

Sedimentary dynamics of coastal organic matter: An assessment of the porewater size/reactivity model by spectroscopic techniques



Duc Huy Dang^a, Véronique Lenoble^a, Gaël Durrieu^a, Jean-Ulrich Mullot^b, Stéphane Mounier^{a,*}, Cédric Garnier^a

^a Université de Toulon, PROTEE, EA 3819, 83957 La Garde, France

^b LASEM-Toulon, Base Navale De Toulon, BP 61, 83800 Toulon, France

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ABSTRACT

Sedimentary organic matter (SOM) mineralization is the driving force in diagenesis activity. This biogeochemical process, which controls the mobility of a huge number of elements and especially SOM transformations in surface and deep (down to –50 cm) sediments, was assessed in this study via seasonal monitoring with sediment core sampling in Toulon Bay (SE France). The SOM diagenetic degradation resulted in an important production of nutrients ($\text{NO}_3^-/\text{NH}_4^+$, PO_4^{3-} , $\text{Si}(\text{OH})_4$, etc.) in porewater associated with dissolved organic matter (DOM) characteristic modifications, which are seasonally dependent. Within this seasonal variation, different elemental ratios (C/P, C/Si) as well as absorbance and fluorescence characteristics were observed in surface and deep sediments, illustrating two pools of SOM, i.e., “fresh” and “buried”. Ultra-filtration results revealed the high proportion of low-molecular-weight DOM and the high-molecular-weight DOM (<3 kDa) was primarily characterized by protein-like fluorophores. The obtained results confirmed and extended the PoreWater Size/Reactivity model that describes diagenetic SOM transformations through the identification of two SOM pools and their reactivity. © 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Mineralization of sedimentary organic matter (SOM) is the driving force of diagenesis (Rullkötter, 2002), and this process affects the following elements/compounds: (1) components of organic matter structure released in porewater through SOM decomposition (C, N, Si, P, etc.); (2) electron-donor elements used by bacterial activity to oxidize the SOM (O, N, Mn, Fe, S); and (3) elements sensitive to the transformation (dissolution/precipitation) of sedimentary phases (e.g., arsenic release by dissolution of Fe/Mn oxides (Couture et al., 2010; Lafferty et al., 2011; Dang et al., 2014)). The carbon cycle in sediments could subsequently control the mobility of several other elements and may impact the coastal ecosystem (Gao et al., 2009). In fact, coastal/marine sediments accumulate OM from different sources: autochthonous (primary production in the seawater column) and allochthonous (OM from eroded sediment and terrigenous origin) (Rullkötter, 2002). The sedimentary OM cycle involves the two inverse processes of mineralization and preservation; the former implies SOM

microbiological degradation, and the latter renders SOM refractory toward mineralization through geo-polymerization and a selective preservation process (Burdige, 2007). The diagenesis process mineralizes the particulate organic carbon (POC) to dissolved inorganic carbon (DIC), and the remaining dissolved organic carbon (DOC) preserved from mineralization is usually qualified as biologically refractory OM (Burdige, 2002).

The PoreWater Size/Reactivity (PWSR) model was proposed to assess SOM diagenetic transformation (Burdige and Gardner, 1998). According to this model, POC hydrolysis releases high-molecular-weight DOC (HMW-DOC), which is degraded into low-molecular-weight DOC (LMW-DOC). The LMW-DOC fermentation produces short-chain organic acids/alcohols, and finally, DIC and inorganic nutrients (Burdige and Gardner, 1998; Komada et al., 2013). Using ultra-filtration, Burdige and Gardner (1998) demonstrated that most DOC has a molecular weight (MW) of less than 3 kDa, representing the LMW-DOC dominant form. Recent studies based on sediment incubation (Robador et al., 2010; Komada et al., 2012) have suggested the hydrolysis of refractory POC to refractory DOC, which could create a second SOM pool. Sulfate-reducing organisms could also directly oxidize LMW-DOC to DIC (Komada et al., 2013).

Among the analytical techniques used to describe OM quality, spectroscopic methods (UV–Vis absorbance, 3D fluorescence) are

* Corresponding author.

