optically active constituents by inverting the spectral remote-sensing reflectance. The QAA can be used in both ocean and coastal waters [Lee et al., 2007]. For example, Qin et al. [2007] achieved higher accuracy retrieving total absorption coefficient, backscattering, and backscattering by particles in Australian tropical coastal waters using QAA than with other semi-analytical algorithms such as the Carder [Carder et al., 2003] and GSM01models [Maritorena et al., 2002]. Furthermore, Green et al. [2008] using QAA in the northern Gulf of Mexico retrieved CDOM absorption ($a_{443}$) from SeaWiFS data of coastal waters influenced by the Mississippi River.

[7] Global estimates of particulate organic carbon can also be obtained using ocean color data. Empirical algorithms to derive POC concentration link particle concentration to optical backscattering [Stramski et al., 1999; Loisel et al., 2002; Stramski et al., 2008]. These algorithms use the remote sensing reflectance in a spectral band at 555 nm to retrieve the backscattering coefficient due to the small effect of phytoplankton absorption. These empirical solutions have provided general global estimates of the POC ocean reservoir, valuable in understanding the global carbon pools.

[8] In this study we hypothesize that the conservative behavior of CDOM and DOC in river-plume-influenced coastal waters, along with the possibility of detecting CDOM with Ocean Color remote sensing, allows for a globalize approach in the estimation of organic carbon export by large rivers. To address this hypothesis, we examined the seasonal transport of organic carbon by the Orinoco River into the eastern Caribbean using the entire SeaWiFS data set. A general goal was to expand and generalize the previous approach of Del Castillo and Miller [2008] by incorporating the use of the QAA semi-analytical algorithm to estimate CDOM and to estimate river discharge using hydrological models and data from NASA’s Tropical Rainfall Measuring Mission (TRMM). Unlike the Mississippi River system which is instrumented and there exists a large set of field measurements, the Orinoco River is not instrumented, field data is scarce, and it is difficult to obtain permission to conduct field campaigns. Therefore, as a large river, the Orinoco River is an ideal system in which to develop a remote sensing approach to estimate terrestrially derived flux and dynamics of DOC and POC to coastal waters.

2. Materials and Methods

2.1. Study Area

[9] The Orinoco River drains a basin of $1 \times 10^6$ km² characterized by a mixture of geological domains largely covered by floodplain forests and savanna forest environments [Latrubesse et al., 2005]. In general, waters originate from two main sources: the northwest portion of the watershed contributing “white waters” containing large amounts of dissolved and suspended materials; and the “black waters” of the southwest portion containing high concentrations of terrestrially derived dissolved material and small amounts of suspended solids [Lewis and Saunders, 1989]. The discharge of the Orinoco into the eastern Caribbean is mostly through the Gulf of Paria between the island of Trinidad and the east coast of Venezuela (Figure 1). Variations in discharge correspond to the seasonal meridional migration of the Intertropical Convergence Zone (ITCZ). Low discharge occurs from January to May (dry season) and high discharge from July to October (wet season). During the wet season the Orinoco floods 79% of the forested floodplain and 21% of the unforested floodplain, which is predominately covered by macrophytic algal mats [Lewis et al., 2000]. Flooding of these regions contributes to the dark colored dissolved organic matter in the main stem river. During low discharge periods, humic substances are estimated as 25% of DOC in the main stem and 40% of DOC in the black waters of the tributary Caroni River [Lewis and Saunders, 1990]. The maximum observed discharge in the wet season is around $7 \times 10^3$ m³ s⁻¹ and the minimum dry season discharge is approximately $1 \times 10^3$ m³ s⁻¹ [Vörösmarty et al., 1998]. During high flow, the river plume extends throughout the eastern Caribbean and can influence surface waters up to distances of 1000 km from the river delta [Müller-Karger et al., 1989]. Figure 2 shows a SeaWiFS diffuse attenuation coefficient (kd490) image of the plume extent into the eastern Caribbean during a high-flow period.
Field measurements used in this study were obtained during the Orinoco River Plume Experiment (ORIPEX) 3 and 4 [Del Castillo et al., 1999], ORIPEX 7 (19–24 November 2005) and a field campaign to the northeastern Caribbean [Méndez Silvagnoli, 2008]. Stations occupied during these field campaigns covered the near-field region directly influenced by the ORP from the Gulf of Paria toward the northeastern Caribbean. Since we intend to develop a global CDOM-DOC relationship to apply to remote sensing estimates of DOC export in poorly instrumented rivers, we pooled data from the northern Gulf of Mexico [Del Castillo and Miller, 2008] and the Orinoco River (as noted above) to investigate the suitability of our approach.

The primary study area used for the analysis of SeaWiFS images and organic carbon transport associated with Orinoco River discharge was a small region ~20 km north of the Dragons’ Mouth (DM in Figure 1) near the entrance of the ORP to the eastern Caribbean. This area was chosen as the closest entry point of the ORP into the Caribbean that was far enough from adjacent landmasses to avoid contamination of the remotely sensed signal from land reflectance. Sampling this area also permitted an analysis of the ORP during the rainy season as the plume flows east around Trinidad and Tobago into the Caribbean and the Guiana current. This study area was repeatedly sampled during the field campaigns and these measurements were used to develop and validate our remote sensing algorithms.

2.2. Water Sampling and Analysis

Temperature and salinity were measured using a SBE19 or SBE25 (SeaBird Electronics) CTD mounted on a SBE32 (SeaBird Electronics) carousel sampler. Water samples were immediately filtered by gravity under low-intensity red lights using Whatman GF/F filters mounted on an all-stainless steel filtration manifold (ORIPEX 3, 4) or using a polycarbonate filtration system under low vacuum (all others). Filters and sample bottles were baked (450°C–12 h). All other components were cleaned with acetonitrile and Nanopure water. The filtration system was flushed with sample (~20 ml) before collecting CDOM and DOC subsamples. DOC samples were placed in baked vials with caps lined with clean Teflon septa. Vials contained phosphoric acid to lower the sample pH below 2. CDOM samples were stored in baked amber-colored bottles. All samples were stored refrigerated until analysis.

