Microtidal subterranean estuaries as a source of fresh terrestrial dissolved organic matter to the coastal ocean

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Microtidal subterranean estuaries as a source of fresh terrestrial dissolved organic matter to the coastal ocean

Mathilde Couturier, Christian Nozais, Gwénaëlle Chaillou

Abstract

This paper reports on the distribution of DOM along the subterranean estuary (STE) of a microtidal beach located in the Gulf of St. Lawrence (Iles-de-la-Madeleine, Quebec, Canada). We combined porewater DOC concentrations as well as CDOM absorbance- and fluorescence-derived indices (SUVA254, FL and BIX) to explore the groundwater-borne DOM transformations along the groundwater flow path to the outflow face of the beach. Based on these optical indices and multivariate analysis, results reveal a highly complex environment where biogeochemical processes and water-rock interaction alter molecular composition of DOM. Marine and groundwater end-members exhibited significantly different optical derived indices. Along the STE, however, DOC and CDOM showed non-conservative behaviour with the production of both “new” high molecular weight (MW) and lignin-derived compounds as well as microbially-derived CDOM. There is no significant relationship between DOC and CDOM optical properties because of the complex and dynamic system. A redundancy analysis (RDA) revealed a relationship between redox conditions and DOM pool signature. The RDA results highlighted a negative correlation between DOC and dissolved Fe, particularly in the suboxic zone of the STE where Fe-oxides are reduced. The RDA showed that the increase of SUVA254 (i.e., from high MW CDOM compounds with low aromaticity to low MW CDOM compounds with high aromaticity) is inversely correlated to dissolved metals, particularly total dissolved Mn. Whatever the processes involved in the carbon behaviour, our results showed the dominance of terrestrial DOM pool all along the STE. Despite the fact that marine-derived particulate solutes are considered as the primary source of DOM in tidal sands, our study illustrated how groundwater-borne solutes may affect reaction in STE and opens questions about the terrestrial DOM export to a coastal bay.

1. Introduction

While sandy beaches have long been considered as biogeochemical deserts (Huettel et al., 1996), recent studies have shown that tidal sands act as active zones for organic matter transformation and mineralization (Anschutz et al., 2009; Loveless and Oldham, 2010; Rocha et al., 2009; Suryaputra et al., 2015). When a sandy beach is hydraulically connected to an aquifer, fresh groundwater discharges occur in the coastal ocean. These discharges, which take place at the tidal beach face or below the ocean surface, are now recognized as critical pathways for carbon and inorganic nutrients to reach the coastal ocean (Beck et al., 2007; Chaillou et al., 2015; Santos et al., 2009). Like surface estuaries, the distribution of freshwater and seawater in the STE controls the geochemical conditions and may affect the fate of chemicals exported to the coastal ocean. Recent studies have investigated the behaviour of organic carbon (OC) from the aquifer to the coastal ocean. Transport of dissolved organic carbon (DOC) was reported to be conservative in the STE of a large tidal flat in Hampyeong Bay (South Korea; Kim et al., 2013) and in the STE of West Neck Bay (NY, USA; Beck et al., 2007). In contrast, other studies have reported the production and loss of DOC along STEs, for example, in the Gulf of Mexico (Santos et al., 2009), in South Carolina (Gohi and Gardner, 2004), and, more recently, in the Gulf of St. Lawrence (Chaillou et al., 2015). These non-conservative behaviours indicate either additional DOC sources or removal processes along the pathway, depending on redox conditions. Marine-derived particulate solutes are considered as the main source of DOC in tidal
sands (Anschutz et al., 2009; Kim et al., 2012; McLachlan and Brown, 2006). However, terrestrial carbon could be another important carbon source in STEs where groundwaters flow from the aquifer to the coastal zone.

Dissolved organic matter (DOM) represents a fundamental link between terrestrial and aquatic carbon cycles and plays a significant role in the biogeochemistry of aquatic ecosystem (Hedges and Keil, 1995). Nevertheless, our knowledge on groundwater-borne DOM in STEs is scarce compared to the available information on inorganic nutrients (Kim et al., 2012; Suryaputra et al., 2015). In natural settings, DOM is derived from terrigenous and aquatic macro- (e.g., plants, animals) and micro- (e.g., algae and bacteria) organisms from fresh and marine systems. Chromophoric dissolved organic matter (or CDOM) is the fraction that absorbs ultraviolet (UV) and visible light and, consequently, is the fraction that controls the optical properties of waters (Green and Blough, 1994). The biogeochemical origin and nature of DOM can be determined by examining the optical signatures of CDOM (Boyd and Osburn, 2004; Coble, 1996; Fellman et al., 2010; Jaffé et al., 2014; Stedmon et al., 2003). This has been done in rivers, lakes, and estuarine systems (e.g., Glaz et al., 2015; Huguet et al., 2009, 2010; Massicotte et al., 2013; Retamal et al., 2007; Stedmon et al., 2010), in subsurface and cave waters (Baker and Genty, 1999; Baker and Lamont-Black, 2001; Birdwell and Engel, 2010), in the coastal ocean (Benner et al., 2005; Guéguen et al., 2005; Kowalczyk et al., 2013; Stedmon et al., 2000), and, more recently, in the porewater of tidal sands and submarine discharges (Kim et al., 2012; Suryaputra et al., 2015). The optical characteristics of CDOM in STEs are supposed to reflect those of the DOM sources and may be controlled by microbial activity, mixing processes (i.e., flocculation), and sorption onto mineral particles, as observed in estuaries (Asmala et al., 2014b; Coble, 2007).

