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Precise indices based on *n*-alkane distribution for quantifying sources of sedimentary organic matter in coastal systems

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ABSTRACT

Precise indices based on *n*-alkane signatures were developed in order to determine the sources and composition of sedimentary organic matter (SOM) in coastal systems. The Arcachon Bay (France), a well-studied temperate lagoon, was used as an example of a complex coastal system sheltering a wide diversity of OM sources. Three main groups of sources were well discriminated from their *n*-alkane signatures: seagrass (*Zostera* sp.) produced mainly *n*-C_{17}, *n*-C_{19}, *n*-C_{21}, *n*-C_{23} and *n*-C_{25} alkanes, algae (Rhodophyta, Chlorophyta) produced *n*-C_{15} and *n*-C_{17} and the terrigenous input [*Quercus* sp., *Spartina* sp. and river suspended particulate OM (SPOM)] was characterized by *n*-C_{25}, *n*-C_{27}, *n*-C_{29}, *n*-C_{31} and *n*-C_{33}. From the above and literature *n*-alkane fingerprints, we developed a set of indices (*n*-alkane ratios) to quantify the contribution of these three major sources of the SOM. At the Arcachon Bay scale, they indicated that SOM was composed mainly of seagrass (ca. 53 ± 19%) and terrestrial (ca. 41 ± 17%) material, followed by algae (ca. 6 ± 9%). Moreover, the new *n*-alkane indices exhibited more relevant spatial patterns than classical ones – the TAR ($C_{27} + C_{29} + C_{31}/C_{15} + C_{17} + C_{19}$; terrestrial to aquatic ratio) and the P_{aq} ($C_{23} + C_{25}/C_{23} + C_{25} + C_{29} + C_{31}$; aquatic plant %) – with a greater contribution from marine sources in the central part of the lagoon where a high density of *Zostera* seagrass was observed. Therefore, the development of precise indices adapted to the local diversity of OM sources is needed when using *n*-alkanes for quantifying the source composition of SOM in complex coastal systems.

1. Introduction

Coastal ecosystems are characterized by high biological productivity due to a significant amount of organic matter (OM) and nutrients from different reservoirs affected by oceanic input and continental input (Hedges and Keil, 1995). The presence of several different settlements such as shores, channels, intertidal mudflats, river input or seagrass meadows associated with the presence of a wide diversity of primary producers such as phytoplankton, seagrass, benthic macroalgae and terrigenous/aquatic higher plants, creates a pool of coastal OM comprising a wide diversity of sources and may exhibit significant spatial variability.

In these coastal areas, sedimentary OM (SOM) plays an important role in ecosystem functioning, especially in trophic transfer, and corresponding mainly to major potential food resources for benthic primary consumers, depending on biochemical composition (Tenore and Dunstan, 1973; Grémare et al., 1997). SOM is also a key component of the main biogeochemical cycles involved in diagenesis (e.g. Jaffé et al., 2006; Medeiros and Simoneit, 2008; Blair and Aller, 2012). Bulk properties of SOM, such as stable carbon isotopic composition ($\delta^{13}C_{TOC}$) and total organic carbon to total nitrogen ratio (TOC/TN) are frequently used to evaluate sources of OM (e.g. Parker, 1964; Hedges and Parker, 1976; Peters et al., 1978; Andrews et al., 1998; Alt-Epping et al., 2007; Perdue and Koprivnjak, 2007; Ramaswamy et al., 2008; Dubois et al., 2012). However, TOC/TN is strongly affected by preferential N remineralization in marine sediments or N sorption onto clay minerals (cf. Schubert and Calvert, 2001) and $\delta^{13}C_{TOC}$ values of a C_3 and C_4 plant mixture could mimic those of marine algae (e.g. Goñi et al., 1998).