Absorption spectra of filtered samples were obtained between 250 and 700 nm at 1 nm intervals using a Perkin Elmer Lamda-18 double-beam spectrophotometer equipped with
with matching 10-cm quartz cells. Nanopure water was used in the reference cell. Absorption coefficients, \( a(\lambda) \), were calculated using \( a(\lambda) = \frac{2.303}{A(\lambda)/l} \), where \( A \) is the absorbance (\( \log_{10}(I_0/I) \)) and \( l \) is the path length in meters. Absorption coefficient at 443 nm was used as an index of CDOM abundance and will be referred to as \( a_g(443) \).

[14] DOC concentration was determined by the thermal catalysis method using a Shimadzu TOC-5000 for ORIPEX 3 and 4 samples and a MQ1001 carbon analyzer [Qian and Mopper, 1996] for the ORIPEX 7 and Mississippi River Plume samples [Del Castillo and Miller, 2008]. Each instrument was equipped with a quartz catalyst and CO\(_2\) detector. Potassium hydrogen phthalate or glucose was used as the standard. An instrument blank was determined daily by reinjection of post-column condensation water that assumed to be carbon free. Instrument stability was monitored by repeated injection of Nanopure water and a standard (1.2 mg C L\(^{-1}\)) every 10 samples and full standard sets (0.60, 0.90, 1.20, 1.50, 3.00, and 6.00 mg L\(^{-1}\)) before and after each sample run. The effect of inter-instrument variability was considered minimal based on the use of standards, similar calibration procedures and the monitoring of instrument stability during the analyses. Comparative analyses of inter-instrument variability have shown that instrument operation rather than design is the major determinant of measurement variability [Hedges et al., 1993].

2.3. River Discharge Climatology

[15] Orinoco river hydrological data only spans the years 1923 to 1989 [Vörösmarty et al., 1998]. Hence, no data were available for our study period. Instead, the model WBM\(_{\text{plus}}\) [Wisser et al., 2010], a macroscale hydrological model, was used to estimate Orinoco River discharge. The WBM\(_{\text{plus}}\) is a fully coupled water balance and transport model that simulates vertical water exchange between the land surface and atmosphere and the horizontal water transport along a prescribed river network. This model was compared to monthly rainfall estimates obtained from the NASA-JAXA Tropical Rain-fall Measuring Mission (TRMM) rainfall algorithm 3B43(V6) with a 0.25° grid [Simpson et al., 1988; Kummerow et al., 2000]. This algorithm is continuously updated and has been successfully validated with global rain gauges including South America [Nicholson et al., 2003; Islam and Uyeda, 2007; Su et al., 2008; Ud din et al., 2008; Nair et al., 2009; Santos e Silva et al., 2009]. TRMM data were downloaded from the Goddard Distributed Active Archive Center (GDAAC) Tropical Rainfall Measuring Mission Web site (http://trmm.gsfc.nasa.gov/). Monthly averages of accumulated TRMM rainfall over the Orinoco River basin were linearly compared to monthly averages of river discharge obtained from the WBM\(_{\text{plus}}\) model. The resulting relationship was used to develop a climatology for the 1998 to 2010 period (Figure 3a).

2.4. Satellite Image Processing

[16] SeaWiFS Level 1a data from 1998 to 2010 were acquired from the NASA Ocean Color website (http://oceancolor.gsfc.nasa.gov/). Level 1a images were processed to monthly composites of remote sensing reflectance, \( R_{rs} \), using NASA’s SEADAS 6.1 software. Batch processing was
performed using SeaBatch 1.1 (Mike Brown, Dalhousie University). Monthly composites were used to minimize the effect of cloud cover that occurs throughout the region due to the ITCZ, with approximately 25 images per month each with variable cloud cover. Rs were extracted from all ocean color bands using a 9 × 9 pixel centered at 11° N, 61.8° W (DM area) from the monthly composites. This area is seasonally influenced by the ORP and was sampled during the field campaigns. Match-ups between field and satellite data were performed for samples associated with the river plume. However, some samples could not be matched due to high cloud coverage over the area. For waters outside the influence of the river plume (Case 1 waters) images collected within a day of sampling were also used. This was required due to the high amount of cloud cover in the region. MODIS-Aqua data could not be used in this study because the limited cloud free images were frequently contaminated with sun glint.