In this study, we focussed on DOC and CDOM to explore the origin of DOM in the system and the biogeochemical processes that affect the DOM pool. We used fluorescence and absorbance CDOM indices in combination with porewater chemistry and DOC analyses, and linked the optical properties of the DOM pool to environmental conditions along the STE. UV spectroscopy was used to characterize the structure and molecular composition of CDOM, and fluorescence allowed the discrimination of a few fluorophores that may vary between environments (Coble, 1996; Stedmon et al., 2003). Fluorescence indices can also be used to determine CDOM origin and dynamics (Huguet et al., 2009; Para et al., 2010). Here, we focussed on five optical CDOM indices: (i) the spectral absorption \(a_\lambda\) coefficient, which is a tracer of CDOM concentrations (Blough and Del Vecchio, 2002), (ii) the specific UV absorbance (SUVA\(_{254}\)) to estimate the aromaticity of the organic carbon (Weishaar et al., 2003), (iii) the slope ratio \(S_\lambda\) to estimate the molecular weight (MW) of the CDOM pool (Helms et al., 2008), (iv) the biological index (BIX) to determine the autotrophic productivity of fluorescent CDOM (Huguet et al., 2009), and (v) the fluorescence index (Fl), which is a tracer of the origin of fluorescent CDOM (McKnight et al., 2001). Our approach provides novel information on groundwater-borne DOM transformations along the groundwater flowpath to the beach discharge face and on the signature of exported DOM to the coastal ocean from sandy beach systems.

2. Materials and methods

2.1. Study area

This study was conducted in the intertidal zone of Martinique Beach (îles-de-la-Madeleine, Québec, Canada; Fig. 1). Martinique Beach originates from a recent transgression sequence. The rapid rates of sea-level rise along the Atlantic coast of Canada over the middle to late Holocene buried terrestrial systems that are now covered by tidal sediments as sedimentation kept pace with the rising high tide. Such buried environments are geological evidence of local and regional submergences over the last millennia (Gehrels, 1994; Juneau, 2012; Scott et al., 1995a,b). This old-age horizon, which was dated to ~900 BP (\(^{14}\)C dating; Juneau, 2012), is carbon-rich (total organic carbon [TOC] = 20% weight percent [w.t.]). Since it is buried below tidal sediments, it undergoes active erosional processes and is strongly fragmented. The old-age horizon now occurs on the landward part of the beach, 25 m from the shoreline; it is at ~30 cm below the beach surface and has a thickness of ~10–15 cm. Except for this organic-rich horizon, beach sediments are organically poor [TOC < 0.2% w.t.], consisting of quartz sand (95%) with an average particle size of 0.3 mm mixed with small amounts of silt (<5%); Chaillou et al., 2014). The underlying sandstone aquifer is composed of fine red-orange sands (~100 μm) containing silicate and aluminosilicate with Fe-coated silicate grains. The site experiences little wave action except during storm events. Tides are semi-diurnal, with a mean range of 0.8 m. The sandy Martinique Beach acts as a shallow unconfined aquifer at the shoreline and releases diffuse fresh groundwaters to the coastal embayment. Within the beach, fresh and cold groundwater flows towards the seaward discharge region below a narrow intruding saline circulation cell located near the top of intertidal sediments (Chaillou et al., 2014, 2015). Based on piezometric measurements, Darcy estimates of fresh groundwater discharge flow ranged from 1.5 m\(^2\) m\(^{-1}\) day\(^{-1}\) in the sandstone aquifer to 2.1 m\(^2\) m\(^{-1}\) day\(^{-1}\) at the beach face (Chaillou et al., 2015). The residence time for groundwater to transit through the system was estimated to be 32 days for a beach transect of 35 m (Chaillou et al., 2015). Even though groundwater-borne C accounts for ~5% of the total DOC discharge, fresh groundwater here is clearly a pathway for DOC produced within the beach to reach the coastal ocean (Chaillou et al., 2015).

2.2. Sampling approach

Sampling was conducted from 18 May to 8 June 2013. Multi-level samplers were deployed (M\(_1\), M\(_2\), Fig. 1C) along a ~35 m cross-shore transect of the beach face; stations were located at 0, 20, 22, 24, 26, 30, and 35 m from the shore. These stations were chosen to cover the intertidal zone and the underlying STE, where fresh meteoric groundwater comes in contact with recirculated seawater and discharges to the coastal embayment. Multi-level samplers consisted of 2.5 m PVC pipes with eight pores distributed vertically and connected to flexible Tygon® tubing, as described in Martin et al. (2003). These samplers were designed to collect porewater at 10, 30, 50, 80, 110, 150, 190, and 230 cm below the beach surface. Samplers were inserted at least two days before sampling to allow sediments around the samplers regain equilibrium. Porewaters were continuously pumped towards the surface using a peristaltic pump, and physicochemical parameters (temperature, dissolved oxygen saturation [DO], salinity) were directly measured using an on-line flow cell with a calibrated multi-parametric probe (600Q5S, YSI Inc.). After these parameters had stabilized, porewater samples were collected for measurements of CDOM, DOC, chlorophyll \(a\) (chl \(a\)), phaeopigments, and total dissolved trace metals (Fe and Mn) in a total extracted volume of ~80 mL. CDOM samples from stations M\(_1\), M\(_2\), M\(_3\), M\(_4\), M\(_6\), and M\(_7\), were filtered onto 0.7 μm Whatman Polycap 75S filters and stored in pre-combusted glass bottles. DOC samples from all stations were filtered on pre-combusted Whatman GF/F 0.7 μm filters, stored in baked vials, and acidified with 25 μL of high purity 10% HCl. Samples for chl \(a\) and phaeopigments were filtered on Whatman GF/F 0.7 μm filters and stored at ~80 °C in the dark. Samples for total dissolved Fe and Mn were filtered onto 0.2 μm Whatman Polycap 75S filters, acidified with nitric acid, and stored at 4 °C. The fresh and saline end-member concentrations of DOC (N = 5), and CDOM, chl \(a\), phaeopigments, Fe, Mn (N = 3) were also measured. Samples from the fresh groundwater aquifer were collected in the manner described above from private and municipal water wells located 50 to 2000 m inshore of the cross-shore transect. Samples of deep bay water (~50 cm above the seabed) were collected by submersible pump from a small boat that was from 50 to ~900 m offshore in Martinique Bay; analyses...
were performed on board using an on-line flow cell and the multiparametric probe. All CDOM, DOC, and pigment data reported here are original, while the physicochemical data set was described in a companion paper (Chaillou et al., 2015).

