

Tidal variability in benthic silicic acid fluxes and microphytobenthos uptake in intertidal sediment

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ABSTRACT

Silicic acid (DSi) benthic fluxes play a major role in the benthic–pelagic coupling of coastal ecosystems. They can sustain microphytobenthos (MPB) development at the water–sediment interface and support pelagic diatoms when river DSi inputs decrease. DSi benthic fluxes have been studied at the seasonal scale but little is known about their diurnal variations. This study measured the amplitude of such variations in an intertidal area over an entire tidal cycle by following the alteration of DSi pore water concentrations at regular intervals over the flood/ebb period. Furthermore we independently estimated the potential DSi uptake by benthic diatoms and compared it to the variations of DSi pore water concentrations and fluxes. The microphytobenthos DSi demand was estimated from primary production measurements on cells extracted from the sediment. There were large changes in DSi pore water concentration and a prominent effect of tidal pumping: the DSi flushed out from the sediment at rising tide, occurs in a very short period of time, but plays a far more important role in fueling the ecosystem ($800 \mu\text{mol-Si m}^{-2} \text{d}^{-1}$), than diffusive fluxes occurring throughout the rest of the tidal cycle ($2 \mu\text{mol-Si m}^{-2} \text{d}^{-1}$). This process is not, to our knowledge, currently considered when describing the DSi cycling of intertidal sediments. Moreover, there was a large potential MPB requirement for DSi ($812 \mu\text{mol-Si m}^{-2} \text{d}^{-1}$), similar to the advective flow periodically pumped by the incoming tide, and largely exceeded benthic diffusive fluxes. However, this DSi uptake by benthic diatoms is almost undetectable given the variation of DSi concentration profiles within the sediment.

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1. Introduction

Silicic acid (DSi) inputs to shallow coastal systems originate predominantly from rivers and adjacent seas but internal recycling in the water column and at the sediment–water interface also play an important role (Ragueneau et al., 2002; Ní Longphuirt et al., 2009a). We focus here on benthic fluxes. At the sediment subsurface, pore waters are often substantially enriched in DSi, driving strong gradients and creating conditions favorable to high diffusive fluxes into the water column. This release of DSi from benthic sediments can significantly contribute to phytoplankton requirements and influence the dominance of this specific group in coastal

waters (Fouillaron et al., 2007). In a temperate ecosystem (Bay of Brest, France), Ragueneau et al. (2002) demonstrated the importance of DSi benthic fluxes in sustaining diatom demand throughout the productive period, particularly in late spring when river supplies are decreased.

DSi benthic flux estimates have previously been based on samples collected either monthly or seasonally (Sigmon and Cahoon, 1997; Marinelli et al., 1998; Ragueneau et al., 2002; Srithongouthai et al., 2003). However, DSi flux across the sediment–water interface is affected by a number of tightly connected physical, chemical, and biological processes (Aller, 1980; Yamada and D'Elia, 1984; Van Cappellen et al., 2002) occurring on shorter (e.g. intratidal) time scales. Consequently, due to the impact of these processes, benthic fluxes also fluctuate over short temporal scales. Clavier et al. (2008) and Ní Longphuirt et al. (2009a) have recently reported DSi fluxes over a full diurnal cycle in subtidal zones and revealed large variations over the day period, comparable to

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alterations observed at the seasonal scale. These studies indicated the importance of natural rhythms of biological and chemical processes to provide more accurate flux calculations and indeed more precise up-scaling to daily and seasonal scales. Nonetheless, in the intertidal zone, although there are major daily changes in environmental conditions due to the alternation of atmospheric exposure and tidal inundation, benthic DSi flux variations at the short time scale have scarcely been studied. Feuillet-Girard et al. (1997) are among the few to describe the tidal influence on DSi diffusive fluxes. However, they studied the emersion period only, and while they observed fluctuations, they could not detect any clear pattern.

Among the processes that play a role in altering short-term DSi flux oscillations, the uptake by microphytobenthos (MPB) has been identified. Situated at the sediment–water interface and within the sediment, MPB biomass and production can often reach levels comparable to phytoplankton in overlying waters and drive a need for a large amount of nutrients. This need has also been shown to vary considerably over the diurnal period most probably linked to light and MPB migration within the sediment. It is however, still not possible to determine the role of microalgae uptake from all the other processes regulating the benthic flux. A few studies have addressed this issue (Sundbäck et al., 1991; Sigmon and Cahoon, 1997; Bartoli et al., 2003) by considering the shift between light and dark incubations. They all described significantly lower DSi out-flux rates in cores exposed to a light/dark cycle in comparison to cores kept in the dark. However, it has been shown that silicon metabolism is not directly connected to photosynthesis (Brzezinski, 1992; Claquin and Martin-Jézéquel, 2005) and we cannot thus assume that the direct availability of light is necessary for DSi uptake. Ní Longphuirt et al. (2009a) made a first quantification of DSi uptake by the microphytobenthic community using the ^{32}Si

isotope. They showed that the uptake was within the same order of magnitude as the variation in benthic fluxes observed over a 2-day experimental period. MPB was thus potentially the main reason for the decrease in DSi fluxes between morning and midday on both days studied.

The present study followed *in situ* variations of DSi pore water concentrations to further appreciate their short-term (day, tide) dynamics in surface sediment (3 cm). Independent estimates of the potential DSi demand of the MPB were performed to evaluate its potential role in the regulation of DSi benthic fluxes over the flood/ebb periods.