2.5. QAAv5 Algorithm

The quasi-analytical algorithm (QAAv5) [Lee et al., 2002, 2007, 2009] was used to derive total absorption...
Table 1. Modeled Orinoco River Flow and Organic Carbon Transport Estimates During the 1998–2010 Period\(^a\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Mean (±CI)</th>
<th>SD(^c)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>(4.65 \times 10^3)–8.54 (\times 10^4)</td>
<td>3.55 (\times 10^4) (±2.96 (\times 10^3))</td>
<td>1.93 (\times 10^4)</td>
<td>155</td>
</tr>
<tr>
<td>Wet season</td>
<td>2.52 (\times 10^4)–8.54 (\times 10^4)</td>
<td>4.84 (\times 10^4) (±3.11 (\times 10^3))</td>
<td>1.25 (\times 10^4)</td>
<td>77</td>
</tr>
<tr>
<td>Dry season</td>
<td>4.65 (\times 10^3)–7.27 (\times 10^4)</td>
<td>2.53 (\times 10^4) (±4.31 (\times 10^3))</td>
<td>1.72 (\times 10^4)</td>
<td>78</td>
</tr>
<tr>
<td>River Flow(^d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daily</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>1.15 (\times 10^0)–3.49 (\times 10^1)</td>
<td>1.43 (\times 10^1) (±1.44 (\times 10^0))</td>
<td>8.51 (\times 10^0)</td>
<td>136</td>
</tr>
<tr>
<td>DOC(^b)</td>
<td>1.56 (\times 10^0)–3.21 (\times 10^1)</td>
<td>1.44 (\times 10^1) (±1.22 (\times 10^0))</td>
<td>6.95 (\times 10^0)</td>
<td>136</td>
</tr>
<tr>
<td>POC</td>
<td>3.39 (\times 10^1)–1.89 (\times 10^2)</td>
<td>4.95 (\times 10^1) (±6.63 (\times 10^0))</td>
<td>4.14 (\times 10^0)</td>
<td>152</td>
</tr>
<tr>
<td>TOC</td>
<td>1.54 (\times 10^0)–4.95 (\times 10^1)</td>
<td>1.96 (\times 10^1) (±2.10 (\times 10^0))</td>
<td>1.24 (\times 10^0)</td>
<td>136</td>
</tr>
<tr>
<td>Annual</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>4.22 (\times 10^1)–1.28 (\times 10^2)</td>
<td>5.29 (\times 10^1) (±5.26 (\times 10^1))</td>
<td>3.10 (\times 10^2)</td>
<td>136</td>
</tr>
<tr>
<td>POC</td>
<td>1.24 (\times 10^1)–6.91 (\times 10^1)</td>
<td>1.81 (\times 10^2) (±2.42 (\times 10^1))</td>
<td>1.51 (\times 10^2)</td>
<td>152</td>
</tr>
<tr>
<td>TOC</td>
<td>5.61 (\times 10^1)–7.15 (\times 10^2)</td>
<td>7.10 (\times 10^1) (±7.68 (\times 10^1))</td>
<td>4.53 (\times 10^2)</td>
<td>136</td>
</tr>
</tbody>
</table>

\(^a\)DOC–DOC transport estimate using only in situ ORP data.

\(^b\)Confidence interval.

\(^c\)Standard deviation.

\(^d\)Units: m³ s⁻¹.

\(^e\)Units: g C y⁻¹.

\(\alpha(\lambda)\), the detritus and CDOM absorption coefficient \((a_d(\lambda))\) and the backscattering coefficient \((b_b(\lambda))\). Because of the similarity between the spectral shapes of CDOM absorption \((a_d(\lambda))\) and absorption by non-algal particles \(a_d(\lambda)\) and \(a_d(\lambda)\), both cannot be partitioned into \(a_d(\lambda)\) and \(a_d(\lambda)\) [Lee et al., 2002]. Hence, our analysis is based on \(a_d(\lambda)\) against in situ measured \(a_d\). QAAv5 provides an empirical approximation of the \(a_d(\lambda)\) spectral slope (S) based on Rrs443 and Rrs555 [Lee et al., 2009]. Qin et al. [2007] using an earlier version of the QAA observed that the QAA and other similar semi-analytical algorithms performed poorly in separating the components of total absorption spectra in coastal waters as a result of using fixed spectral slopes. In highly variable coastal environments \(S\) varies in relation to the proportion of marine and terrestrial end-members [Carder et al., 1989; Del Castillo et al., 1999; Del Castillo, 2005]. \(S\) is more or less constant in waters dominated by a fresh water end-member (e.g., salinities <30) and changes rapidly above the salinity threshold when marine CDOM becomes dominant [e.g., Del Castillo, 2005]. Therefore, with the addition of deriving an estimate of \(S\), we expected QAAv5 to be better suited for estimating CDOM in the ORP.

[18] Performance of the QAAv5 algorithm was assessed comparing SeaWiFS-derived \(a_d(\lambda)\) (i.e., 443 nm) with field measurements (i.e., in situ \(a_d(\lambda)\)). Statistical analysis used to assess differences in \(a_d(\lambda)\) and \(a_d(\lambda)\) samples means included a t-test, standard deviation of the absolute percent difference (APD), root mean square error (RMSE) and linear regression. The statistical analysis was performed using StatPlus:mac LE, version 2009 (AnalystSoft Inc., Vancouver, B.C., Canada). The RMSE and APD were calculated following [Bailey and Werdell, 2006; Mannino et al., 2008; Kowalczyk et al., 2010] and given by:

\[
\text{RMSE} = \left[ \frac{1}{N} \sum (a_d(\lambda)_\text{SeaWiFS} - a_d(\lambda)_\text{in situ})^2 \right]^{1/2}
\]

Mean APD\% = \[
\sum \left( \frac{(a_d(\lambda)_\text{SeaWiFS} - a_d(\lambda)_\text{in situ})}{a_d(\lambda)_\text{in situ}} \right) \times 100 / N
\]

2.6. Particulate Organic Carbon Calculation

[19] Estimates of particulate organic carbon (POC) concentration (mg C m⁻³) were obtained using SeaWiFS Rrs bands at 443, 490 and 555 nm following the algorithms of Stramski et al. [2008] and Stramska [2009]:

\[
\text{POC}_{443} = 203.2 \left( \frac{\text{Rrs443}}{\text{Rrs555}} \right)^{1.034}
\]

\[
\text{POC}_{490} = 308.3 \left( \frac{\text{Rrs490}}{\text{Rrs555}} \right)^{1.639}
\]

Our analysis was based on the average of both algorithms due to the uncertainties in precision discussed by Stramska, [2009]. These POC estimates represent the concentration present in the river plume (POCp). Adjustments of these values with in situ averages allowed us to approximate POCp to the amounts present on the Orinoco River, (POC_R). This modification is described further in section 3.