2.3. Analytical methods

Chl \( \alpha \) concentrations were estimated using the Welschmeyer (1994) method. Chlorophyll pigments were extracted for 24 h in 90% acetone at 5 °C in the dark without grinding. Phaeopigments were then analyzed on the same sample after acidification with 5% HCl. A measure of fluorescence was made on a Turner Designs fluorometer (10-005R) for chl \( \alpha \) and after acidification for phaeopigments. The analytical error was estimated at 10%. The estimation of chl \( \alpha \) degradation was calculated by the proportion of phaeopigments divided by the sum of chl \( \alpha \) and phaeopigments (Bourgeois et al., 2011; Josefson and Conley, 1997). Total dissolved Fe and Mn were analyzed in acidified and filtered porewater samples using a 5100PC Flame Atomic Absorption spectrophotometer (5100ZL Zeeman furnace). Analytical uncertainties were <5%. DOC samples were analyzed by high-temperature combustion (HTC) using a Total Organic Carbon (TOC) analyzer (TOC-V<sub>500</sub>, Shimadzu) based on the method proposed by Wurl and Tsai (2009). Analytical uncertainties were <2% for concentrations higher than 1 mg L<sup>-1</sup>.

2.3.1. Absorbance measurements and absorbance-derived indices (\( a_{375}, S_R, SUVA_{254} \))

CDOM absorbance was measured with a Lambda 850 UV–VIS spectrophotometer (Perkin Elmer) throughout the UV and visible spectra domains (230–800 nm) in quartz cuvettes with 1 cm and 5 cm path lengths to increase sensitivity. Freshly deionized water was used as a blank. Between each sample, the quartz cuvette was flushed first with HCl and then with Milli-Q water. Three absorbance indices were calculated as described in Table 1.

The spectral absorption coefficient, \( a_{\text{CDOM}}(\lambda) \), at 375 nm (\( a_{375} \)) was used as a tracer of CDOM absorption, as proposed by Blough and Del Vecchio (2002). Another parameter, the dimensionless slope ratio (\( S_R \)), was used as an indirect measure of the average molecular weight (MW) of DOM (Helms et al., 2008). Finally, SUVA<sub>254</sub> is a measure of the absorbance by mg of carbon present in the sample (Weishaar et al., 2003). This parameter is strongly correlated with DOM aromaticity and has been used to trace the lignin component of DOM in rivers (Spencer et al., 2012).

2.3.2. Fluorescence measurements and fluorescence-derived indices (BIX, FI)

All fluorescence measurements were made using a Varian Eclipse Fluorometer equipped with a 450 W Xe lamp, double excitation, emission monochromators, and an extended red, high-sensitivity, multi-
Table 1: Description and definition of optical indices used.

<table>
<thead>
<tr>
<th>Absorbance indices</th>
<th>Calculation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption coefficient at 375 nm − a(375) (m−1)</td>
<td>According to the relationship ( \alpha_{\text{DOM}}(\lambda) = 2.303A(\lambda)/l ), where A(\lambda) is the optical density at wavelength ( \lambda ) (dimensionless) and l is the length of the cell used in the absorbance measurement (m)</td>
<td>Tracer of CDOM distribution (Blough and Del Vecchio, 2002)</td>
</tr>
<tr>
<td>Spectral slope ratio (S5)</td>
<td>The ratio of the slope of the shorter wavelength region (275-295 nm) to that of the longer wavelength region (350-400 nm) using the non-linear regression technique described by Stedmon et al. (2000)</td>
<td>An indirect measure of the average MW of DOM, where low values (0 &lt; S5 &lt; 1) indicate higher MW and high values (1 &lt; S5 &lt; 2) indicate lower MW (Helms et al., 2008)</td>
</tr>
<tr>
<td>Specific ultra violet absorbance (SUVA) at 254 nm (L mg C−1 m−1)</td>
<td>The sample UV absorbance at 254 nm divided by the DOC concentration measured in liters per mg C per m</td>
<td>A higher number is associated with greater aromatic content (Weishaar et al., 2003)</td>
</tr>
</tbody>
</table>