2. Methods

2.1. Study site and experimental approach

The study site is situated in the Nakdong estuary ($35^{\circ}05'\text{N}$, $128^{\circ}55'\text{E}$; Fig. 1) at the southern end of the Korean peninsula. Its expansive tidal flats are of international importance being a main stopover location for wild birds that migrate between East Asia and Oceania. As with other wetlands, they also serve as a breeding ground and they support a rich coastal biodiversity. These areas have suffered profoundly from ecologically destructive development related to commercial interests, such as dam constructions and reclamation for housing and industry. However, since the turn of the 21st century, the management approach to Korea's tidal flats has shifted from reclamation projects to preservation efforts (Hong, S.-K. et al., 2008).

The sampling site flats are protected by sand dunes that run parallel to the coastline. The surface sediment is composed mostly of muddy sand (Choy et al., 2008). Core sampling was conducted

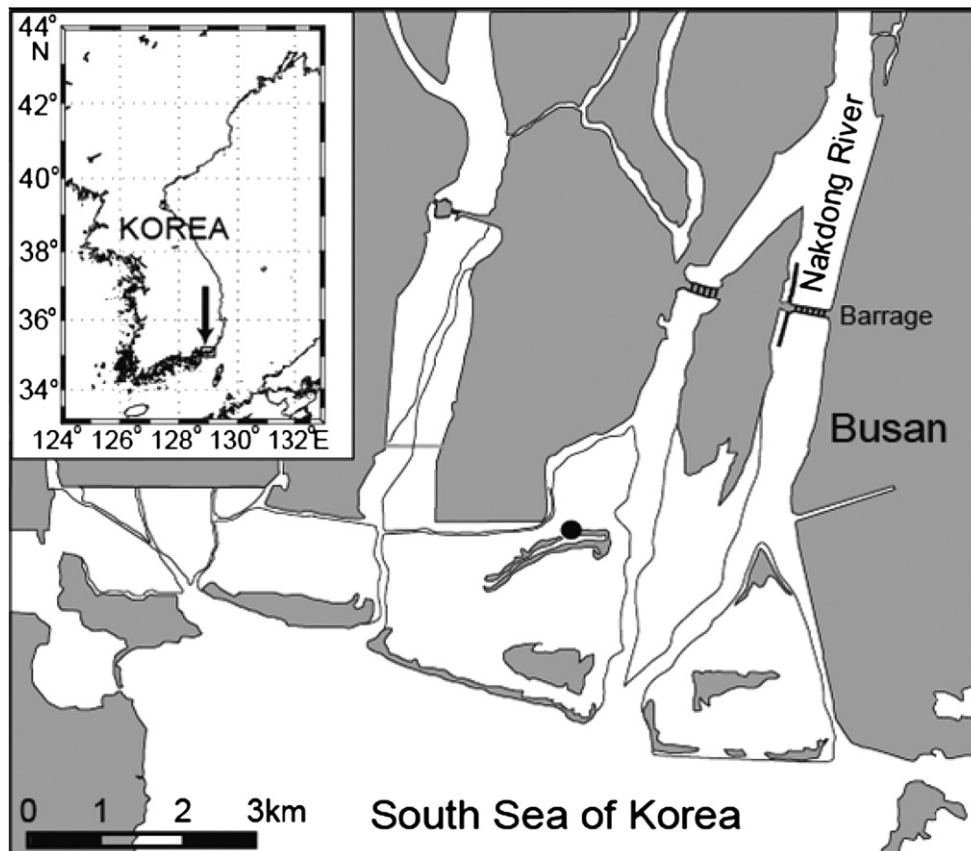


Fig. 1. The Nakdong Estuary on the southeast coast of the Korean Peninsula. The black dot indicates the study site.

during a 12-h period to determine the variation of nutrient pore water concentration profiles over diurnal and tidal cycles. Concentration profiles were used in this study instead of other methods based on incubations of various durations (either *in situ* with benthic chambers or in the laboratory with undisturbed cores) as this technique is best adapted for analyzing rapid changes in the sediment and takes into account variation at the interface during both immersion and emersion periods. To assess the potential effect of MPB on these variations, the migration of the MPB was tracked concurrently through a study of the variation in Chl *a* concentrations within the sediment over a depth range of 2 cm. Following this measurement, the primary production of the MPB was assessed using the ^{14}C isotope technique on cells extracted from the sediment at the site (Hartig et al., 1998), and the potential nutrient demand by the MPB was then estimated using conversion factors.