3. Results

[20] Average river flow calculated for the Orinoco River during the period 1998 to 2010 based on the WBM data and TRMM 3B43 (V6) rainfall data were comparable to the flow of 3.6 \(\times 10^4\) m³ s⁻¹ reported by Spitz and Leenheer [1988] and Vörösmarty et al. [1998] (Table 1). River discharge varied from 4.6 \(\times 10^3\) m³ s⁻¹ to 8.5 \(\times 10^4\) m³ s⁻¹ with an average of 2.5 \(\times 10^4\) m³ s⁻¹ during the dry season, increasing to an average of 4.8 \(\times 10^4\) m³ s⁻¹ during the wet season.

3.1. In Situ Data

[21] Surface values of \(a_d(\lambda)\) measured in situ in the eastern Caribbean varied from 0.01 m⁻¹ to 0.83 m⁻¹ with the maximum associated with the ORP. For areas under the direct influence of the ORP, \(a_d(\lambda)\) ranged from 0.03 m⁻¹ to 0.83 m⁻¹ (Table 2). DOC, as expected, showed a gradient with highest concentrations at stations close to the Orinoco River mouth, ranging from 0.9 mg C l⁻¹ to 5.2 mg C l⁻¹ (Table 2). Surface salinity in the region varied from 19.7 to
Table 2. In Situ and Modeled Concentrations of DOC, Salinities and CDOM Absorption Coefficient at 443 nm at the Eastern Caribbean

<table>
<thead>
<tr>
<th>Sampled Area</th>
<th>Parameter</th>
<th>Range</th>
<th>Mean</th>
<th>SD µ</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>In situ ORP</td>
<td>$a_{443}$</td>
<td>0.03–0.83</td>
<td>0.31±0.1</td>
<td>0.24</td>
<td>33</td>
</tr>
<tr>
<td>DOC</td>
<td>0.90–5.20</td>
<td>1.9±3.5</td>
<td>1.03</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Salinity</td>
<td>19.70–35.0</td>
<td>30.3±1.6</td>
<td>4.8</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Gulf of Paria</td>
<td>$a_{443}$</td>
<td>0.61–0.83</td>
<td>0.73±0.1</td>
<td>0.09</td>
<td>5</td>
</tr>
<tr>
<td>DOC</td>
<td>1.8–3.6</td>
<td>2.51±0.9</td>
<td>0.73</td>
<td>5</td>
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<tr>
<td>Salinity</td>
<td>19.7–22.1</td>
<td>20.6±1.2</td>
<td>0.99</td>
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<tr>
<td>DM Zone</td>
<td>$a_{443}$</td>
<td>0.08–0.68</td>
<td>0.35±0.02</td>
<td>0.2</td>
<td>8</td>
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<tr>
<td>DOC</td>
<td>1.0–3.3</td>
<td>1.6±0.6</td>
<td>0.73</td>
<td>9</td>
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</tr>
<tr>
<td>Salinity</td>
<td>24.4–35.0</td>
<td>31±2.5</td>
<td>3.0</td>
<td>9</td>
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<tr>
<td>Eastern Caribbean Zone</td>
<td>$a_{443}$</td>
<td>0.01–0.83</td>
<td>0.15±0.1</td>
<td>0.21</td>
<td>75</td>
</tr>
</tbody>
</table>

<table>
<thead>
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<tbody>
<tr>
<td>SeaWiFS</td>
<td>$a_{443}$</td>
<td>0.02–0.86</td>
<td>0.24±0.2</td>
<td>0.29</td>
<td>10</td>
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<tr>
<td>All Data</td>
<td>$a_{443}$</td>
<td>0.01–0.96</td>
<td>0.04±0.001</td>
<td>0.11</td>
<td>517</td>
</tr>
<tr>
<td>DM Zone (12-year period)</td>
<td>$a_{443}$</td>
<td>0.02–0.91</td>
<td>0.24±0.03</td>
<td>0.21</td>
<td>148</td>
</tr>
<tr>
<td>DOC</td>
<td>0.961.1–2.8</td>
<td>1.66±0.1</td>
<td>0.44</td>
<td>148</td>
<td></td>
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<tr>
<td>Salinity</td>
<td>21–36</td>
<td>30.4±0.9</td>
<td>3.6</td>
<td>148</td>
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<tr>
<td>POC</td>
<td>0.09–0.66</td>
<td>0.24±0.02</td>
<td>0.1</td>
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<td></td>
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<tr>
<td>DOC®</td>
<td>1.5–9.52</td>
<td>4.3±0.11</td>
<td>0.75</td>
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<tr>
<td>DOC®</td>
<td>3.5–6.96</td>
<td>4.70±0.2</td>
<td>0.89</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>POC®</td>
<td>0.56–3.4</td>
<td>1.44±0.1</td>
<td>0.62</td>
<td>152</td>
<td></td>
</tr>
<tr>
<td>TOC®</td>
<td>2.33–8.9</td>
<td>5.8±0.2</td>
<td>1.2</td>
<td>148</td>
<td></td>
</tr>
</tbody>
</table>

35 showing correlation with DOC ($r^2 = 0.50$, n = 31) along the ORP gradient. This relationship persisted when pooled with samples from the Mississippi River Plume (MRP) area ($r^2 = 0.73$, n = 262) (Figure 4a). There was also a strong correlation between salinity and $a_{443}$ within the ORP ($r^2 = 0.71$, n = 31). Again, this relationship was maintained when samples were added from the MRP ($r^2 = 0.93$, n = 661) (Figure 4b). DOC and $a_{443}$ within the ORP were also correlated ($r^2 = 0.62$, n = 27) suggesting that a large proportion of DOC in the region is colored material. When pooled with the Mississippi River Plume data, a stronger correlation between DOC and $a_{443}$ was observed ($r^2 = 0.70$, n = 159) (Figure 4c). Analysis comparing the slopes of the regression lines of the ORP and pooled (ORP+MRP) data sets showed no statistically significant differences between them, $t = 0.95$ (2,184) = 1.97 calculated $t = 0.77$ P = 0.001 [Zar, 2010]. These regression lines presented different elevations, $t = 0.05$ (2,184) = 1.97 calculated $t = 1.98$ P = 0.001 (Figure 4c). This suggest that the variability around the regression lines may be attributed to the lower number of samples for the ORP, but retaining the underlying CDOM-DOC relationship of the pooled data set.