Fluorescence indices

| Biological index (BIX)                                   | The ratio of the fluorescence intensity at an emission wavelength of 380 nm and the fluorescence intensity at an emission wavelength of 430 nm, from an excitation at 310 nm. | Values between 0.8 and 1.0 correspond to freshly produced DOM of biological or microbial origin, whereas values below 0.6 are considered to contain little autochthonous OM (Huguet et al., 2003). |
| Fluorescence index (FI)                                  | The ratio of emission intensity at 450 nm to that at 500 nm, obtained with an excitation at 370 nm | FI values > 1.9 are interpreted as indicating a predominance of autochthonous-derived organic matter, whereas FI values of 1.4 or less indicate DOM of terrestrial origin (McKnight et al., 2001). |

Fluorescence index was used to determine the autotrophic productivity of fluorescent CDOM in an estuarine system. The BIX value was influenced by the presence of a distinct fluorophore (\( \beta \)) in EEM spectra that was attributed to autochthonous biological activity, i.e., microbial components (Burdige et al., 2004; Coble, 1996, 2007). A second fluorescence-derived index was also determined according to McKnight et al. (2001) for distinguishing CDOM derived from terrestrial and microbial sources. It is influenced by humic-like fluorophores and allows one to distinguish between microbially derived fulvic acids and terrestrially derived DOM. Fig. 2 presents the EEMs associated with the coloured samples collected from sampler M7 at different depths (from 80 cm to 230 cm) and EEMs of the groundwater and seawater end-members.

2.4. Multivariate analyses

Salinity is often used to discriminate the mixing zone as well as the freshwater and saline circulation cell in the STE (Burnett et al., 2003; Moore, 1996). However, this discrimination does not provide sufficient information on the processes controlling the porewater chemistry in these zones. Here, an approach based on multivariate analysis was used to describe the distribution of the DOM pool not only based on salinity but also as a function of environmental parameters. The distribution of the environmental parameters measured can provide insight into STE chemical heterogeneity as well as to the processes controlling porewater chemistry. Seidel et al. (2015) recently used this approach to explain variations in DOM composition depending on environmental conditions in tidal flat porewaters (Wadden Sea, Germany).

A redundancy analysis (RDA) was performed to assess which environmental factors significantly explained variations in the optical properties of DOM. The main axes (components) were constrained to be linear for the best combinations of the environmental variables (Ramette, 2007), and multiple regressions were used to model variations between environmental (explanatory) and optical (response) variables. The statistical significance of the RDA was tested with 1000 permutations (\( \alpha \) level 0.05). The centered and scaled environmental data used for the RDA were temperature, salinity, dissolved oxygen, and total dissolved Mn and Fe (i.e., explanatory variables). DOC, chl \( a \), and the five optical indices were used to define the DOM pool (i.e., response variables). To remove environmental variables that did not significantly explain residuals variations in the optical data, an automatic stepwise selection procedure was applied. Other variables (i.e., ammonium, pH; data not shown) were removed based on the output of the automatic forward selection procedure because they did not significantly explain any variations in the optical index (Legendre and Legendre, 2012). This procedure yielded a reduced RDA consisting of the environmental variables having the greatest effect on the variance in optical data. Statistical analyses were performed using the ape and vegan packages of the R software.

3. Results

Physicochemical parameters measured in June 2013 are the same as those presented in Chaillou et al. (2015). The distribution of salinity, dissolved oxygen saturation, and temperature in STE and end-members will be briefly described, but we will mainly focus on the distributions of DOC, fluorescence, and absorbance-derived CDOM indices.

3.1. End-member characteristics

End-member characteristics are summarized in Table 2. The salinity of groundwater in municipal and private wells, i.e., the fresh groundwater end-member, averaged 0.14 ± 0.09, the temperature was 7 °C, and DOC concentrations averaged 0.19 ± 0.03 mmol L−1. Due to dark conditions, chl \( a \) and phaeopigments concentrations were null. CDOM concentration was low (\( \lambda_{375} = 0.76 ± 0.25 \) m−1), with an SUVA254 value of 1.73 ± 0.57 L mg C−1 m−1 and \( S_p \) of 0.80 ± 0.10. Groundwater BIX and FI values were low, with values of 0.36 ± 0.03 and 1.30 ± 0.03, respectively. The salinity of the seawater, i.e., the marine end-member, was 30.58 ± 0.30 and the temperature was approximately 11 °C. Temperature increased during the day to a maximum of 12.4 °C in the afternoon. DO saturation was >100% due to wind and wave action, and DOC values were 0.14 ± 0.01 mmol L−1. Seawater samples exhibited low concentrations of chl \( a \) (1.61 ± 0.24 µg L−1) and phaeopigments (0.70 ± 0.32 µg L−1). Absorbance-derived indices showed low
concentrations of CDOM ($a_{375} = 1.42 \pm 0.50$ m$^{-1}$). SUVA$254$ values were high, with a mean value of $4.09 \pm 1.64$ L mg C$^{-1}$ m$^{-1}$, and a slope ratio value, SR, of $1.33 \pm 0.49$. Seawater BIX and FI values were $1.13 \pm 0.30$ and $1.58 \pm 0.54$, respectively.

3.2. Environmental conditions in the STE

The salinity ranged from 0.58 to 24 along the STE. The 2D profile revealed fresh groundwater with low salinity values in the deepest samples ($<5$; Fig. 3A) and a narrow intruding saline circulation cell at the surface, with salinity values higher than 10 that decreased sharply beneath this surficial saline circulation cell. For example, salinity at $M_6$ was 12 in the upper 20 cm and dropped to 1 at 30 cm. This sharp vertical gradient is characteristic of a microtidal beach system dominated by fresh groundwater discharge, where most of the STE is stratified (Heiss and Michael, 2014; Robinson et al., 2007b).