2.2. Field sampling

On 16 August 2007, sampling took place every two hours, from before sunrise (05:00 local time) to after sunset (20:00). Core sampling was done on foot as the water depth never exceeded 1 m. Triplicate cores of 9 cm \emptyset were recovered at each time step for the determination of pore water nutrient concentration. Interstitial water was immediately sampled from the cores on the site, every 0.5 cm, from the interface down to 2.5 cm depth, using the Rhizon (Rhizosphere Research Products, NL-6706, Wageningen) method (Seeberg-Elverfeldt et al., 2005). Pore water samples were then stored in 15-ml tubes and refrigerated until analysis for DSi. Sediment samples were also collected for pigment analysis using a modified version of the cryolander method (Wiltshire et al., 1997). During low tide, 3-cm \emptyset tubes were pushed into the sediment, and the sediment was frozen by gently pouring liquid nitrogen into the core. A total of six cores were sampled at each time period. During submersion periods, larger cores (9 cm \emptyset) were sampled and immediately sub-sampled with the smaller cores. The sediment was kept frozen at -80°C until sectioning for pigment analysis. Environmental parameters (salinity, temperature, and water depth) were recorded every minute over the entire sampling period using a Hydrolab DataSonde 4 (Hydrolab, TX, USA) multi-parameter logging system. Photosynthetically available radiation (PAR, $\mu\text{mol photon m}^{-2} \text{s}^{-1}$) for the site was recorded at the sediment surface with a Hobo Light Intensity probe (Onset Computer Corp.).

2.3. Sample processing and analysis

2.3.1. General methods

Nutrient concentrations in water samples were analyzed according to Strickland and Parsons (1968). In this paper, we present DSi results only as results for NO_3 and NH_4 are reported elsewhere (Ní Longphuirt et al., 2009b). The sediment cores taken for pigment analyses were sectioned at thicknesses of 0.2, 1, 3, 5, 10 and 20 mm, using a cryotome (Leica, CM 1500). The pigments were then extracted with 5 ml of acetone (90%) for 24 h at -20°C and analyzed using high-performance liquid chromatography as described in Kang et al. (2006). Additional samples were weighed, dried and reweighed to calculate water content. MPB cell counts and identification were carried out using an inverted microscope (Leica).

2.3.2. Diffusive flux estimation

Diffusive fluxes across the sediment–water interface were estimated using Fick's first law of diffusion adapted to sediment conditions (Bernier, 1980):

$$J = -\phi \times D_i \times dC/dz \left(\text{mmol} - \text{Si m}^{-2} \text{d}^{-1} \right) \quad (1)$$

where the sediment porosity (ϕ) was calculated through the sediment water content, D_i is the bulk sediment diffusion coefficient at the interface ($D_i = 3.3 \times 10^{-5} \text{ m}^2 \text{d}^{-1}$; Douchement, 1987), dC is the concentration gradient at the sediment–water interface, and dz is the thickness of sediments across which diffusion takes place.

2.3.3. Primary production measurements

Surface sediment was collected from the study site and placed in a basin overnight, after which MPB was isolated on the following morning using lens tissue. Subsequently, the cells were transferred from the lens tissue into a beaker and diluted in filtered water from the study site. Nutrients were added to reach concentrations consistent with those found in the superficial sediments. At this point, a 100-ml sample was filtered onto a GF/F filter and stored at -20°C for determination of pigments. Another 100-ml sample was also fixed with Lugol's solution for species determination and cell counts. The rest was dispensed into 32 disposable, sterile, 150-ml Nunc culture flasks. It is of note that there is a possible bias by applying the lens tissue technique as strongly adhered and hardly motile diatoms may not be caught. However, this method had previously been found to give statistically acceptable results (Eaton and Moss, 1966; Hickman, 1969) and is widely used in microphytobenthos studies (Hartig et al., 1998; Underwood et al., 1998).

To measure the gross primary production over the diurnal period, incubations were started before sunrise (at 05:00) and run every 2 h until 20:00, after sunset. During each incubation, four bottles were inoculated with ^{14}C - NaHCO_3 . One of the bottles was placed in the dark while the other three were exposed to natural light conditions. The temperature over the entire incubation period was $31.2^\circ\text{C} \pm 0.85$. After incubation, samples were collected on 25-mm GF/F filters. Filters were immediately rinsed with filtered seawater and placed in 7-ml scintillation vials. After addition of 100 μl of 0.5 N HCl, the vials were dried for 24 h at 50°C before addition of 5 ml of Ultima Gold scintillation liquid to each vial. ^{14}C particulate uptake was determined using a liquid scintillation counter Packard model TRI-CARB 1600-TR. For each experiment, total activity introduced into incubation samples was measured by counting 100- μl triplicates of each sample in vials containing 5 ml Instagel and 50 μl of Carbo-Sorb.

3. Results

3.1. Environmental parameters and sediment characteristics

The estuary has semi-diurnal tides with a maximal tidal range of 1 m during the experimental period. High tide was recorded at 10:30 on the day of sampling (Fig. 2). The system is largely influenced by the Nakdong River, with low salinity values oscillating with the tidal cycle from 2.75 PSU during the flooding tide up to 10.5 PSU just following high tide. Because of the high turbidity level of the Nakdong River, the PAR (Fig. 2) recorded at the sediment surface was strongly related to the tidal and diurnal cycles, with the highest values being recorded at low tide, at approximately 17:00. Sediment temperature (Fig. 2) showed a clear diurnal variation, with the lowest value (25°C) at dawn and maximum values in the early afternoon (33°C). Also, the temperature difference between the surface and 2.5-cm sediment depth was maximal (2°C) at the beginning of the afternoon, and this difference was reversed between night and day. The sediment surface cooled faster at night, while during the day, the sediment remained cooler at depth. Water content and porosity varied with the tidal cycle (data not

