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Transient biogeochemistry in intertidal sediments: New insights from tidal pools in *Zostera noltei* meadows of Arcachon Bay (France)

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ABSTRACT

Several studies highlighted the occurrence of circular pools in intertidal flats of different coastal systems and their transient water chemistry over both tidal and diurnal cycles. However, little is known about (1) the response of benthic biogeochemical reactions and fluxes at the sediment-water interface over such short time scales, and (2) the role of these tidal pools in the biogeochemical functioning of coastal systems. Based on in situ microprofiles and water sampling, we investigated the dynamics of dissolved oxygen (O_2), nutrients, sulfides and metals, and the associated fluxes at the sediment-water interface in tidal pools from the Arcachon Bay (Atlantic coast of France). Our integrative approach included several tidal and diurnal cycles over two different seasons in the presence and absence of *Zostera noltei*. The results show that water temperature and light irradiance were the main factors driving the biogeochemical functioning of the tidal pools, as they controlled the physiological activity of the microphytobenthos. Changes in light radiations induced diurnal fluctuations of O_2 concentrations within surficial sediment, thus resulting in fluctuations of the O_2 diffusive fluxes at the sediment-water interface and of the O_2 penetration depth in sediment. At high tide, the increase in turbulence above the sediment induced the advection of oxygenated water within the first millimeters of sediment, resulting in a significant increase in porewater O_2 concentrations and sediment O_2 penetration depth. Porewater sulfide concentrations and apparition depth were concomitant with the O_2 dynamic over both diurnal and tidal cycles, indicating that intermediate redox diagenetic processes were impacted by O_2 dynamic over such short time-scale. The rapid changes in redox processes in the sediment column are confirmed by a significant flux of dissolved manganese toward the water column during nighttime. The consumption of nitrate and the release of ammonium and phosphate, associated to the mineralization of the organic matter in the surface sediment did not appeared related however to such short time cycles. The efflux of dissolved silica from the sediment was most likely associated with the enhanced dissolution of Si-bearing particles in surface sediment at higher temperatures, although silica uptake by *Z. noltei* was also noted. This study clearly shows that tidal pools function as natural incubators of transient biogeochemical processes. A rough assessment of the nutrient budget at the scale of the bay indicates the tidal pools may contribute significantly to the biogeochemical functioning of Arcachon Bay.

1. Introduction

In shallow coastal areas, the functioning of pelagic and benthic compartments is tightly coupled (Soetaert et al., 2000). Physical and chemical properties, such as temperature light, salinity, concentration of dissolved oxygen and nutrients, strongly vary over time scales ranging from hours to years in the coastal water column due to tidal, diurnal and seasonal cycles. These environmental evolutions profoundly impact the sediment biogeochemistry and chemical exchanges at the sediment-water interface, which in turn impact the water column chemistry. Assessing the transient dynamics of sedimentary biogeochemical processes is of primary importance to better understand the functioning of coastal ecosystems and to predict their evolution in a changing world.

Intertidal zones are particularly suitable to investigate the transient dynamics of sedimentary biogeochemical processes as they undergo strong changes in light, temperature, nutrient availability and hydrodynamic conditions over time, from tidal to seasonal time scales (e.g., Taillefert et al., 2007; Jansen et al., 2009). Recent works showed that the intensity of light irradiance was the main factor controlling the short-term O_2 dynamic in intertidal sediments over diurnal and tidal cycles (Jansen et al., 2009; Denis et al., 2012; Delgard et al., 2012).

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During the daytime, O_2 generally presents higher concentrations and penetration depths in sediments due to the photosynthetic activity of microphytobenthos, which may result in a net O_2 production in surface sediments and O_2 flux from the sediment to the water column (Böttcher et al., 2000; De Beer et al., 2005; Werner et al., 2006; Jansen et al., 2009; Delgard et al., 2012). Moreover, Denis et al. (2012) indicated that benthic photosynthetic production was generally higher during emersion periods than during inundation periods, as the light irradiance could be strongly attenuated through the water column. Previous studies also reported a vertical migration of microphytobenthos during tidal cycles in intertidal sediments that significantly modified the photosynthetic activity in surficial sediments (Consalvey et al., 2004; Migné et al., 2009; Denis et al., 2012; Delgard et al., 2012). The changes in O_2 concentration in surficial sediments directly impact the fate of redox species through modifications of early diagenetic processes such as denitrification, nitrification, and metal (e.g., Fe and Mn) and sulfide oxidation (Deflandre et al., 2002; Dalsgaard, 2003; Taillefert et al., 2007; Glud, 2008; Rigaud et al., 2013). Indeed, the increase in O_2 penetration depth in sediments lowers the sulfate reduction rates (Billerbeck et al., 2006) and intensifies the oxidation of reduced species produced in the anoxic part of the sediment (NH_4^+, Fe^{2+}, sulfides S(-II) and FeS; Taillefert et al., 2007; Delgard et al., 2012), thereby directly modifying the exchanges of nutrients and metals at the sediment-water interface (Rigaud et al., 2013).

The main limitation in understanding the biogeochemical processes and chemical transfers at the sediment-water interface in intertidal environments is the specific conditions occurring at low tide, notably the emersion periods that interrupt the exchanges at the sediment-water interface and induce perturbations such as the evaporation of porewater and desiccation of the top layer of sediments. Interestingly, intertidal flats may present topographic depressions where water can be trapped during low tide (e.g., Van der Laan and Wolff, 2006). These environments, referred as tidal pools, are particularly exposed to temporal variations in light and temperature because of their small volumes and shallow depths (e.g., Morris and Taylor, 1983; Clavier et al., 2011). Tidal pools have transient chemical compositions over tidal cycles due to chemical exchanges at the sediment-water interface (Lillebø et al., 2004; Murray et al., 2006). Thus, tidal pools can be considered as natural incubators, where it is possible to investigate the dynamics of sedimentary biogeochemical processes in response to changes in the environmental conditions in the overlying water. Indeed, the benthic-pelagic coupling is expected to be amplified due to the reduced volume of the pelagic compartment.