A strong vertical decline in oxygen concentration was also observed below the saline circulation cell (Fig. 3B). At the depth of 110 cm, the porewater was suboxic, with DO around 20%, whereas the surficial saltwater was the most oxygenated layer (DO above 60% saturation). Total dissolved Fe concentrations ranged from 50 to 1700 μmol L$^{-1}$, with the lower concentrations measured at the surface near the top of the beach ($M_1$; Fe $< 300$ μmol L$^{-1}$; Fig. 3C). The highest values were in the middle of the transect ($M_4$ and $M_5$), where hotspots of Fe concentrations were observed with values $>1500$ μmol L$^{-1}$ (i.e., $M_4$ at 150 cm below the surface). Mn concentrations showed the same trends but with concentrations two orders of magnitude lower (i.e., 0 to 34 μmol L$^{-1}$; Fig. 3D).

3.3. DOM in beach porewaters

DOC concentrations at $M_1$ and $M_2$ averaged 2.18 mmol L$^{-1}$ with a maximum value of 6.18 mmol L$^{-1}$ (Fig. 4A). DOC concentrations decreased towards the discharge area, even though the distribution was patchy with some hotspots (i.e., $M_3$–$M_4$; DOC ranged from 4.68 to 15.26 mmol L$^{-1}$ at 80 cm below surface). In the intertidal zone, DOC concentrations were also high relative to the marine end-member (from 0.54 to 1.86 mmol L$^{-1}$). Fig. 4 presents the distributions within the cross-shore section of the STE, of DOC, % degradation of chl $a$, and the five optical indices calculated from the data. The $a_{375}$ absorption coefficient varied greatly (from 0.60 to 14.2 m$^{-1}$; Fig. 4B), with sharp horizontal and vertical gradients and maximum concentrations within the upper layer of the sediment. Hot spots of $a_{375}$ values were found in the

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**Table 2**

Average and standard deviation of DOC, chl $a$ degradation, absorbance, and fluorescence indices of groundwater and seawater end-members.

<table>
<thead>
<tr>
<th>End-member</th>
<th>Groundwater</th>
<th>Seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>N = 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC (mmol L$^{-1}$)</td>
<td>0.19 ± 0.03</td>
<td>0.14 ± 0.01</td>
</tr>
<tr>
<td>N = 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chl $a$ degradation (%)</td>
<td>100 ± 0.00</td>
<td>33.80 ± 13.24</td>
</tr>
<tr>
<td>$a_{375}$ (m$^{-1}$)</td>
<td>0.76 ± 0.25</td>
<td>1.42 ± 0.50</td>
</tr>
<tr>
<td>SUVA$254$ (L mg C$^{-1}$ m$^{-1}$)</td>
<td>1.73 ± 0.57</td>
<td>4.09 ± 1.64</td>
</tr>
<tr>
<td>$S_R$</td>
<td>0.80 ± 0.10</td>
<td>1.33 ± 0.30</td>
</tr>
<tr>
<td>FI</td>
<td>1.30 ± 0.03</td>
<td>1.58 ± 0.54</td>
</tr>
<tr>
<td>BIX</td>
<td>0.36 ± 0.03</td>
<td>1.13 ± 0.30</td>
</tr>
</tbody>
</table>
tidal zone, a few centimetres below the surface (−30 to 80 cm), with values ten times higher than those found for marine end-members (i.e., −10 m−1 and 1.42 m−1, respectively). In the landward part of the transect, a375 values were also high near the surface (>5 m−1). The values of chl a degradation estimated for each sample were also reported (Fig. 4C). Chl a concentrations were relatively low in the STE, and the proportion of degraded chl a was estimated to be 55% (i.e., M5, M6; Fig. 4C). Below 80 cm depth, there were no chl a and phaeopigments due to the absence of light and the weak influence of tide and waves on the STE. SUVA254 values ranged from 0.10 to

Fig. 3. Cross-section of transect M1–M7 (see Fig. 1C) showing the topography and distribution of (A) salinity, (B) dissolved oxygen saturation (%), (C) Fe and (D) Mn concentrations (μmol L−1) in sediment porewater samples. Depths are relative to mean sea level (i.e., 0 m is mean sea level). Contour lines were determined by linear interpolation (kriging method) of data points; the interpolation model reproduced the empirical data set with a 97% confidence level. Black dots represent the depths at which samples were collected using multi-level samplers.
7.97 L mg C\(^{-1}\) m\(^{-1}\) and increased with depth (Fig. 4E), with the highest values in the deep landward portion of the transect (e.g., M4, M6, SUVA\(_{254}\) > 5 L mg C\(^{-1}\) m\(^{-1}\)). The lowest SUVA\(_{254}\) values (<0.20 L mg C\(^{-1}\) m\(^{-1}\)) were observed below the tidal zone, i.e., at M7, in the freshwater lens. Finally, the slope ratio values were generally low (SR < 1.75); most samples had SR < 0.75 with maxima in the tidal zone (i.e., M6, M7, 1 < SR < 2; Fig. 4D). In the upper part of the STE, SR values decreased with depth (from 1.15 at 50 cm to 0.40 at 190 cm).

To interpret EEMs, a focus on the FI and BIX indices was done. BIX (Fig. 4F) ranged from 0.31 to 0.99, with a mean value of 0.59 ± 0.14 and maximum values at the top of the intertidal zone (i.e., M3, M4, 1 < SR < 2; Fig. 4D). In the upper part of the STE, BIX indicated different character but no noticeable trends.