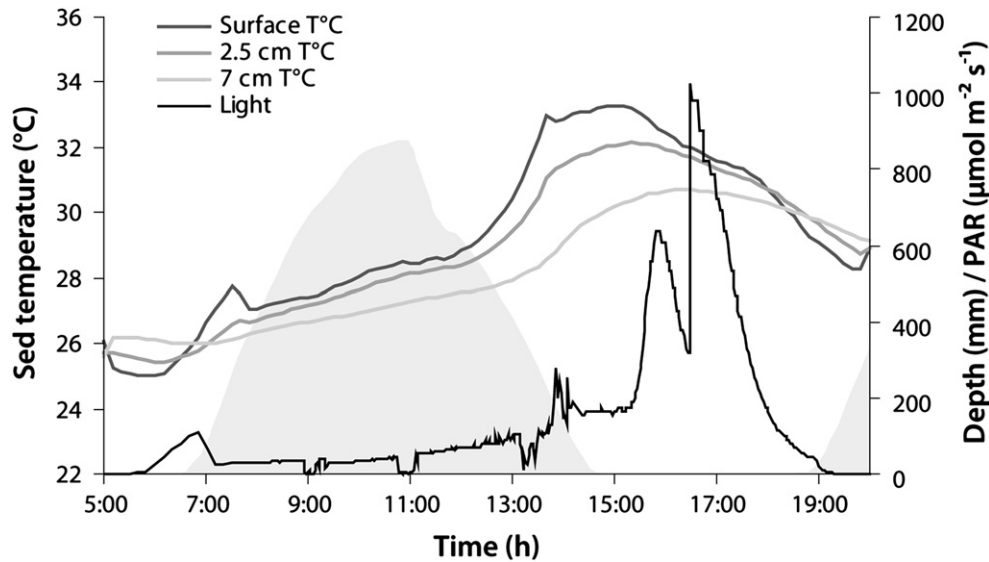


Fig. 2. Variations of sediment temperature, PAR (photosynthetically active radiation) and water depth (gray area), over the entire tidal cycle.

given), ranging from 46.6 to 54.2% and 24.7 to 35.9%, respectively, from high tide to low tide.

3.2. DSi pore water profiles

The concentrations of DSi in sediment pore water showed clear fluctuations between emersion and immersion periods during the 12 h of sampling. Fig. 3 shows the profiles; a missing section of the curve between the surface of the sediment and 0.5 cm of depth is the result of little to no extractable water during emersion periods. Gradients appear sharper during low tide (from 15:00 to 19:00) as compared to immersion periods (from 07:00 to 11:00) when profiles become nearly vertical. At the surface of the sediment, DSi concentrations varied from 140 up to 170 $\mu\text{mol L}^{-1}$, with the lowest value occurring at the beginning of the immersion period because of dilution by tidal currents. Greater changes occurred in the deeper layers. At 2.5 cm depth, DSi concentrations increased more than twofold (from 145 to 330 $\mu\text{mol L}^{-1}$) over the day period. This trend is clearly shown in the contour plot with overlaid arrows pointing

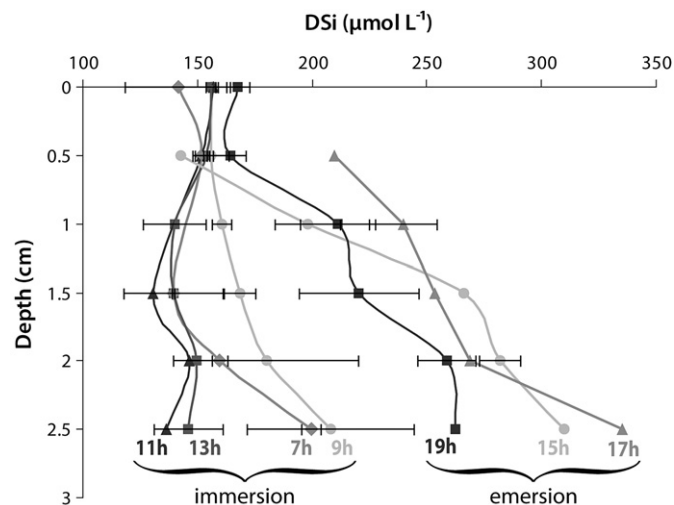


Fig. 3. Evolution of pore water Si(OH)_4 concentration profiles within the sediment (mean value for 3 replicates) over immersion/emersion periods. The missing section of the curve between the surface of the sediment and 0.5 cm of depth is the result of little to no extractable water during emersion. Error bars indicate standard deviations.

in the direction that DSi diffused (Fig. 4). This plot also indicates a local decrease in DSi concentration around high tide between 0.5 and 1 cm depth in the sediment.

3.3. DSi diffusive fluxes across the sediment–water interface

Theoretical DSi diffusive fluxes across the water–sediment interface were calculated from concentration gradients over the immersion period according to Fick's first law (Eq. (1); Berner, 1980). They varied from release to uptake within a day but the overall range of fluxes was weak (Fig. 5). Maximum flux out of the sediment at the very beginning of the immersion period reached 12 $\mu\text{mol m}^{-2} \text{h}^{-1}$. The flux was then reversed during the remaining flooding period but remained low, with a maximum rate of $-3.7 \mu\text{mol m}^{-2} \text{h}^{-1}$ toward the sediment.

