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The role of benthic biofilm production in the mediation of silicon cycling in the Severn Estuary, UK

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ABSTRACT

The biological mediation of benthic biogenic silica (BBSi) by the diatom-dominated biofilms on the intertidal mudflats of the Severn Estuary (UK) was assessed *in situ* under different environmental conditions using measurements of productive biomass (chlorophyll *a*), photosynthetic activity of undisturbed microalgal assemblages, benthic biogenic silica (BBSi) and benthic dissolved silica (BDSi). We show low BBSi standing stocks in the mudflats compared to other European estuaries, under both warmer summer conditions (0.6%) and colder winter conditions (0.5%). Dissolved forms of Si (BDSi) dominated the estuary, with significantly higher concentrations during the sampled winter (22.6 ± 1.0 mg L^{-1}) compared to the sampled summer (2.9 ± 0.5 mg L^{-1}). Benthic algal biomass was higher under cold conditions compared to warmer conditions (24.0 ± 2.3 and 13.2 ± 1.9 mg g^{-1} *sed. dw.*, respectively), following reduced migratory behaviour in the winter increasing surficial biomass. Relative maximum Electron Transport Rate ($rETR_{max}$), used as a proxy for relative primary productivity, was higher under warm conditions (254.1 ± 20.1 rel. units) compared to cold conditions (116.0 ± 27.1 rel. units). The biofilms sampled in the summer biologically mediated Si by the productive, high light acclimated diatoms that were highly motile during fluorescence measurements, and exhibited migratory behaviour, which despite nutrient limitation, evidenced by low F_v/F_m, increased the accumulation of BBSi. The biofilms sampled in the winter that were subject to relatively colder temperatures, consisted of low light acclimated diatoms of reduced migratory capabilities, and induced NPQ that suppressed productivity, and mediated BBSi to a lesser extent. Environmental stresses reduced the biofilm biological mediation of Si, which controlled Si to a lesser extent compared to the high hydrodynamic energy increasing biofilm re-suspension and terrestrial/coastal inputs.

1. Introduction

Most research on the global silicon (Si) cycle has focused on weathering (Hurd, 1977; West et al., 2005; Fortner et al., 2012) or oceanic Si cycles (Brzezinski et al., 1998; Yool and Tyrrell, 2003). Few have explored the complexity of the marine-terrestrial interconnecting cycles, leaving estuarine processes poorly constrained despite their importance in determining marine Si budgets. The present study intends to address the lack of research on Si cycling in the coastal transition zone. This was achieved by analysing the variations in Si fractions in the Severn Estuary, resulting from environmental driven changes in the ecosystem functioning, in the form of biomass and relative primary productivity, by the exposed diatom-dominated (Underwood, 2010) microphytobenthos (MPB) biofilms on the intertidal mudflats.

The high water turbidity, typical of a sediment-dominated estuary, limits the growth of large pelagic phytoplankton communities (Underwood, 2010). Subsequently, the MPB biofilms have high rates of biogeochemical cycling, with complex rhythms of photosynthetic activity (Pickney and Zingmark, 1991), and are likely to mediate nutrient dynamics in an estuary. MPB are characterised by the absence of photo-inhibition at high irradiance, due to the combination of physiological (e.g. effective photochemical and non-photochemical quenching, NPQ; *see* Maxwell and Johnson, 2000; Jesus et al., 2006; Lavaud and Kroth, 2006) and behavioural mechanisms (bulk migratory response), and cell surface turnover in the form of micro-cycling, minimizing the risk of overexposure to

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damaging light intensities (Kromkamp et al., 1998; Serôdio et al., 2006b, 2008; Perkins et al., 2001, 2002, 2010a). No previously published studies have investigated the diatom-dominated MPB biofilms influence on Si dynamics in the Severn Estuary.

The Severn Estuary is a heterogeneous environment with a complex hydro-geomorphology (Kirby, 2010; Manning et al., 2010), resulting in an important environment for biosphere functioning, primarily through the filter for land-ocean exchange. The hypertidal range is the second highest astronomical tide globally (13.9 m at Avonmouth) (Liang et al., 2013) resulting in substantial intertidal areas of cohesive muddy sediment. This makes the Severn Estuary an important case study for Si cycling, and allows for scaling to quantify other estuarine Si budgets. Few estuarine Si studies exist globally (De'Elia et al., 1983; Rendell et al., 1997; Liu et al., 2005; 2008; 2009; Arndt and Regnier, 2007; Pastuszak et al., 2008; Carbonnel et al., 2009; 2013), and understanding of the controls on the current Si cycle and estuarine budgets are lacking. The Scheldt Estuary, Belgium/The Netherlands, remains one of the only estuaries to have a comprehensive Si dataset, and has proven to enhance biological processes leading to nutrient transformations (Arndt and Regnier, 2007; Carbonnel et al., 2009; 2013). Similarly, the fine-sediment dominated Severn Estuary may exhibit a significant biological control on Si dynamics. Further, the strength of the inter-habitat coupling in the estuary implies that changes in MPB biomass and productivity may propagate into other linked ecosystems, and further afield to the marine pelagic zone in the southwest.