3.4. Link between optical properties and environmental variables based on multivariate analysis

The RDA model reflects the variations in the optical properties of DOM in response to variations in environmental variables in the STE. This approach was used to determine the driving factors that explain the complex optical index distribution of the DOM pool and to estimate the role of transport versus biogeochemical processes within the STE. Fig. 6 presents the distribution of DOC and optical indices made on the end-members with those made on the porewater samples across the salinity gradient. DOC and optical indices did not show clear trends relative to salinity. DOC and a\(_{375}\) exhibited higher concentration than the two end-members (Fig. 5A, B) whereas SR, SUVA\(_{254}\), BIX and FI indicated different character but no noticeable trends.
presents the RDA results in a triplot, by plotting samples (points) and arrows representing environmental parameters (explanatory factors) and optical indices (response factors). Arrows represent the direction of the maximal variation, and vector lengths indicate the contribution to the variation in the data. The angles between arrows represent the correlation between the variables they represent.

The environmental factors in the RDA model and the two first axes were significantly (p < 0.01) correlated with the variability in optical indices, with the first two axes explaining 87% of the variability in the optical indices. None of these environmental parameters dominated the multivariate similarity pattern among samples. The first RDA axis (RDA1; 62% of the explained variability) was mainly linked with total dissolved Fe and to a lesser extent with temperature. The second RDA axis (RDA2; 25% of the explained variability) was correlated with total dissolved Mn and salinity. Finally, the third axis (RDA3; 7% of explained variability, data not shown) was mainly correlated with DO saturation.

The RDA model represents the variance of the DOM’s optical index explained by environmental conditions. Optical indices are represented by red arrows. RDA1 was mainly associated with the Fl and BIX fluorescence indices, which were closely linked to total dissolved Fe, and DOC, which was inversely correlated with Fe content. Finally, chl a and the absorption coefficient $a_{375}$ were also associated with RDA1. The second axis, RDA2, was associated with changes in $S_k$ and SUVA$_{254}$, i.e., DOM composition. These two optical indices are related to MW and aromatic content, which are dependent upon the origin of DOM, and also to the biogeochemical processes altering the DOM structure.

4. Discussion

In Martinique Beach, low oxygen conditions (~20% saturation) and high DOC concentrations (mean value 1.31 ± 0.91 mmol L$^{-1}$) represented suitable conditions for biogeochemical reactions to occur, leading to changes in DOM concentrations and molecular composition due to degradation processes. Moreover, the absence of light and the strong AR presented the RDA results in a triplot, by plotting samples (points) and arrows representing environmental parameters (explanatory factors) and optical indices (response factors). Arrows represent the direction of the maximal variation, and vector lengths indicate the contribution to the variation in the data. The angles between arrows represent the correlation between the variables they represent.

The environmental factors in the RDA model and the two first axes were significantly (p < 0.01) correlated with the variability in optical indices, with the first two axes explaining 87% of the variability in the optical indices. None of these environmental parameters dominated the multivariate similarity pattern among samples. The first RDA axis (RDA1; 62% of the explained variability) was mainly linked with total dissolved Fe and to a lesser extent with temperature. The second RDA axis (RDA2; 25% of the explained variability) was correlated with total dissolved Mn and salinity. Finally, the third axis (RDA3; 7% of explained variability, data not shown) was mainly correlated with DO saturation.

The RDA model represents the variance of the DOM’s optical index explained by environmental conditions. Optical indices are represented by red arrows. RDA1 was mainly associated with the Fl and BIX fluorescence indices, which were closely linked to total dissolved Fe, and DOC, which was inversely correlated with Fe content. Finally, chl a and the absorption coefficient $a_{375}$ were also associated with RDA1. The second axis, RDA2, was associated with changes in $S_k$ and SUVA$_{254}$, i.e., DOM composition. These two optical indices are related to MW and aromatic content, which are dependent upon the origin of DOM, and also to the biogeochemical processes altering the DOM structure.

4. Discussion

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water–rock interaction provided an ideal environment for the transformation and sorption onto mineral particles of terrestrially derived DOM without photochemical oxidation processes (Kaiser et al., 2004).

4.1. Optical signatures of CDOM sources in the STE

As expected, the two end-members (i.e., fresh groundwater and marine water) presented contrasting DOM profiles (Table 2). Firstly, $S_R$ values in groundwater end-members were relatively low (i.e., 0.80 ± 0.10), indicating high MW molecules that were associated with the presence of humic-like fluorophores (i.e., FI values < 1.4) and low BIX values (i.e., 0.36 ± 0.02) and showed no evidence of a microbial component. These values are in the range of FI and BIX values reported in groundwaters. Birdwell and Engel (2010), for example, reported a wider range of BIX values from cave and spring waters, with values ranging from 0.50 to 3.00, and Lapworth et al. (2008) showed a large range of FI values varying between 0.50 and 2.50, depending on the water table level. The values of DOC-normalized absorbance at 254 nm, SUVA$_{254}$, were in the range of those reported for groundwater end-member, suggesting the DOM pool changes when the fresh groundwater transited from the Permian aquifer to the beach.