3.4. MPB and Chl *a* concentrations

Microscopic examination of the MPB extracted revealed that the genus *Navicula* was dominant along with small *Navicula* spp. ($85 \pm 15\%$). *Nitzschia longissima* and *Amphora* sp. were also present

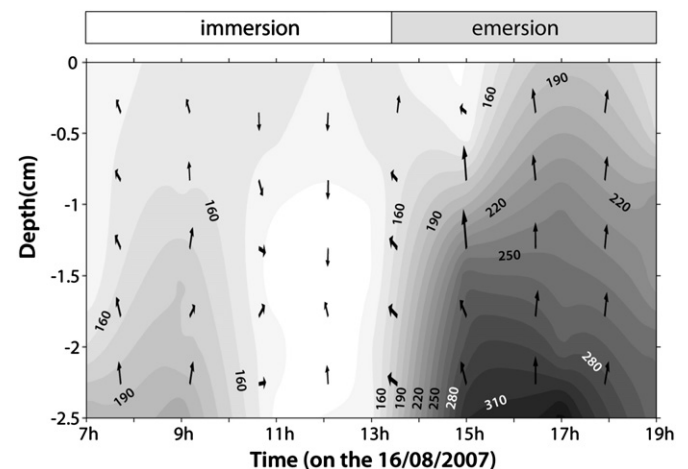


Fig. 4. Contour plot of DSi concentration ($\mu\text{mol L}^{-1}$) in pore water through the sediment depth and its evolution over the tidal cycle. Arrows in the vector map superimposed to the contour plot, point in the direction DSi flows.

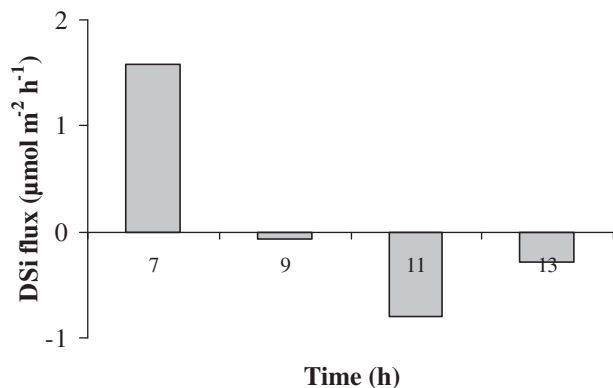


Fig. 5. DSi diffusive fluxes across the water–sediment interface estimated using Fick's first law of diffusion for period of immersion. They varied from release to the water column (values > 0) to uptake within the sediment (values < 0) within the day.

in small numbers. Vertical profiles of Chl *a* within the sediment (Fig. 6) indicated that MPB biomass was spread over a layer of 1–2 cm thickness. A detailed description of the Chl *a* vertical dynamic in the sediment during the day of sampling is described in Ní Longphuirt et al. (2009b). They show that below 1 cm depth, Chl *a* concentration declined strongly most of the time. Major changes in concentration attributable to migration processes occurred between 0 and 0.5 cm depths. Maximum biomass during the emersion periods was concentrated in the first millimeter (70% of the biomass, Ní Longphuirt et al., 2009b). During the immersion period, MPB migrated down into the sediment. At that time, the maximum biomass was found down to a depth of 0.5 cm.

There is no standard method to calculate Chl *a* biomass in the sediment. We have integrated Chl *a* concentration over 2 cm depth,

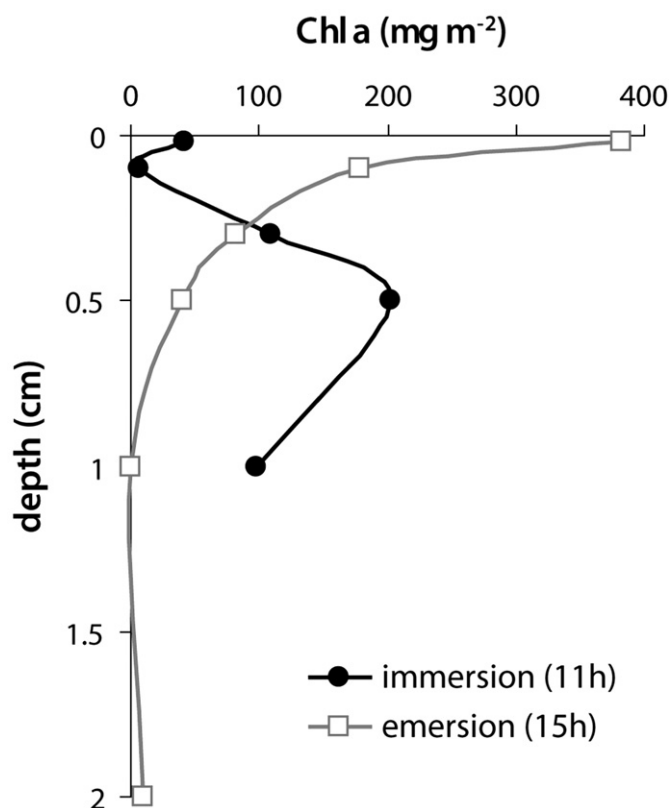


Fig. 6. Variation of Chl *a* concentration profiles in the sediment during immersion and emersion periods.

based on previous studies showing that most vital cells are usually present in this surface layer (De Jonge and Colijn, 1994). Once integrated, Chl *a* concentration varied from 25 to 112 mg m⁻² (with an average concentration for the day of 55 mg m⁻²). It increased slightly during the day (by about 25 mg m⁻²) and appeared to follow the availability of light reaching the seafloor, independently of the tide. For comparison, values encountered in shallow coastal environments commonly range between 20 and 400 mg-Chl *a* m⁻², an amount which is often equal to or greater than the chlorophyll biomass of the phytoplankton in the overlying water (McIntyre et al., 1996; Cahoon, 1999).