[25] Values of $a_{443}$ for the Gulf of Paria stations varied from 0.61 m$^{-1}$ to 0.83 m$^{-1}$. DOC concentration varied from 1.8 mg C L$^{-1}$ to 3.6 mg C L$^{-1}$ and salinity varied from 19.7 to 22.1 (Table 2). In general, $a_{443}$ in the DM area ranged from 0.08 m$^{-1}$ to 0.68 m$^{-1}$. DOC concentration at these stations varied from 1.0 mg C L$^{-1}$ to 3.3 mg C L$^{-1}$ and salinity from 24.4 to 35.0.

[26] The spectral slope remained constant ~0.017 in salinities below 30 suggesting no significant differences in CDOM optical properties through the zone, retaining the optical properties of the riverine organic matter [Blough et al., 1993; Del Castillo et al., 1999; Del Castillo, 2005].

3.2. SeaWiFS Modeled $a_{443}$

[24] Estimates of $a_{443}$ derived from SeaWiFS data were similar to in situ values. However, the QAA algorithm tended to underestimate $a_{443}$ values in optically complex waters of the ORP. SeaWiFS-derived $a_{443}$ and in situ $a_{443}$ values were highly correlated in the ORP ($r^2 = 0.85$, slope = 1.3, n = 10, P < 0.001). When these data were pooled with data from the northeastern Caribbean and the Gulf of Mexico, a similar relationship was observed as for the ORP ($r^2 = 0.86$, slope = 0.93, n = 95, P < 0.001) (Figure 5a). The observed root mean square error (RMSE) for the relationship was 0.041 m$^{-1}$ and the observed mean APD was 0.62%.

This high APD is probably due to the estimates differences at optically complex waters that although proportional where in general less that the observed in situ values. A Student t-Test [Zar, 2010] indicated no significant differences between the means of the SeaWiFS $a_{443}$ and in situ $a_{443}$ estimates, $t = 0.05$ (2,190) = 1.97 calculated $t = 0.76$ P = 0.45. The remote sensing estimates for the DM zone thorough the 1998–2010 period were within the in situ values and varied from 0.015 m$^{-1}$ to 0.91 m$^{-1}$. We also observed a significant correlation between $a_{443}$ and the Orinoco River flow ($r^2 = 0.42$ n = 147; Figures 3a and 3b). This relationship is based on the modeled river flow, which depends on good retrieval of $a_{443}$, the distance from sampling site to the river mouth, and mixing of the plume with neighboring waters.

3.3. DOC Model

[25] An empirical model to estimate DOC was developed based on the relationship between measured in situ salinity and DOC (Figures 3a–3c). This model is defined by:

\[
\text{Salinity} = 36.65 - 26.1 \times a_{443} \quad (5)
\]

\[
\text{DOC}_p = 5.3 - 0.12 \times \text{Salinity} \quad (6)
\]
Modeled salinity in the DM zone for the 12-year period varied from 21 to 36 and the corresponding derived DOC concentration varied from 1.1 mg C L\(^{-1}\) to 2.8 mg C L\(^{-1}\), both within the expected in situ values in this zone (Table 2). Modeled DOC\(_P\) and in situ DOC at the ORP showed a strong relationship (\(r^2 = 0.85, \text{Slope} = 0.72, n = 9, P = 0.001\)), remaining strong when pooled with samples of the MRP (\(r^2 = 0.80, \text{Slope} = 0.78, n = 34, P = 0.001\)) (Figure 5b). The observed overall RMSE between the observed and modeled DOC was 33.9 and the observed mean APD was 17.4%. A Student t-Test to test differences between the means indicated no significant differences between DOC\(_P\) and in situ DOC, \(t_{0.05 (2),62} = 1.99\) calculated \(t = 1.06\) \(P = 0.30\). These results show that our method explained \(~70\%\) of the variability in DOC transport by the Orinoco River. Figure 6

![Figure 4](image-url)

**Figure 4.** (a) Relationship between DOC and salinity from surface samples obtained during the ORIPEX field campaigns throughout the Orinoco River Plume (open circles, \(r^2 = 0.50, n = 31\)) and pooled with samples from the Mississippi River Plume [Del Castillo and Miller, 2008] (solid circles, \(r^2 = 0.73, n = 262\)). (b) Relationship between \(a_g\) and salinity. Data shown include samples from the Orinoco River and Mississippi River plumes (\(r^2 = 0.93, n = 661\)). (c) Relationship between \(a_g\) and DOC. Orinoco River Plume (open circles, \(r^2 = 0.62, n = 27\)) and pooled with samples from the Mississippi River Plume (solid circles, \(r^2 = 0.70, n = 159\)). The statistics for comparison between slopes are: \(t_{0.05 (2),184} = 1.97\) calculated \(t = 0.77\) \(P = 0.001\). For the elevations, \(t_{0.05 (2),184} = 1.97\) calculated \(t = 1.98\) \(P = 0.001\).