E-mail address: mounier@univ-tln.fr (S. Mounier).

suitable for natural conditions without the need for pre-concentration steps and are useful even in salt media. For UV–Vis spectrophotometry, it was demonstrated that the E_2/E_3 ratio (absorbance at 250 nm over 355 nm) was inversely correlated to the molecular weight of chromophorically dissolved OM (CDOM, [Peuravuori and Pihlaja, 1997](#); [Wang et al., 2009](#)). The spectral slopes (in the short wavelength region of 275–295 nm ($S_{275-295}$) or long-wavelength region of 350–400 nm ($S_{350-400}$)) and the ratio of the short/long-wavelength regions ratio (S_R) can be used as an inverse proxy of the OM molecular weight ([Helms et al., 2008](#)). The $SUVA_{254}$ is commonly used as a DOM aromaticity indicator ([Peuravuori and Pihlaja, 1997](#); [Weishaar et al., 2003](#)). The measurement of OM fluorescence capacity (FDOM, Fluorescence Dissolved Organic Matter) can also assess the SOM quality, and the FDOM can be separated into different fluorescent components (humic-like and protein-like; [Coble, 1996](#); [Stedmon et al., 2003](#); [Burdige et al., 2004](#)). For example, in the Chesapeake Bay sediments, the contribution of a humic-like fluorophore appeared to increase with depth, i.e., a SOM fraction attributed to the refractory LMW-DOM, whereas the protein-like fraction was mostly produced near the sediment water interface (SWI) ([Burdige et al., 2004](#)).

The porewater chemistry, and primarily the SOM transformation process, was investigated under different conditions (tidal and coastal sediments, continental slope) through spatial and seasonal variations ([Crill and Martens, 1987](#); [Thamdrup et al., 1994](#); [Alperin et al., 1994, 1999](#); [Beck et al., 2008](#)). The factors leading to the seasonal pattern were demonstrated as variations in temperature, OM deposition, and biological activities ([Arnosti et al., 1998](#); [Magni and Montani, 2006](#); [Gao et al., 2009](#); [Robador et al., 2010](#)). However, the relationships among the diagenesis-involved elements (C, N, P, Si, Mn, Fe, etc.), their sedimentary dynamics and DOM quality through a temporal pattern remain widely unknown.

In this context, the goal of the present study was to further investigate the SOM transformation processes in the coastal sediments of Toulon Bay (France, NW Mediterranean Sea) using seasonal monitoring of (1) the seawater column parameters; (2) the diagenesis tracer dynamics in porewater; and (3) quantity/quality and size fractionation monitoring of the “refractory” DOM. The obtained dataset was expected to validate the usefulness of coupling elemental analysis, size separation, and spectroscopic techniques in the study of sedimentary organic matter diagenesis, which is widely represented by PWSR models. The variation of such a process through time (temporal) and depth (down to –50 cm) is aimed at assessing the PWSR model with respect to the seasonal aspect and extending the PWSR model to anoxic/sulfidic sediments.

2. Materials and methods

2.1. Study site and sediment coring

Sediment cores were collected in Toulon Bay (NW Mediterranean Sea), which is divided by a seawall into two bays ([Fig. 1](#)). The maximum water depth in the small bay is 12 m. The sedimentation rate was estimated as close to 0.2 cm yr^{-1} ([Tessier et al., 2011](#)). The cartography of the surface sediments of the bay demonstrated a high level of multi-contamination by metals/metalloids ([Tessier et al., 2011](#); [Cossa et al., 2014](#)), organo-metals ([Pouget et al., 2014](#)), and organic contaminants (PAH, PCB; unpublished data), especially in the north of the small bay. The benthic macrofauna appeared limited, and no algal population was found in the north of the small bay ([Bernard et al., 2001](#)). The OM in the Toulon Bay primarily originates from the inputs of two urbanized rivers (Las and Eygoutier, [Fig. 1](#)), treated sewage outlets, aquaculture (south of the small bay), and planktonic activities ([Boge et al., 2006](#); [Nicolau et al., 2006, 2012](#)). Small Mediterranean rivers are characterized by