3.5. Primary production

Primary production by MPB extracted from the sediment (Fig. 7) reached 50 μg-C L⁻¹ h⁻¹ around 09:00, as PAR was already very high (1200 μmol photon m⁻² s⁻¹). The rate seemed to then saturate and stayed at the same level until 14:00, when the PAR started to decline. Overall, when integrated for the whole daylight period, 461 μg-C L⁻¹ d⁻¹ was produced (11 μg-Chl *a* L⁻¹), giving an average of gross production of 3.5 mg-C mg-Chl *a*⁻¹ h⁻¹.

4. Discussion

4.1. DSi pore water concentrations: variation between immersion and emersion periods

To our knowledge, this study is the first to report variations of pore water DSi concentrations over a diurnal and tidal cycle. Typically, DSi profiles in marine sediments display a sharp increase in concentration with depth, up to an asymptotic concentration that is highly variable from one site to another (Rutgers Van Der Loeff et al., 1981; Ragueneau et al., 2001). In the tidal flat studied here, we focused on the surface sediment (down to 2.5 cm depth) where DSi concentrations did not reach the asymptotic concentration, and important variations were observed between the emersion and immersion periods. Indeed, results showed that tidal currents induced a dilution of the concentration down to a depth of 2.5 cm during the immersion period (Fig. 4). By contrast, during emersion, a large increase in concentration occurred throughout the sediment profile. This increase suggests high remineralization rates, probably enhanced by the alterations in sediment temperature (Fig. 2, Wollast, 1974), salinity, pH (Yamada and D'Elia, 1984; Van Cappellen et al., 2002) and bacterial action (Bidle et al.,

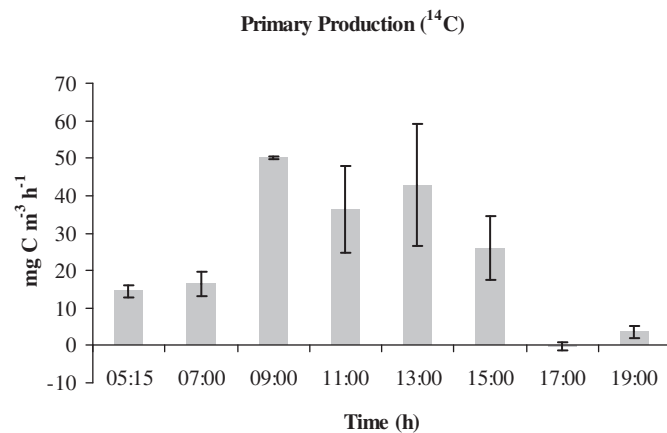


Fig. 7. Microphytobenthos primary production measured on cells extracted from the sediment and incubated over the diurnal period at in situ light and temperature conditions (mg-C m⁻³ h⁻¹).

2002). Part of this increase in concentration may also come from the diffusion of DSi from deeper, more concentrated, pore waters.

Similar tide-induced variations of ammonium and nitrate pore water concentrations have already been described in other intertidal systems (Usui et al., 1998; Kuwae et al., 2003; Sakamaki et al., 2006) and are reported elsewhere for our experiment (Ní Longphuirt et al., 2009b). All of these studies showed tidal oscillations in DIN (Dissolved Inorganic Nitrogen) concentrations, with an increase in ammonium and a decrease in NO_x in pore water during emersion and the opposite trend during immersion. Thus, it is of note that DSi pore water concentrations here showed a similar fluctuation to ammonium concentrations in the sediment but a distinctly reverse trend with nitrate concentrations. It is also of note that in general, DSi concentrations were not higher at depth during immersion. As discussed below, these results are important when trying to understand what triggers microphytobenthos migration into the sediment.

4.2. DSi fluxes in intertidal sediments: importance of tidal flooding (and advection) over molecular diffusion

Transport of DSi across the sediment–water interface results from a combination of advective and diffusive mechanisms. Advection can be defined as transport responding to a pressure gradient or a body force, whereas molecular diffusion is defined as transport responding to concentration gradients (Corey and Auvermann, 2003). When the tide rose, advection generated by tidal currents drastically altered pore water profiles and significantly decreased and homogenized DSi concentrations to depths greater than 2 cm (Fig. 3). Consequently, concentration gradients and diffusive fluxes became weak. Conversely, after the ebb tide, processes appeared to be governed essentially by remineralization reactions, and molecular diffusion promoted the migration of pore water ions from deeper sediment where DSi concentrations were higher. Because there was no exchange with the water column, the concentration gradient increased and became increasingly stronger throughout the low tide period. Thus, there was a large change between the immersion and emersion periods. In contrast, there was no observed evolution of DSi profiles within the course of each of the periods, emersion or immersion. In the absence of an obvious trend, we drew average profiles for each period (Fig. 8). On the basis of these profiles, the mean pore water DSi content was estimated using trapezoidal depth-integration in the top 2.5 cm of sediment. From the difference in DSi content between high and low tide, the release of DSi to the water column during tidal flooding (Q) can be calculated as $400 \mu\text{mol-Si m}^{-2}$. Because of the tidal rhythm, DSi was removed twice a day to the water column, meaning that this quantity should be multiplied by 2 to be expressed as a daily event. Thus, Q was ultimately estimated at ca. $800 \mu\text{mol-Si m}^{-2} \text{d}^{-1}$.