Molecular biomarkers in sediments can also provide precise information about source characterization and allow, to a certain extent, determination of the degradation state of OM (e.g. Eglinton and Hamilton, 1963; Poynter and Eglinton, 1990; Ten Haven et al., 1992; Wakeham et al., 1997; Volkman et al., 2008;

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He et al., 2014; Ranjan et al., 2015 and references therein). Among these biomarker tools, linear alkanes (*n*-alkanes) are commonly used to discriminate terrigenous from marine SOM (Wang et al., 2013 and references therein). Indeed, *n*-alkanes are degraded more slowly than the bulk OM (most of the early OM transformation and degradation in sediments is mediated by microorganisms) and the other lipid classes and consequently accumulate in sediments (Meyers, 2003; Ranjan et al., 2015). Prevailing odd and high molecular weight (MW; $\geqslant C_{27}$) *n*-alkanes indicate a mainly terrigenous vascular plant input (Eglinton and Hamilton, 1967; Tissot et al., 1977; Prahl et al., 1994; Mead et al., 2005; Sikes et al., 2009; Seki et al., 2010), whereas odd and low MW (such as C_{17}) *n*-alkanes are characteristics of a marine origin (macroalgae, phytoplankton, phanerogams; Boutton, 1991; Meyers and Ishiwatari, 1993; Meyers, 2003; Sikes et al., 2009). Furthermore, odd and mid MW (C_{21} to C_{25}) *n*-alkanes tend to show an origin in freshwater aquatic and marine macrophytes (Huang et al., 1999; Ficken et al., 2000; Mead et al., 2005). Therefore, some indices based on *n*-alkanes were proposed and used to determine the composition of SOM, such as (i) CPI [carbon preference index (odd/even predominance to determine the quality of SOM and the contribution of additional sources, such as microbial and/or petroleum hydrocarbons); e.g. Bray and Evans, 1961; Kolattukudy, 1976; Collister et al., 1994; Peters et al., 2005; Mille et al., 2007], (ii) TAR (terrestrial/aquatic ratio; odd long chain/odd short chain alkanes; Bourbonnière and Meyers, 1996), (iii) P_{aq} (aquatic plants %; odd mid chain alkanes/odd mid and long chain alkanes; Ficken et al., 2000). However, these indices are not really adapted to complex coastal ecosystems characterized by a high diversity of OM sources. Indeed, significant mangrove, marine macrophytes and/or aquatic input introduce sources with non-unique *n*-alkane compositions to the system, making the effective determination of sources from only *n*-alkane chain length data difficult in such complex environments (Sikes et al., 2009).

Here, we studied the major primary producers from a semi-enclosed coastal system characterized by multiple sources of OM (Arcachon Bay, France) in order to investigate their *n*-alkane signatures. We also analyzed the *n*-alkane distributions in the Bay and the riverine suspended particulate OM (SPOM) and in the surface sediments of the Bay. From this, we defined precise relevant *n*-alkane indices, which take into account (i) the diversity of OM sources and (ii) the fact that some individual *n*-alkanes may not come from a unique source, in order to better estimate the composition of surface SOM in such a complex coastal system.

2. Materials and methods

2.1. Study site

Arcachon Bay (44°40′ N, 1°10′ W; Fig. 1) is a mesotidal (tidal amplitude, 0.8–4.6 m) semi-enclosed lagoon of 174 km^2 in southwestern France. This coastal ecosystem receives ocean water through a narrow channel in the southwest and riverine water from the Leyre River (Fig. 1) which represents 73% of the total annual freshwater inflow (ca. 813.10^6 m^3; Plus et al., 2010). The other freshwater streams are distributed mainly along the eastern and southern coastlines (Fig. 1). In the inner lagoon (156 km^2), tidal channels (41 km^2) separate large intertidal areas (115 km^2) covered by the largest European *Zostera noltei* meadow (70 km^2; Auby and Labourg, 1996). The bay is a complex coastal system which displays a wide variety of OM sources – micro- and macroalgae, phanerogams, and terrigenous OM – that together make up the SOM (Dubois et al., 2012).