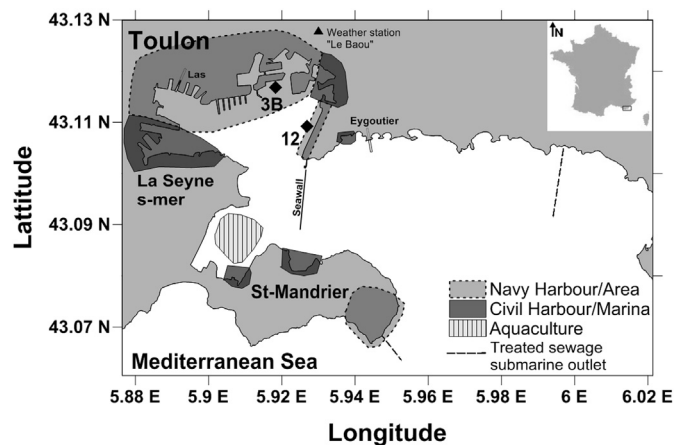


Fig. 1. Map of the study site and location of the sampled cores.

a base flow and intermittent storm flooding. In the case of Eygoutier, storm floods are responsible for ~90% and ~70% of annual POC and DOC discharge, respectively ([Nicolau et al., 2012](#)). Wastewater treatment plant inputs were also demonstrated to significantly increase the base flow OC discharge (e.g., in Marseille, [Oursel et al. \(2013\)](#)). The dissolved nutrients (NO_3^- and Si) in Eygoutier were at low concentrations in summer and higher concentrations in winter, resulting in a seasonal nutrient discharge into the sea ([Nicolau et al., 2006](#)). It was also demonstrated that algal biomass was the most important in winter (February), whereas bacterial and zooplanktonic abundances were high in spring and early summer ([Boge et al., 2006](#)).

In the current study, two specific stations (3B and 12, [Fig. 1](#) and [Table A.1](#)) were investigated, and seasonal monitoring was conducted at station 12 (every two months for 14 months). Sediments from station 12 (NE of the small bay, $43^\circ 6' 37.26'' \text{N} - 5^\circ 55' 42.15'' \text{E}$) appeared to be weakly mixed, which resulted in a high contamination of surface sediments and, to a lesser extent, of deep sediments ([Tessier et al., 2011](#)). Station 3B ($43^\circ 7' 0.48'' \text{N} - 5^\circ 55' 5.78'' \text{E}$) is situated in the Navy area. The constant profile of inorganic contaminants throughout the sediment core (down to –50 cm, a depth that normally corresponds to ~250 years of recorded history in the Toulon Bay, according to the average sedimentation rate; data not shown) suggest that the sediments from this area were highly mixed due to historical events (World War II) and frequent traffic/maritime operations.

Sediment sampling campaigns were performed in June 2009, April 2011, and every two months from May 2012 to July 2013 at station 12 and February 2013 at station 3B ([Dang et al., 2014](#)). The French Navy supported the sampling with the use of its ships and divers to collect sediment cores (Interface Corer, 10-cm diameter and 1-m long Plexiglas[®] tube) to preserve SWI integrity. For each campaign, a duplicate core (Plexiglas[®] tube with predrilled holes each cm) was used to measure the pH and Eh profiles.

Each core was sliced every 2 cm in a glove box under an inert atmosphere (N_2) to preserve the redox conditions. Slices were subsequently homogenized and centrifuged (in 50-mL Corning tubes for 15 min at 4000 g at 20 °C, Sigma 3–18 K). The porewater was recovered under a nitrogen atmosphere and filtered through 0.2- μm on-line syringe filters (cellulose nitrate, Sartorius). For DOC and DIC, samples were stored in pre-calcinated glass tubes (24 mL with a Teflon/silicon septum, Wheaton). An aliquot was reserved in polypropylene (PP) tubes for major element and nutrient analysis. For minor and trace elements, samples were stored in high density polyethylene (HDPE) bottles (6 mL, Wheaton), pre-cleaned with 10% HNO_3 , and rinsed three times with mQ water ($18.2 \text{ M}\Omega\text{cm}^{-1}$,

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