The magnitude of this DSi release to the water column at tidal flooding may be compared with the input that may result from molecular diffusion across the sediment–water interface during immersion. Because there was no diffusion during low tide, benthic fluxes were calculated using Fick's first law of diffusion for the immersion period only. The results ranged from -0.8 to $1.5 \mu\text{mol-Si m}^{-2} \text{h}^{-1}$. This range of variation, as well as the magnitude of these fluxes, is very low when compared to fluxes measured in coastal environments, which can reach some tens of $\text{mmol-Si m}^{-2} \text{d}^{-1}$ (Gomez-Parra and Forja, 1993; Ragueneau et al., 2002; Srithongouthai et al., 2003). However, this agrees with the difference observed in DSi concentration in overlying water. In coastal environments, DSi concentrations in the bottom water are typically low (i.e., often $<10 \mu\text{M}$), inducing stronger gradients at the water–sediment interface and driving fluxes of the greatest magnitude. When DSi bottom water concentrations are high, as in rivers and

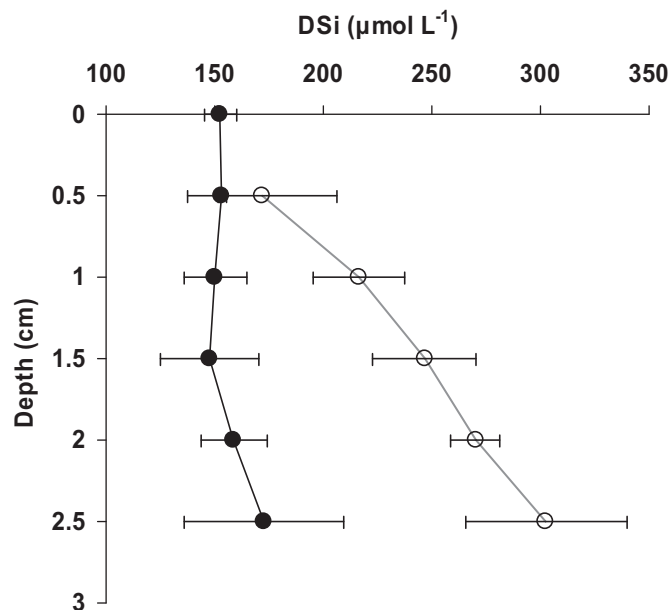


Fig. 8. Average DSi concentration profiles through the sediment depth for immersion (black line, black circles) and emersion (gray line, open circles) periods. Horizontal bars represent the standard deviation for all measurements made during the period, at the depth considered.

estuaries (i.e., often $>100 \mu\text{M}$) and as in this study, concentration gradients with pore water sediment are weak and consequently benthic diffusive fluxes are lower.

Our estimate of a daily diffusive flux of $1.7 \mu\text{mol-Si m}^{-2} \text{d}^{-1}$ is minor compared to the $800 \mu\text{mol-Si m}^{-2} \text{d}^{-1}$ that are flushed at tidal flooding. Thus, it seems clear that advection during the first few minutes of immersion, rather than diffusion at high tide, is responsible for most of the DSi transfer from intertidal sediment to the water column. This outcome is of major importance because this release to the water column is not accounted for during measurements performed with other methods, such as benthic chambers or permanently flooded cores. This sudden nutrient pulse to the water column may also affect the physiology of the phytoplankton in the overlying water (Fouillaron et al., 2007; Clauquin et al., 2010).

4.3. DSi concentration in the sediment, DSi benthic fluxes, and DSi requirements by MPB

As the nutrient pulse results in decreased DSi pore water concentrations, it may also play a role in the physiology of MPB, which migrates within the first centimeter of sediment depending on tidal and light cycles (Serôdio et al., 1997; Guarini et al., 2000). The hypothesis that MPB organisms burrow into deeper sediments during immersion to gain access to higher DSi/nutrient concentrations at depth has been proposed (Barranguet et al., 1998; Kingston, 2002; Leynaert et al., 2009). By studying the variation of concentrations in the sediment, we discovered that contrary to what was previously thought, concentrations of DSi and also DIN are not higher at depth during immersion; rather, concentrations at the surface are higher during the exposure period (when the cells are at the surface) than through the entire immersion period. Therefore, the hypothesis that MPB organisms migrate down during immersion to access higher concentrations does not hold, at least for intertidal sediments.