In the present study, we characterized the transient biogeochemistry of sediments in response to the variation of external forcing (temperature, light, water depth) over tidal and diurnal cycles in tidal pools from the Arcachon Bay. Biogeochemical processes and fluxes at the sediment-water interface were characterized and quantified from continuous in situ measurement of O_2, H_2S and pH in porewaters using an autonomous miniprofiler and from temporal variations of major biogeochemical species concentration (O_2, NO_3^-, tCO_2, PO_4^{3-}, NH_4^+, Si_d, Mn_d and Fe_d) in the overlying water trapped in the pool at low tide. The contribution of driving factors was evaluated by statistical treatments. A chemical budget at the scale of the bay is proposed to estimate the role of tidal pools to the biogeochemical functioning of Arcachon Bay.

2. Material and methods

2.1. Study area and sampling

The tidal pools were located in an intertidal mudflat of Arcachon Bay (44°42.737 N; 1°08.097 W), a macrotidal lagoon along the French Atlantic coast characterized by a semi-diurnal tide with an amplitude ranging from 1.2 m to 4.4 m (Fig. 1A). The pools at the study site were topographic depressions, a few meters wide and up to 20 cm depth (Fig. 1B). Lagoon water was trapped in the pools for approximately 4–5 h around low tide, until the rising tide reached the study site. The intertidal flat consisted of silty loam sediment colonized by a dense meadow of the dwarf eelgrass *Zostera noltei*. Although their origin is still not known (i.e., hydrodynamic vs. biological structure; see discussion in Van der Laan and Wolff, 2006; Takeuchi and Tamaki, 2014), the tidal pools presented consistent features in Arcachon Bay. Aerial photos of the sampling site enabled to estimate a surface coverage of 20% for the tidal pools (Fig. 1C). Arcachon lagoon pools were similar to those previously described by van der Laan and Wolff (2006) in the Banc d'Arguin (Mauritania).

Three field campaigns were carried out in July 2010 and August and October 2013. In July 2010, four different pools were studied during the same day: two pools densely covered by *Zostera noltei* and two unvegetated pools (Table 1). The water trapped in the four pools was sampled in triplicate every hour throughout an emersion period in the daytime (between 13:30 and 16:20). Pools studied in August and October 2013 were both unvegetated. In August 2013, the pool water was sampled during two consecutive periods of emersion, including one daytime (between 14:40 and 18:40) and one night (between 02:20 and 06:30). In October 2013, the pool water was sampled during emersion periods occurring during three consecutive days (between 12:00 and 18:00). Both in August and October 2013, sampling of the pool water started approximately one hour before the complete disconnection of the pool during the ebb tide and finished about one hour after the pools reconnected with the bay water during the flood tide. Water samples were collected in the central part of the pool using a 250 mL Nalgene beaker fixed on a long rod with a sampling frequency of 20–30 min. Samples were immediately filtered using acetate cellulose 0.2 µm syringe filters and were partitioned in either plastic or glass vials according to the type of analysis to be performed. The subsamples were stored untreated in gastight glass vials for total dissolved inorganic carbon ($tCO_2 = CO_2 + HCO_3^- + CO_3^{2-}$) analysis or collected in polyethylene vials and acidified with a 1% equivalent volume of concentrated HNO_3 for dissolved Fe and Mn analysis. The subsamples for dissolved nutrients (NO_3^-, NH_4^+, PO_4^{3-}, Si_d) analysis were transferred into two 12 mL polyethylene vials. Samples for tCO_2, metals and Si_d were kept refrigerated until analysis, while those for other nutrients were immediately frozen. The analysis of these samples was completed within a month after sampling.

At the end of 2013 campaigns, three 10 cm long and 2.5 cm diameter sediment cores were collected and sliced at 2 mm vertical resolution for porosity assessment. Porosity was obtained on each sediment slice by mass differences between fresh and freeze-dried sediment following correction for salt content, and assuming a sediment particle density of 2.65 g cm^{-3}.

2.2. In situ measurements in the pool water

Temperature, salinity, dissolved O_2 concentration, photosynthetically active radiation (PAR) reaching the sediment surface and water pressure (i.e., depth) were continuously monitored in the pools using in situ autonomous probes. Oxygen concentration and temperature were recorded using a SDOT300 data logger (*NKE Instruments*) equipped with an *Aanderaa* optode 3835. Salinity, temperature and water pressure were recorded using a STPS 100-SI data logger (*NKE Instruments*). PAR was monitored using a SPAR data logger (*NKE Instruments*) equipped with a flat LI-192 sensor (*LI-COR Corporate*). The SDOT and STPS probes were mounted on a foot of the miniprofiler MP6 system (see below) and positioned to be immerged in the pool water, while the SPAR probe was directly inserted into the pool sediment. During the 2010 campaign, the SDOT and STPS sensors were deployed in only one of the four pools, while temperature was manually recorded in the other at each sampling time. Oxygen concentrations were compensated for salinity, temperature and depth using the Interactive TD 280 spreadsheet (AADI, *Aanderaa*). The precisions of measurements were ± 5% for oxygen, 0.1 °C for temperature, 0.1 for salinity and