Marine Chemistry 186 (2016) 46–57

Contents lists available at ScienceDirect

Marine Chemistry

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

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

Mathilde Couturier [a,b,*], Christian Nozais [b], Gwénaëlle Chaillou [a,b]

[a] Canada Research Chair on the Geochemistry of Coastal Hydrogeosystems, Université du Québec à Rimouski, Rimouski, Québec G5L3A1, Canada
[b] Département de Biologie, Chimie et Géographie, Université du Québec à Rimouski, 300 Allée des Ursulines, Rimouski, Québec G5L3A1, Canada

ARTICLE INFO

Article history:
Received 14 March 2016
Received in revised form 2 August 2016
Accepted 5 August 2016
Available online 08 August 2016

Keywords:
Biogeochemistry
Subterranean estuary
Coloured dissolved organic matter (CDOM)
Groundwater-borne carbon

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 (Îles-de-la-Madeleine, Quebec, Canada). We combined porewater DOC concentrations as well as CDOM absorbance- and fluorescence-derived indices (S_R, $SUVA_{254}$, FI 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 S_R and $SUVA_{254}$, (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 DOC 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., 2008; Chaillou et al., 2015; Charette et al., 2013; Cyronak et al., 2013; Dorsett et al., 2011; Maher et al., 2013). The chemical composition of groundwater discharge is controlled by both groundwater-borne concentrations and biogeochemical reactions that occur as fresh groundwater transits to the ocean and mixes with seawater.

The subterranean estuary (STE), where fresh groundwater and recirculated seawater mix, is a critical component of the coastal aquifer (Moore, 1999) that must be considered when estimating regional chemical fluxes from aquifers to coastal waters and the impact of these chemical fluxes on coastal ecosystems (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 (Goñi 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

* Corresponding author at: Canada Research Chair on the Geochemistry of Coastal Hydrogeosystems, Université du Québec à Rimouski, Rimouski, Québec G5L3A1, Canada.
E-mail address: Mathilde.Couturier@uqar.ca (M. Couturier).

http://dx.doi.org/10.1016/j.marchem.2016.08.001
0304-4203/

sands (Anschutz et al., 2009; Kim et al., 2012; McLachlan and Brown, 2006). However, terrestrial carbon could be another important carbon source in STE systems 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-BIack, 2001; Birdwell and Engel, 2010), in the coastal ocean (Benner et al., 2005; Guéguen et al., 2005; Kowalczuk 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_λ) 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_R) 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 (FI), 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 $m^3\ m^{-1}\ day^{-1}$ in the sandstone aquifer to 2.1 $m^3\ m^{-1}\ day^{-1}$ 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_{1-7}; 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 (600QS, 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_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