![Figure 5](image-url)

**Figure 5.** (a) Relationship between SeaWiFS \(a_g\) and in situ \(a_g\) for samples in the Orinoco River Plume (solid circles, \(r^2 = 0.85, \text{slope} = 1.3, n = 10\)) and pooled with samples from the eastern Caribbean and Mississippi River Plume (open circles, \(r^2 = 0.86, \text{slope} = 0.93, n = 95\)). (b) Relationship between modeled river plume DOC\(_P\) and in situ DOC for samples in the Orinoco River Plume (open circles, \(r^2 = 0.85, \text{slope} = 0.72, n = 9\)) and pooled samples (solid circles, \(r^2 = 0.80, \text{slope} = 0.78, n = 34\)). Dashed lines represents correlation line, solid line represent 1-to-1 relationships.
shows a SeaWiFS image of the distribution of the Orinoco River Plume DOC throughout the eastern Caribbean during high-flow season, the image is from 20 September 2006. Statistical analysis of 2,000 points selected at random over this image showed a DOC average of 1.03 mg C L$^{-1}$ (SD = 0.11 mg C L$^{-1}$), a normal value for these oceanic surface waters.

We extrapolated DOC$_P$ concentrations to the expected concentrations at the river itself, DOC$_R$ applying a two end-member mixing model [Del Castillo et al., 2000; Del Castillo and Miller, 2008]. This model assumed a riverine end-member salinity of 0, and a marine end-member with salinity 35 and a DOC concentration of 1.14 mg C L$^{-1}$. The DOC and salinity values of the marine end-member were determined from the in situ ORP data used in this study. The resulting modeled DOC$_R$ concentrations were observed to vary throughout the sampled period from 1.9 mg C L$^{-1}$ to 5.2 mg C L$^{-1}$, average of 4.3 mg C L$^{-1}$ (Table 2). These estimates were then multiplied by the modeled river flow to obtain the DOC transport per day of the Orinoco River, which varied from 1.15 x $10^9$ g C day$^{-1}$ to 3.49 x $10^9$ g C day$^{-1}$ with average of 1.43 x $10^9$ g C day$^{-1}$ throughout the 1998 to 2010 period (Table 1).

Similar analysis of DOC transport considering only the in situ ORP data (Figure 4c) showed river DOC concentrations varying from 3.52 mg C L$^{-1}$ to 6.96 mg C L$^{-1}$ and average of 4.70 mg C L$^{-1}$ (Table 2). The average DOC transport per day was 1.44 x $10^9$ g C day$^{-1}$, ranging from 1.56 x $10^9$ g C day$^{-1}$ to 3.21 x $10^9$ g C day$^{-1}$ (Table 1). Even though DOC concentration showed to be higher that the estimate with the pooled data set, the DOC transports are comparable. The poling of both data sets into a single data set favored conservative DOC estimates similar to the in situ values. This observation denotes the importance of river discharge over concentration of DOC in estimating carbon export.

3.4. Particulate Organic Carbon

The POC$_P$ concentrations estimated from SeaWiFS imagery presented a range of 0.09 mg C L$^{-1}$ to 0.66 mg C L$^{-1}$. It is well known that a large fraction of river particulate organic matter is initially deposited near the river mouth, decreasing sharply within a few km of the mouth [Trefry et al., 1994; Dagg et al., 2004]. Therefore, calculating river POC (POC$_R$) from SeaWiFs imagery collected over the DM area is not straightforward. To get a coarse approximation of the quantities present in the river we introduced a correction factor based on the observed in situ average for the river it self. The historically recorded in situ average for the Orinoco River is about 1.45 mg C L$^{-1}$ [Lewis and Saunders, 1989; Paolini, 1995], and our estimate of POC$_P$ was 6 times less than this value. By applying a correcting factor of 6 to POC$_P$ to correct for the missing portion we obtained an average of 1.44 mg C L$^{-1}$ of POC$_R$ for the period 1998–2010, that is similar to the historical average from which we derived the proportion. These new estimates of POC$_R$ ranged from 0.56 mg C L$^{-1}$ to 3.4 mg C L$^{-1}$ (Table 2).

Even though our POC$_R$ estimates are an approximation, we considered that its seasonal variations respond to the observed POC fluxes interpreted from ocean color data. In fact our estimates where within the historical variations, the lowest in situ record for POC during dry season is 0.82 mg C L$^{-1}$ increasing to 3.6 mg C L$^{-1}$ in the wet season [Paolini, 1995], which places our estimates within the
expected range of the river. In summary the daily $\text{POC}_R$ transport of the Orinoco River varied from $3.39 \times 10^9$ g C day$^{-1}$ to $1.89 \times 10^{10}$ g C day$^{-1}$ throughout the sampled period (Table 1).

3.5. Orinoco River Total Organic Carbon Transport

[30] Total organic carbon values ($\text{POC} + \text{DOC}$) ranged from $2.33 \text{ mg C L}^{-1}$ to $8.9 \text{ mg C L}^{-1}$ of TOC$R$ (Table 2). Daily transport varied from $1.54 \times 10^9$ g C d$^{-1}$ to $4.95 \times 10^{10}$ g C d$^{-1}$ (Table 1). Annual transport based on satellite imagery averaged $5.29 \times 10^{12}$ g C y$^{-1}$ of DOC and $1.81 \times 10^{13}$ g C y$^{-1}$ of POC, for a total of $7.10 \times 10^{12}$ g C y$^{-1}$ of organic carbon (Table 1) about a 3.1% of the total estimated organic transport by the world major rivers, $236 \times 10^{12}$ g C y$^{-1}$ [Schlunz and Schneider, 2000].