Secondly, in marine end-members, $S_R$ values were higher than in their groundwater counterparts, indicating lower MW molecules associated with the presence of biological compounds (mean BIX value = 1.13 ± 0.30). SUVA$_{254}$ Values were higher in marine samples than in groundwater end-members, and this was associated with the occurrence of aromatic contents often linked to terrestrial compounds. High SUVA$_{254}$ values could be associated with surface runoff or alterations of CDOM due to physical processes in marine water (Asmala et al., 2014a). SUVA$_{254}$ values reported in the literature vary widely from site to site in the coastal environment. For example, Asmala et al. (2014b) reported high SUVA$_{254}$ values in river discharge (5.03 L mg C$^{-1}$ m$^{-2}$) while Dixon et al. (2014) reported SUVA$_{254}$ values between 2.8 and 3.8 L mg C$^{-1}$ m$^{-2}$ in an estuary (Neuse River Estuary, North Carolina, USA). In our study, the surface samples presented SUVA$_{254}$ values close to those reported for coastal systems.

4.2. From the aquifer to the coastal ocean

DOC data (Fig. 5A) clearly showed an addition from sediments comparing to the DOC measurements in groundwater and seawater end-members. This supports the idea that carbon porewater content was not simply the result of dilution by fresh groundwater and seawater in the STE of Martinique Beach. This distribution was already observed at this site by Chaillou et al. (2015) and suggests the presence of a permanent production, or input, of DOC throughout the groundwater flow path over the year. The origin of this DOC is not yet well known. In addition to fresh and marine end-members, the hydrolysis of particulate organic carbon (POC) and the release of DOM from reduced metal oxides are potential sources of DOC; this has been observed in other tidal flat sediments (Reckhardt et al., 2015; Seidel et al., 2014). Based on the $^{13}$C signatures of DIC in beach groundwaters and the old-age horizon POC content, Chaillou et al. (2015) proposed that the buried carbon-rich soil is a potential source of the DOM pool. They noted the addition of $^{13}$C-depleted DIC, with values at −30 and −34‰, along the STE, which should be similar to the organic matter from which it is derived, including buried organic-rich horizons with $^{13}$C values varying between −32 and −34‰. As was the case with DOC, a375 values (Fig. 4B) indicate that there is CDOM production in the landward part of the STE (i.e., M1, M3, and M4, 50–80 cm depth), with $S_R$ values lower than groundwater samples (Table 2). This is concomitant with FI values (Fig. 4C), and suggests the presence of terrestrially derived organic matter. This also suggests in situ production of the high MW CDOM fraction in the system, which is in agreement with the hydrolysis of old-age POC (Komada et al., 2012; Kowalczyk et al., 2009; Weston et al., 2006).

In the downstream part of the STE, low DOC and high BIX values (Fig. 4A, F) indicated heterotrophic degradation of DOC and the presence of organic matter with an autochthonous origin (i.e., microbial production). It was not possible to discriminate which of these two processes was the main source of DOM. Only isotopic investigations of DOC can provide further insight into the origin of porewater DOC and DOM. Whatever its origin, DOM produced locally was transported seaward by groundwater flow. This local production may significantly increase the exported fluxes of DOC by groundwater discharge at the beach face. Based on groundwater end-members flow and the fresh groundwater flow estimated in the beach, local production could account for ~15% of the total DOC exported to seawater (Chaillou et al., 2015). The behaviour of these compounds within the STE will control the reactivity of the exported CDOM.

4.3. Relationship between DOM parameters within the STE

The relationships between DOM characteristics (i.e., DOC, chl a, and optical indices) are often used to reveal the biogeochemical source and processing of organic matter through physical and biogeochemical conditions of surface estuaries. For example, the absorption coefficient of CDOM (a$_{CDOM}$) has been used as a proxy for DOC in rivers and the coastal ocean (Fichot and Benner, 2011; Spencer et al., 2012; Stedmon et al., 2003; Yamashita et al., 2008). The relationship between DOC and a$_{CDOM}$ was based on the assumption of the conservative behaviour of these parameters along a salinity gradient, (i.e., invariant proportion of CDOM in the DOC pool). However, a decoupling and nonlinear correlation between DOC and CDOM occurs in many environments, depending on mixing, photochemical oxidation, and microbial degradation (Del Vecchio and Blough, 2004; Nelson et al., 1998; Nelson and Siegel, 2013; Skoog et al., 1996).

In the Martinique Beach STE, there was no significant relationship between the optical indices of DOC and CDOM. For both DOC and
CDOM, absorbance and fluorescence-derived indices showed clearly different behaviours along the transect (Fig. 5B–F). This was not unexpected because CDOM distribution in STEs results from a complex interaction of variables related to physical mixing, biogeochemical processes, and water–rock interactions. These behaviours of CDOM have already been reported in certain surficial systems where flocculation, photobleaching, microbial production and turbidity are important processes that control CDOM behaviour (Kowalczyk et al., 2003; Rochelle-Newall et al., 2014).

Firstly, microbial degradation could be responsible for the removal of lignin and other components of CDOM as well as for the production of specific DOM (Inamdar et al., 2011; Kaiser et al., 2004). Microbial degradation leads to changes in the optical properties of CDOM by the ability of heterotrophic bacteria to degrade high MW DOM and also to produce new CDOM (Asmala et al., 2013; Chapelle et al., 2009). In our study, the presence of microbial production is suggested by the BIX indices. The low signal of compounds derived from microbes was due to 1) the strong presence of terrestrial compounds and 2) the rapid turnover of freshly produced CDOM due to the highly active environments (Rusch et al., 2000). However, the concomitant occurrence of high DIC concentrations (Chailou et al., 2014, 2015), elevated concentrations of reduced species such as Fe and Mn, and the low oxygen saturation as well as high DOC concentrations (mean value = 1.31 ± 0.91 mmol L⁻¹) support the idea of active anaerobic microbial degradation of the DOM pool. This is also supported by the significant correlation between the BIX indices and dissolved Fe, as shown by the RDA results (Fig. 6). Nevertheless, it is unclear if the correlation between BIX and dissolved Fe is related to the reduced conditions that favoured heterotrophic degradation or if the relationship is due to the interaction between Fe and CDOM.

