Estuarine, Coastal and Shelf Science 148 (2014) 36–47

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

Alkalinity production in intertidal sands intensified by lugworm bioirrigation

Alexandra M.F. Rao [a, *], Sairah Y. Malkin [a, 1], Francesc Montserrat [a, b], Filip J.R. Meysman [a, b]

[a] Laboratory of Analytical, Environmental & Geochemistry, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium
[b] Department of Ecosystem Studies, Royal Netherlands Institute for Sea Research, P.O. Box 140, 4400 AC Yerseke, The Netherlands

ARTICLE INFO

Article history:
Received 16 September 2013
Accepted 5 June 2014
Available online 26 June 2014

Keywords:
diagenesis
bioirrigation
bioturbation
Arenicola
calcium carbonate
alkalinity

ABSTRACT

Porewater profiles and sediment-water fluxes of oxygen, nutrients, pH, calcium, alkalinity, and sulfide were measured in intertidal sandflat sediments from the Oosterschelde mesotidal lagoon (The Netherlands). The influence of bioturbation and bioirrigation by the deep-burrowing polychaete *Arenicola marina* on the rates and sources of benthic alkalinity generation was examined by comparing measurements in intact and defaunated sediment cores before and after the addition of *A. marina* in summer and fall 2011. Higher organic matter remineralization rates, shallower O_2 penetration, and greater sediment-water solute fluxes were observed in summer, consistent with higher sediment community metabolic rates at a higher temperature. Lugworm activity stimulated porewater exchange (5.1 × in summer, 1.9 × in fall), organic matter remineralization (6.2 × in summer, 1.9 × in fall), aerobic respiration (2.4 × in summer, 2.1 × in fall), alkalinity release (4.7 × in summer, 4.0 × in fall), nutrient regeneration, and iron cycling. The effects of lugworm activity on net sediment-water fluxes were similar but more pronounced in summer than in fall. Alkalinity release in fall was entirely driven by metabolic carbonate dissolution, while this process explained between 22 and 69% of total alkalinity production in summer, indicating the importance of other processes in this season. By enhancing organic matter remineralization and the reoxidation of reduced metabolites by the sediment microbial community, lugworm activity stimulated the production of dissolved inorganic carbon and metabolic acidity, which in turn enhanced metabolic $CaCO_3$ dissolution efficiency. In summer, evidence of microbial long distance electron transport (LDET) was observed in defaunated sediment. Thus, alkalinity production by net carbonate dissolution was likely supplemented by anaerobic respiration and LDET in summer.

1. Introduction

Oceans are an important sink for the excess CO_2 released by human activities including fossil fuel burning, land use change, industrialization and deforestation, which have resulted in a >30% rise in atmospheric CO_2 during the industrial era (Sabine et al., 2004; Forster et al., 2007). In this time, the oceans have absorbed approximately 30% of anthropogenic CO_2 emissions by air-sea gas exchange, resulting in a decline in surface ocean pH of about 0.1 (Feely et al., 2010). In the last century, ocean acidification has had a significant negative effect on calcification, survival, growth, development, and abundance among corals, mollusks, echinoderms, coccolithophores, and other taxonomic groups (Kroeker et al., 2013). With an additional expected decline of 0.3–0.4 pH by the end of this century, ocean uptake of anthropogenic CO_2 will likely have strong adverse effects on calcareous and noncalcareous marine organisms alike (Gazeau et al., 2007; Guinotte and Fabry, 2008; Hutchins et al., 2009).

In coastal waters, the accumulation of anthropogenic CO_2 can exacerbate low pH conditions resulting from natural respiration processes (Feely et al., 2008; Bates and Mathis, 2009; Feely et al., 2010), thereby compounding the stress exerted on coastal ecosystems. While sediments represent an important site of organic matter remineralization in nearshore environments, recent studies suggest that coastal sediments are also a source of alkalinity to the overlying water, favoring the role of the coastal ocean as a potential sink for atmospheric CO_2 (Thomas et al., 2009; Faber et al., 2012). During early diagenesis, alkalinity can be produced by several different processes, including $CaCO_3$ dissolution, denitrification, and iron and sulfate reduction coupled to the subsequent

* Corresponding author. Present address: Université du Québec à Rimouski, Institut des sciences de la mer, 310 allée des Ursulines C.P. 3300, Rimouski QC, G5L 3A1 Canada.
E-mail address: alexandra_rao@uqar.ca (A.M.F. Rao).
[1] Present address: Department of Marine Sciences, University of Georgia, Athens, GA, USA.

http://dx.doi.org/10.1016/j.ecss.2014.06.006

burial of iron sulfide minerals such as iron monosulfide (FeS) and pyrite (FeS_2) (Stumm and Morgan, 1996). It is crucial to better understand the actual mechanisms and rates of benthic alkalinity generation.

In the North Sea, it has been estimated that as much as one-quarter of the overall CO_2 uptake may be driven by alkalinity production in the intertidal flats of the southern North Sea (Thomas et al., 2009). These deposits support rich macrofaunal communities (Reise et al., 1994; Seys et al., 1994) and high sediment community metabolic rates (de Beer et al., 2005; Werner et al., 2006; Roy et al., 2008). The macrofaunal activity in these sediments exerts an important influence on carbon and nutrient cycling and fluxes of solutes across the sediment-water interface by altering the balance between solute transport and reaction rates in sediments (Kristensen, 2001). An understanding of the influence of benthic macrofauna in regulating alkalinity production may therefore help to elucidate the rates, controls, and spatiotemporal variability in alkalinity sources and CO_2 uptake in ocean margin environments. Experimental and modeling studies have shown that biological particle mixing (bioturbation) exerts a strong control on the permeability, stability, composition, and metabolic rates in sediments, and that bioirrigation flushes out reduced metabolites and supplies terminal electron acceptors and organic substrates for microbial metabolism (Banta et al., 1999; Kristensen, 2001; Volkenborn et al., 2007; D'Andrea and DeWitt, 2009; Volkenborn et al., 2010; Kristensen et al., 2012). However, the influence of benthic macrofaunal activity on alkalinity generation has so far received little attention.