Si is a key element for siliceous organisms in aquatic habitats. Land-sea interactions and transfers control the proportions of Si in the form of silicic acid $Si(OH)_4$, hereafter called 'dissolved silica' (DSi), and particulate biogenic silica (BSi). These vary seasonally and geographically due to the transformation from DSi to BSi (~240 t mol y^{-1}) by photoautotrophic motile epipelic diatoms (accounting for >95% of eukaryotic living cells on intertidal mudflats) (Underwood, 2010), and weathering processes, a factor of river flow regime and temperature (Ragueneau et al., 2000). The variation in the natural abundance of Si fractions has often been used as a proxy for diatom production and Si utilization (Conley and Malone, 1992). Therefore, characterizing the difference in Si fractions provides important information on Si biological uptake in the estuary.

Si cycling is poorly quantified from local to global scales due to the lack of Si data compared to other key nutrients (Moosdorf et al., 2011). Previous studies (Conley and Malone, 1992; Aure et al., 1998; Gilpin et al., 2004) have noted non-Redfield ratios (Redfield et al., 1963) in estuaries. For example, in sub areas of the Baltic Sea, the doubling of phosphate and nitrate inputs increased BSi production causing a reduction in DSi, and induced Si limitation (Pastuszak et al., 2008). Such nutrient ratios can diminish the relative importance of diatoms, resulting in non-siliceous phytoplankton becoming dominant (Correll et al., 2000). Despite the Severn Estuary's ecological and economic importance, its role in benthic BSi (BBSi) and benthic DSi (BDSi) transformations, to our knowledge, has not been addressed quantitatively. This gap leaves little understanding of the terrestrial disturbances by anthropogenic activities, land-use changes, and climate change expected over the twenty-first century (Met Office, 2011). The aim of this study was to analyse the biological mediation of Si by the diatom-dominated MPB biofilms in the Severn Estuary under different environmental conditions, resulting from investigating three separate survey sites under summer and winter conditions. This was achieved through the analysis of different environmental conditions experienced during the summer (relatively warmer, lower rainfall) and a winter (relatively colder, higher rainfall), and over a spatial scale of the three sample sites that differed in sediment water content and site exposure.

2. Methods

2.1. Study site and sampling method

The study was carried out on intertidal mudflats located in the Severn Estuary between southeast Wales and southwest England (Fig. 1). Three intertidal mudflat sites were surveyed: site 1, Severn Beach (002°66′W, 051°56′N); site 2, Portishead (002°77′W, 051°49′N); and site 3, Newport Wetlands (002 °58′W, 051°32′N). Site 1 mudflats located at the mouth of the River Severn, subject to a small tidal prism, were exposed to the full-force of the prevailing south westerly winds, and had sediments of high sand content (>63 μm). Site 2 mudflats were less exposed to the south westerly winds, and had higher mud content (<63 μm), and crevasses perpendicular to the shoreline. Site 3 mudflats, subject to a large tidal prism, were sheltered from the south westerly winds, and had high mud content (<63 μm), and laid adjacent to a saltmarsh and wetlands.

In situ MPB biofilms were sampled during daytime low tide periods in the summer and winter of 2014. Air temperature records for the Severn Estuary show a significant difference ($t(df) = 13.224$, $p < 0.001$) between the relatively warmer summer and relatively colder winter sampling periods (Met Office, 2015). The benthic biofilms sampled during the summer were exposed to longer sunshine hours and lower rainfall (225 h sunshine, 79.6 ± 28.2 mm of rain) compared to biofilms sampled during the winter (64 h sunshine, and 136.8 ± 28.6 mm of rain) (Met Office, 2015).

At each site, 12 sampling stations were surveyed, equally spaced along a linear transect parallel to the lower shore. Sampling involved extracting sediment mini-cores of a diameter of 2.54 cm for the surficial 5 mm biofilm for analyses of chlorophyll *a* content (chl *a*) (Smith and Underwood, 1998), key benthic diatom species, and BBSi content. Pore fluids (25 ml) at each station were sampled for BDSi and orthophosphate (P) concentrations using a simplified peeper method (Teasdale et al., 1995).

2.2. BBSi

Approximately 25% of the surficial 5 mm biofilm sediment was placed in an oven at 85 °C for 24 h to determine the percentage loss of weight upon drying. BBSi concentrations were determined following the standard alkaline extraction method for marine sediment (DeMaster, 1981) and presented as percentage of dried Si mass (g/g). Dried sediment was crushed using a pestle and mortar, and ~0.05 g of the sediment was leached in hydrogen peroxide (5 ml of 10% H_2O_2 solution), followed by acid (5 ml of 1 M HCl solution). To each sample, 40 ml of 0.1 M of $NaCO_3$ was added. Samples were placed in a covered, constant temperature water bath at 85 °C. After 1 h, 3 h and 5 h, sub samples were taken, diluted, neutralized, and analysed for BBSi content using the standard Heteropoly Blue Method, and measured using a Hach Lange DR3900 spectrophotometer.

2.3. BDSi and orthophosphate (P-PO_4^-)

Pore fluid samples were centrifuged for 10 min at 1000 rpm for BDSi and P-PO_4^- concentrations. BDSi was analysed using the Heteropoly Blue method with concentrations (mg L^{-1}) measured using a Hach Lange DR3900 spectrophotometer. P-PO_4^- concentrations (mg L^{-1}) from pore fluids were measured using a Hach Lange DR3900 spectrophotometer, where 2.0 ml of each sample were analysed following the LCK 349 method. All P-PO_4^- concentrations recorded in both seasons, were below 50 mg L^{-1} and did not interfere with BBSi measurements.