4. Discussion

[31] This study analyzed the transport of organic carbon associated with the Orinoco River Plume (ORP) into the eastern Caribbean. Previous studies have shown that the ORP directly influences the optical properties of eastern Caribbean surface waters [Müller-Karger et al., 1989; Blough et al., 1993; Del Castillo et al., 1999; Corredor et al., 2003, 2004]. The distribution of CDOM determined by surface patterns of $a_{443}$ indicates that CDOM concentration changes as the ORP mixes with oceanic waters throughout the eastern Caribbean. The direct relationship of DOC and $a_{443}$ in this region and constant spectral slope throughout the Gulf of Paria suggests that CDOM and DOC concentration is governed in large-part by the concentration and mixing of river waters indicating a conservative behavior throughout the plume [Blough et al., 1993; Del Castillo et al., 1999; Odriozola et al., 2007]. This also suggests that CDOM and DOC co-verify significantly in the ORP, which is a fundamental requirement to appropriately estimate organic carbon transport from the ORP to the eastern Caribbean.

[32] SeaWiFS imagery for the eastern Caribbean are often contaminated by cloud coverage. This especially occurs when the ITCZ is situated in its northern most position and lead to a variable amount of usable daily images per month. The variable number of usable images may create a bias in monthly averages. For the SeaWiFS global annual mean, Gregg and Casey [2007] reported a bias of about 6%. Even though this bias may not be an issue in global estimates, it must be considered at regional scales where there may be a amplified effect, especially when dealing with the processes associated with river discharge and plume dynamics. Kwiatkowska et al. [2007] showed that at higher spatial resolution the percentage of the ocean observed by the sensor is reduced, for SeaWiFS at 1 km resolution its coverage is about 6% of the total ocean. In the eastern Caribbean it must be considered then that remotely sensed information is subject to a higher bias during the season of high cloud coverage (rainy season). Monthly estimates that would typically include dozens of daily samples will probably include fewer samples and potentially under sampling the variability of in-water constituents intended in the analysis. Müller-Karger et al. [1990] reported that remote sensing may underestimate phytoplankton blooms due to clouds contaminating a study area when the highest concentration of chlorophyll occurs. During this study, the uncontaminated SeaWiFS images may have failed to capture various pulses of CDOM and related organic material transported by the Orinoco River. As stated earlier, MODIS images could not be used due to high cloud cover and sun glint contamination.

[33] Associated to image variability is the possible in-pixel variability, especially in optically complex waters. There is an intrinsic variation due to spatial and even temporal differences that may arise when matching up in situ to the remote sensed signal. In general comparisons with satellite data assume that there is uniform in-pixel variation with low standard deviations, which may not be a reality in optically complex waters. Yuan et al. [2005] addressed this issue and observed that in Case II waters [i.e., those in which the optical properties are substantially affected by colored dissolved organic matter CDOM or suspended particulate matter from sources other than phytoplankton] the large discrepancy between remote sensing and in situ data was caused by large in pixel variation. In Case I waters the dominance of one property (e.g., phytoplankton) and low spatial and temporal variations, result in low standard deviations and a better correlation with the remote sensed signal. Our correlation performed better in Case I waters increasing in error as the ORP influence increased. Therefore the large intrinsic variability in eastern Caribbean waters, and especially those influenced by the ORP, makes in-pixel variability another factor to consider. This clearly represents a limitation on how well our remote sensing retrievals may match field measurements. Simply put, a perfect remote sensing retrieval may not match a field measurement if this field measurement is different from the mean within the pixel. This shows that, in areas with high spatial variability, it is better to use underway measurements (binned to pixel size) to evaluate remote sensing retrievals.

[34] Ocean currents and eddies are another source of variability in the region. The ORP area is affected by the meridional overturning circulation and the North equatorial current through the Grenada passage. This flow creates instabilities that favors the formation throughout the zone of the most energetic eddies in the Caribbean Sea [Canal-Silander, 2006; Jouanno et al., 2009]. These are enhanced by eddy potential vorticity gradients created by the presence of the fresh water inputs from the Orinoco River and the Amazon River [Cherubin and Richardson, 2007]. The Amazon Plume seasonally has some effect on the zone, when its surface area peaks during June–July entering the Caribbean region through the Lesser Antilles [Müller-Karger et al., 1988, 1989; Hu et al., 2004]. The observed moderate relationship of the modeled parameters with river flow could be explained by the intrinsic variability within the region and the nature of a river plume itself.

[35] There is high degree of uncertainties in QAA derived IOPs when applied to optically complex waters. In general the QAA protocol includes uncertainties retrieving total $a_{443}$ that can be as much as 37% due to its dependence upon accurate retrieval of particles backscattering ($b_{wp}$) [Lee et al., 2010]. In waters such as the ORP, the presence of inorganic suspended particles may affect backscattering retrievals. Wozniak and Stramski [2004] reported that high minerals concentrations modify the reflectance spectra rendering the remote sensing algorithms useless. Rosado-Torres [2008] observed effects on QAA estimates by abnormal values in red portions of the total absorption spectra ($a_{\text{total}}(\lambda)$), leading
to negative values for the phytoplankton absorption coefficient ($a_{ph}$). Some of our estimates seem to show the same pattern with QAA $a_{ph}(667)$ in negative values, and abnormally low values in the red portion of the visible spectra for the $a_{total}(\lambda)$. There is no evidence to suggest that our results are derived from the effect of clays, but the abnormal behavior of the $a_{total}(\lambda)$ suggest failure of the model in modeling $b_{hp}(\lambda)$, one of the first steps in the inversion algorithm. Stramski and Kiefer [1991] showed that non-living organic and mineral particles are the primary contributors to $b_{hp}$ in oceanic environments, an effect that should be amplified in coastal areas. To summarize, even though QAAv5 in the ORP seemed to underestimate the in situ values, it accomplished a seamless transition from open ocean to coastal waters detecting the natural variations of the ORP.