Secondly, the effect of CDOM–particle interactions in STEs can significantly contribute to CDOM removal (Asmala et al., 2014a; Shank et al., 2005; Sun et al., 2014). Here, SR indices—and to a lesser extent SUVA₂₅₄ indices—exhibited a removal process in brackish waters of the STE (Fig. 5C–D). The significant relationship between SR and SUVA₂₅₄ values in our samples (p < 0.05; data not shown) and the RDA analysis (Fig. 6) highlighted the link between these two optical parameters along the transect. According to the RDA results, the increase of SR and SUVA₂₅₄ (i.e., from high MW CDOM compounds with low aromaticity to low MW CDOM compounds with high aromaticity) was inversely correlated to dissolved metals, particularly total dissolved Mn. These results suggest that the high concentration of total dissolved metals may have played a role in the removal process of CDOM compounds (i.e., SR and SUVA₂₅₄). DOM may be bound to metal-oxides in the oxic layer leading to a buried phase of high MW and humic DOM. This is also supported by the significant correlation of the RDA results between FI and total dissolved Fe (Fig. 6). An increase in FI values, even by 0.1 unit, could suggest that humic compounds were removed from the systems, as shown by McKnight et al. (2001). In marine sediments as well as in soil horizons, metal oxides, and especially Fe oxides, promote OM preservation through co-precipitation of OC and iron (Barber et al., 2014; Lalonde et al., 2012; Wagai and Mayer, 2007). The RDA results highlight the negative correlation between DOC and dissolved Fe (Fig. 6). In the STE, DO saturation is low (~20%), enhancing the reductive dissolution of Fe oxides and inducing high dissolved Fe concentrations (Fig. 3B–C). However, in such a system, where tides, water table fluctuations, storms, and swash induce transient behaviours of the recirculating cell and the associated mixing zone (Abarca et al., 2013; Heiss and Michael, 2014; Robinson et al., 2007a), redox oscillations are probably strongly involved in the heterotrophic degradation of organic matter, as is the case in coastal sediments (Sundby, 2006, and reference therein). Because the sorption of CDOM on metal oxides is highly reversible under similar conditions of sorption (Kaiser and Guggenberger, 2000; Lalonde et al., 2012), these redox oscillations could lead to a constant phenomenon of trapping/releasing of DOM and consequently affect the optical indices of CDOM.

4.4. CDOM behaviour in a microtidal STE

Fig. 7 is a conceptual model of the behaviour of DOM in an STE. As previously proposed to describe the connection between soil and groundwater, the hydrological connectivity between groundwater and ocean through sandy beaches drives the lateral segregation of organic molecules (see the regional chromatographic model of Shen et al., 2015). Groundwater-borne DOM originates from the percolation of rain through the soil to the aquifer and thus has a terrestrial signature. As groundwater transits, groundwater-borne DOM may be transformed by three dominant processes: POC hydrolysis, microbial degradation, and sorption/desorption onto metal oxides. These processes concomitantly produce/trap high MW and lignin-enriched compounds and microbial autochthonous compounds. Regardless of the process, most of the high MW DOM compounds seem to be trapped in the STE and do not reach the overlying coastal waters.

In contrast to the literature on beach systems, there is little evidence here of the occurrence of biological compounds of marine origin within the whole system, even in the recirculation cell where tides and waves continuously force seawater to infiltrate and recirculate in the system. As previously modelled by Abarca et al. (2013) and Robinson et al. (2007b), microtidal STEs with high fresh groundwater discharge have limited mixing with seawater because of low seawater infiltration and the narrow recirculating seawater cell. The distribution of both chl a and phaeopigments at the top of the intertidal zone agreed with weak marine particle infiltration into the STE system (Fig. 4C). The temperature as well as the sampling period may explain the low productivity conditions at the time of sampling, but the site-specific hydrogeological context also appeared to limit the input of marine compounds into the

Fig. 7. Schematic representation of CDOM behaviour through the subterranean estuary.
system. Whether the terrestrial-marked DOM that occurs within the discharge zone is bioavailable remains an open question that is still being debated (Bianchi, 2011; Burdige, 2005).

5. Conclusion
This study has provided a snapshot of CDOM behaviour and characteristics through the STE of Martinique Beach using the optical properties of CDOM. Optical indices are a useful tool to study CDOM behaviour in aquatic environments. However, interpretation should be done with caution since the biogeochemical environment may strongly influence changes in these indices. Marine and groundwater end-members were significantly different, but CDOM along the STE is clearly not simply the result of end-member dilution. Thus DOC and CDOM are transformed in the complex and dynamic system. Coupled with RDA analysis, optical indices gave better insight than univariate interpretation and revealed a relationship between optical parameters and redox conditions. Thus, DOM transformations may be attributed to several processes. The hydrolysis of an old buried soil may be responsible for the production of DOM with high MW that enhanced the CDOM’s fluorescence. Whether the terrestrial-marked DOM that occurs within the coastal ocean is a changing paradigm and the priming effect. Proc. Natl. Acad. Sci. 108, 1947–1950.


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