Nevertheless, although the reason for the migration remains elusive, it is a fact that benthic microalgae burrow at depth during

immersion. Moreover, it cannot be discounted that during immersion, and superimposed over advection and diffusion processes, uptake by benthic diatoms also influences the distribution of pore water DSi. A close examination of the DSi profile during immersion indicates a slight inversion in the concentration gradient 0.5–1 cm down into the sediment (Fig. 4) around midday. This depth coincides with the depth of the biomass maximum during flooding (Fig. 6), when most diatoms had migrated down into the sediment. This inversion is reflected also by diffusive fluxes directed toward the sediment at that period (Fig. 5). Such flux reversal is probably the result of MPB assimilation. At this depth, no light is available, but light is not necessary for DSi uptake because silicon metabolism is not directly connected to photosynthesis (Brzezinski, 1992; Claquin et al., 2002). These results highlight the fact that benthic diatoms very probably take up DSi at depth while buried in the sediment. It does not mean, however, that they do not also consume nutrients when they are at the surface. It is possible that benthic diatoms take DSi throughout the entire day (as do pelagic cells), whether at low tide when they are concentrated at the surface or at high tide when they have migrated into the sediment. Indeed a recent study on subtidal MPB showed that DSi uptake continues over the entire diurnal period (Ní Longphuirt et al., 2009a).

The MPB DSi requirement per day can be approximated from primary production rates measured on MPB cells extracted from the sediment (Fig. 7) and the Si:C molar ratio. On the day of the experiment, the MPB received 12 h of daylight, but only 5 h of that occurred during low tide. To ensure a conservative estimate, we consider that MPB organisms photosynthesized only during those 5 h; in addition, because of the strong attenuation of light within the first 200 μm of the sediment, we consider that only the Chl *a* present in the top 200 μm of sediment was active (the average concentration in this layer is $4.3 \pm 2.0 \text{ mg-Chl } a \text{ m}^{-2}$). Based on these assumptions, the MPB gross primary production is at least $15 \text{ mg-C m}^{-2} \text{ h}^{-1}$ (or $75 \text{ mg-C m}^{-2} \text{ d}^{-1}$). This photosynthetic activity of MPB falls in the high range of values reported for other intertidal environments (Goto et al., 1998; Guarini et al., 2002), but it is almost certainly related to the high level of PAR encountered in such an area. To extrapolate the inferred carbon production of $15 \text{ mg-C m}^{-2} \text{ h}^{-1}$ into a DSi requirement per day, we assume a Si:C molar ratio of 0.13, an average determined for planktonic diatoms (Brzezinski, 1985), although some results tend to show that benthic diatoms are more heavily silicified than pelagic diatoms (Sigmon and Cahoon, 1997). We can therefore estimate that benthic microalgae will require $812 \mu\text{mol-Si m}^{-2} \text{ d}^{-1}$.

When related to Chl *a* biomass, the DSi productivity ($18 \mu\text{mol-Si mg-Chl } a^{-1} \text{ d}^{-1}$) is approximately one-quarter of that reported previously by Ní Longphuirt et al. (2009a) for MPB in a shallow subtidal site. Thus, this estimate seems reasonable and conservative although despite this the current value is still three orders of magnitude higher than the diffusive fluxes measured at the sediment–water interface during the immersion period. This large difference indicates that the magnitude of diffusive fluxes measured, as well as the extent of their variations, is not related to the MPB DSi demand. However, the DSi requirement by the MPB does coincide with the amount of DSi released during flooding. If the effect of DSi assimilation by the MPB is not visible neither on concentrations in the sediment, nor on the diffusive flux, it might be because:

(1) The diffusive fluxes are underestimated. Indeed, it is possible that the diffusive flux predicted from the concentrations in the sediment may be distorted if the sampling interval (at 0.5 cm scale) is not sufficiently fine to account for discontinuities in profiles that could exist at the interface at millimeter scale due

to biological activity, and in particular to the presence of a biofilm;

- (2) Another explanation could be that there is a kind of balance between remineralization (which include all processes such as weathering, desorption, diffusion, dissolution) and assimilation rates, whereby DSi is released as the same rate as MPB remove DSi from the system. This would obscure the effect of MPB uptake on DSi concentrations in the sediment;
- (3) Finally, it is also possible that MPB takes up much of its DSi requirement from the water column. Uptake of $800 \mu\text{mol-Si m}^{-2} \text{ d}^{-1}$ from the water column will decrease concentration by less than $1 \mu\text{mol L}^{-1}$ at high tide. This effect will not be seen at this site where seawater concentrations are very high ($>120 \mu\text{mol L}^{-1}$) especially since it could be offset by the advective flow at high tide.

5. Conclusions

Although diffusive fluxes at the sediment–water interface have been often studied, to our knowledge this study is the first to show the variability of DSi concentrations and fluxes in an intertidal area over an entire tidal cycle. First, our results suggest that DSi pore water concentrations show large fluctuations and contrary to what we previously thought, concentrations are at their highest at low tide because of remineralization and DSi diffusion from deeper and more concentrated pore waters. These alterations are similar to those exhibited by ammonium concentrations in the sediment, but they exhibit a distinctly reverse trend compared to nitrate concentrations. In addition, with the incoming tide, a large pulse of DSi is flushed out of the sediment by advective processes. Diffusion at high tide represents only a very small part of the fluxes to the water column. Furthermore, MPB organisms show a high DSi requirement but its effect on sediment concentration, on diffusive fluxes or in the water column is not detectable by in situ observations.

This study is of major concern for the accurate quantification of benthic fluxes and their role in the ecosystem in intertidal areas. The results show the importance of considering small-scale variations to better understand the processes at play and to prioritize their significance in ecosystem functioning. In the future, a model of silica early diagenesis in the sediment, including an MPB compartment, would help greatly in bringing all the pieces together and for assessing the impact of the MPB on the silica cycle and benthic–pelagic coupling.

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