[36] Despite image variability and methodology biases, our analysis captured the dynamics of organic carbon in the Orinoco River Plume. The variability in organic carbon fluxes responded mostly to the seasonality of the river flow, and not to variations in the DOC and POC concentrations within the river waters. This is apparent also when we restricted our DOC model to in situ ORP data, observing similar results even with slightly higher river DOC estimates. The lower number of samples in the ORP data set favored higher DOC estimates influenced by the variability in the samples. The collection of ORP and MRP into a single data set favored a decrease in the variability and into conservative DOC estimates. On average, our estimates of DOC in the plume were similar and within the observed range in the eastern Caribbean area. The extrapolated river concentrations for the 12-year period covered in this study were similar to those reported by Lewis and Saunders [1989] for 1982 to 1985. In a similar analysis for the Mississippi River Plume [Del Castillo and Miller, 2008], observed that the variability in DOC transport estimates was driven mainly by changes in the river flow, not in the concentrations of organic carbon in the river. Thus, it is then reasonable to consider that, in a watershed such as the Orinoco River were the hydrologic regime has not been severely impacted by anthropogenic effects [Lewis, 1988; Lewis et al., 2000], the concentrations of organic materials does not change enough to impact total carbon export by the river. It has been documented that the organic carbon concentrations in the Orinoco River remain relatively constant and respond to seasonal variations in water flow with biogenic substances maintaining concentrations similar to those of the drier watersheds [Lewis and Saunders, 1989]. Contrary to the inorganic dissolved constituents of the river waters, the organic components are not diluted with increasing water flow, but increases in concentration during flooding. This phenomenon is known as the purging effect and it may involve the removal of organic carbon from concentrated terrestrial sources that had accumulated during dry season [Cushing et al., 2006]. Most of the organic matter that arrives to the Orinoco main stem comes from the southeast region of the watershed, or the Guyana shield, and from the floodplains. The floodplain is made from approximately 2300 basins, each with a floodplain lakes surrounded by macrophytes mats and forest. During dry season organic matter accumulates in the floodplain area, from the desiccation of macrophytes mats and the litter fall of the forested floodplain [Lewis et al., 2000]. It is from these areas where most of the organic matter is purged into the Orinoco River. Consequently, seasonal variations of dissolved organic carbon are small and the purging effect offset dilution, which constrains concentrations to a small range.

[57] In terms of organic carbon transport by the river our estimates reflect a 6.1% increase in DOC transport over the reports from Lewis and Saunders [1989]. These differences may reflect changes in the hydrology and the fact that organic carbon historical data for the river is limited, ~3 years [Lewis and Saunders, 1989] This data set may not capture natural climate variations throughout the basin, like those induced by the El Niño-La Niña Southern oscillations (ENSO). Long-term rainfall analysis for the region confirms that El Niño events are associated with negative rainfall anomalies and La Niña with positive anomalies in northern South America [Poveda and Mesa, 1997]. In an analysis of the relationship of ENSO and the climate of Venezuela between 1950 and 2004, Guevara [2006] reported droughts and low river flows during ENSO events in the Caroni River, one of the tributaries of the Orinoco River. About 85% of ENSO years coincided with rainfall deficits bigger than 35%. One of those events occurred within the period of 1982 to 1985, the sampling period reported by Lewis and Saunders [1989], a lower precipitation period that probably lead to a lower carbon transport estimate.

[38] The limitations in estimating POC within the river let us to constrain our ocean estimates within the variability of historical values for the river. Even though, our POC concentrations were within the expected range and its transport is similar to the observed for the Orinoco River, we cautiously propose them as the particulate carbon concentrations during the 1998 to 2010 period. In large rivers suspended organic material is very small and primarily detrital in origin. In tributaries of the upper Orinoco 1% or less of the POC is larger than 500 $\mu$m, and >97% of coarse particulate organic material is allochthonous (mostly leaves) [Cushing et al., 2006]. For the Orinoco main stem, autochthonous particulates (bacteria, phytoplankton and zooplankton) account for only 1% of the POC [Lewis and Saunders, 1990]. Consequently, is reasonable to expect that, due to its dimensions and nature, large portions of these particulate materials would remain suspended in river waters. This may explain why our oceanic estimates adjusted for the fraction lost during its transit throughout the Gulf of Paria, were within the reported range for the river. Furthermore, Ittekkot [1988] observed that at least 65% of the POC load of large rivers is refractory because it has been subject to microbial attacks in soils, for the Orinoco River the refractory portion is 75% of the POC load. Therefore we would expect that most of the particulate would travel farther and conservatively throughout the Gulf of Paria into the Caribbean region.

5. Conclusion

[39] In conclusion our results corroborates the possibility of estimating organic carbon transport by large rivers, such as the Orinoco River, using remote sensing data and hydrological models. We propose that, because river flow is the dominant term in organic transport, a global CDOM-DOC relationship can be used to estimate carbon export in rivers with sparse or no field data. The flexibility of the semi-analytical algorithm QAAv5 in estimating $a_{ph}(443)$ within waters of variable optical complexity showed its efficacy in
the Orinoco River Plume. Our methodology here applies only to river plumes where there is a conservative behavior between salinity, CDOM, and DOC. This is why our data sets of the Orinoco River and the Mississippi River plumes correlated and were successful tools in the analysis. In areas where the influx of multiple sources of CDOM and DOC mix with the river plume, such as in estuarine systems, their conservative relationship is expected to deviate. Small rivers for instance not necessarily carry such relationship, and are subject to anthropogenic-induced changes in the landscape and to rain patterns. But at global scales the transport by large rivers such as the Orinoco River outweigh the impact of these areas to the global carbon cycle, our estimates of total organic carbon flow into the eastern Caribbean by the Orinoco River represent a 3.1% of the total continental discharge.

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