To better understand the role of macrofaunal activity (particle mixing and porewater bioirrigation) on alkalinity production in coastal sediments, we investigated the impact of the deep-burrowing lugworm *Arenicola marina* on interfacial fluxes and porewater profiles of oxygen, nutrients, pH, calcium, alkalinity, and sulfide in sediment cores from an intertidal sandflat in the Oosterschelde (The Netherlands). The effect of season was investigated by comparing experiments conducted in summer and in autumn.

A. marina is the dominant bioirrigator in intertidal sediments in the southern North Sea, and at densities that can exceed 50 individuals per m^{-2}, it often dominates the polychaete biomass in this region (Reise et al., 1994; Coosen et al., 1994; Kristensen, 2001). The lugworm is a head-down deposit feeder residing in L-shaped burrows that can conspicuously transform its habitat (Huettel, 1990; Volkenborn et al., 2007). Sediment ingestion in the lower part of the burrow causes sediment to sink into the feeding pocket, and the resulting surface depression traps detritus. The lugworm periodically retreats to the surface and excretes sediment particles around the opening of the tail shaft, producing distinctive faecal casts. This ingestion–egestion behavior reworks the sediments surrounding the burrow structures, and translocates surface sediments with recently deposited labile organic material and solid phase electron acceptors, such as iron and manganese (hydr)oxides, downward into subsurface suboxic or anoxic layers of sediment. At the same time, aged, refractory organic particles and reduced iron sulfide minerals are transported upward to the oxic surface layer. The peristaltic motions of *A. marina* result in the irrigation of burrow water with oxygenated bottom water in a rhythmic fashion and the percolation of suboxic or anoxic porewater surrounding the feeding pocket upward into the overlying water, although flow reversals do occur (Kristensen, 2001; Volkenborn et al., 2010). The bioturbation and bioirrigation activities of lugworms enhance aerobic and anaerobic mineralization of organic carbon and nitrogen in sandy coastal sediments (Kristensen, 1988; Huettel, 1990; Banta et al., 1999; Kristensen, 2001).

2. Materials and methods

2.1. Sampling

Sediment cores were collected by hand at low tide at Tholseinde (51° 26′ 52″ N, 04° 05′ 47″ E, Fig. 1), an intertidal region in the inner part of the Oosterschelde (Delta area, SW Netherlands). The Oosterschelde is an euhaline mesotidal basin with extensive intertidal sandflats, which cover about one-third of its surface area (de Jong et al., 1994). Hydrodynamic forces and sediment transport in this coastal embayment have been modified by a storm-surge barrier and two auxiliary dams, completed in 1987 (ten Brinke et al., 1994; de Jong et al., 1994; Nienhuis and Smaal, 1994). The Oosterschelde sandflats are home to a rich macrofaunal community of bivalves, gastropods, and polychaetes, most notably the lugworm *Arenicola marina* (Coosen et al., 1994).

2.2. Core incubations

Sediment cores were collected in July and November 2011, and brought to the Royal Netherlands Institute for Sea Research (NIOZ) in Yerseke, NL for *ex situ* incubations. Plexiglas (PMMA) coreliners, 15 cm inner diameter and 35 cm in length, were used for collection and subsequent incubations. Cores typically contained about 20 cm of sediment and 15 cm of overlying water. Cores were incubated in a darkened water bath, continuously aerated and replaced daily with Oosterschelde seawater, kept in a temperature-controlled room at 16 °C in July and 12 °C in November.

In July, eight cores were collected and immediately sealed with polyoxymethylene lids with gas-tight O-ring seals after collection for a ten day period of defaunation by asphyxia. Cores were then opened and any macrofauna that had migrated to the surface were carefully removed with minimal disturbance to the sediment-water interface. The open cores were then placed in the aerated water bath for a reequilibration period of eight days. Subsequently, O_2, pH and H_2S microsensor profiles were measured in triplicate in each of three cores, as described in Section 2.4, and solute fluxes were determined in all eight cores as described in Section 2.3. Two adult *Arenicola* specimens were introduced in each core, and it was verified that the lugworms burrowed into the sediment. Two days after lugworm addition, flux measurements were repeated in all cores and microprofiles were measured in two cores, both in areas that appeared undisturbed by lugworm activity ($n = 3$ replicate profiles of each solute per core) and in areas covered with *Arenicola* faecal casts ($n = 2$ replicate profiles of each solute per core).

In November, ten cores were collected and brought into the laboratory for incubation. The incubation procedure was largely similar to the July experiment, but in addition to the measurements made in defaunated cores before and after lugworm addition, the initial conditions were also characterized in cores shortly after collection (hereafter referred to as "intact cores"). To this end, porewater O_2, pH and H_2S microprofiles ($n = 5$ replicate profiles of each solute) were measured after one day of reequilibration in two intact cores, P1 and P2, which were dedicated for microprofile measurements throughout the entire experiment. After two days of reequilibration, solute flux measurements (Section 2.3) were made in cores P1, P2, and three additional intact cores. Two of these intact cores were then destructively sampled for solid phase and porewater analyses as described in Section 2.4. The remaining cores were sealed for a twenty-five day defaunation period, reopened and macrofauna that had surfaced were carefully removed. Cores were then kept open in the aerated water bath for a nine day reequilibration period. Subsequently, porewater O_2, pH and H_2S microprofiles ($n = 3$ replicate profiles of each solute) were measured under defaunated conditions, and flux measurements