2.2. Sampling, sample processing and storage

In order to analyze the *n*-alkane signature of pure primary sources, fresh macroalgae (Rhodophyta and Chlorophyta), fresh and degraded leaves and rhizomes of *Zostera* spp., degraded leaves of *Spartina* sp., degraded leaves of *Quercus* sp. (the main terrigenous primary producer in the valley of the Leyre River) and surface sediment for micro phytobenthos extraction, were collected by hand at the intertidal stations (mainly CH, CV, GH and GV) of the bay in March–April 2009 (Fig. 1). The *n*-alkane signature of epiphytes was determined from *Z. noltei* leaves containing epiphytes vs. *Z. noltei* leaves without epiphytes (epiphytes removed from the leaves). Rhizomes of *Z. noltei* in the bay are known to be a habitat for bacteria (Nielsen et al., 2001 and references therein). Therefore, the term "rhizomes" also takes into account the potentially associated bacterial population. Since *Z. noltei* is the main macrophyte in the Arcachon Bay, a 1 yr in situ degradation experiment was carried out to account for possible *n*-alkane alteration during degradation [see Dubois et al. (2012) for details]. All macrophyte samples were cleaned in two successive filtered seawater baths to remove detritus and attached animals and then rinsed with deionized water (DIW) to remove salt, and finally stored at −20 °C.

Micro phytobenthos (epipelic diatoms) was extracted from sediments following the method of cell migration through nets [100 μm mesh; Riera et al. (1999) as modified by Herlory et al. (2007)]. Cells were recovered on GF/F filters and stored at −20 °C.

To explore the terrigenous input from the river compared with the main terrigenous primary producer (degraded leaves of *Quercus* sp.), one continental station on the Leyre River was sampled monthly in 2009 for the *n*-alkane profile of SPOM in surface freshwater. Freshwater was collected 10–20 cm below the surface using a plastic container. Four pelagic stations (Fig. 1) distributed along a gradient from the inner to the outer part of the bay were sampled bimonthly in 2009 at high tide in order to investigate the *n*-alkane signature of SPOM in surface seawater (mixture of many OM sources, including the potential signature of phytoplankton). Seawater was collected 1 m below the surface using a Niskin bottle. Fresh- and seawater were gently filtered (vacuum −0.2b) through precombusted (4 h, 450 °C) GF/F filters, using glass material. Filters were stored at −20 °C.

In April 2009, surface sediment (1 cm) was sampled at 30 benthic stations in the inner bay (Fig. 1) for SOM characteristics based on *n*-alkane indices. The 19 intertidal stations were sampled by hand at low tide; they were distributed over a wide range of particle grain size and density of *Z. noltei*. The 11 subtidal stations were sampled via diving using sediment cores; they were located within major and minor channels. Sediment samples were placed in Al containers and stored at −20 °C back in the laboratory.

All details on sampling, degradation experiment and sample processing are given by Dubois et al. (2012). All samples were stored at −20 °C.

2.3. n-Alkane analysis

Sediment and macrophyte, as well as filter, samples were freeze-dried before further processing. For sediment and primary producer biomass, 3–15 g and 0.3–1 g respectively were used for lipid extraction. GF/F filters of freshwater and seawater SPOM were scraped before lipid extraction in order to increase the number of filters (i.e. amount of material) extracted in a single accelerated solvent extraction (ASE) cell to provide sufficient quantity of material for analysis. In fact, the filters were pooled in order to get two samples for freshwater SPOM and two samples for each pelagic station for seawater SPOM. The size of the ASE cell was too small to put in directly all the filters including the glass matrix. This processing also had the advantage of decreasing the filter blank. Extraction was performed using ASE (ASE-350, DIONEX Corp.) operated with CH_2Cl_2 at 100 °C and 2900 psi for 16 min in 2 cycles. A total hydrocarbon fraction was first isolated from the extract using an Al_2O_3 column via elution with 15 ml CH_2Cl_2. During this