



# The impact of electrogenic sulfur oxidation on the biogeochemistry of coastal sediments: A field study

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## Abstract

Electro-active sediments distinguish themselves from other sedimentary environments by the presence of microbially induced electrical currents in the surface layer of the sediment. The electron transport is generated by metabolic activity of long filamentous cable bacteria, in a process referred to as electrogenic sulfur oxidation (e-SOx). Laboratory experiments have shown that e-SOx exerts a large impact on the sediment geochemistry, but its influence on the *in situ* geochemistry of marine sediments has not been previously investigated. Here, we document the biogeochemical cycling associated with e-SOx in a cohesive coastal sediment in the North Sea (Station 130, Belgian Coastal Zone) during three campaigns (January, March and May 2014). Fluorescence *in situ* hybridization showed that cable bacteria were present in high densities throughout the sampling period, and that filaments penetrated up to 7 cm deep in the sediment, which is substantially deeper than previously recorded. High resolution microsensor profiling (pH, H<sub>2</sub>S and O<sub>2</sub>) revealed the typical geochemical fingerprint of e-SOx, with a wide separation (up to 4.8 cm) between the depth of oxygen penetration and the depth of sulfide appearance. The metabolic activity of cable bacteria induced a current density of 25–32 mA m<sup>-2</sup> and created an electrical field of 12–17 mV m<sup>-1</sup> in the upper centimeters of the sediment. This electrical field created an ionic drift, which strongly affected the depth profiles and fluxes of major cations (Ca<sup>2+</sup>, Fe<sup>2+</sup>) and anions (SO<sub>4</sub><sup>2-</sup>) in the pore water. The strong acidification of the pore water at depth resulted in the dissolution of calcium carbonates and iron sulfides, thus leading to a strong accumulation of iron, calcium and manganese in the pore water. While sulfate accumulated in the upper centimeters, no significant effect of e-SOx was found on ammonium, phosphate and silicate depth profiles. Overall, our results demonstrate that cable bacteria can strongly modulate the sedimentary biogeochemical cycling under *in situ* conditions.

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**Keywords:** Electrogenic sulfur oxidation; Marine sediments; Long-distance electron transport; Redox cycling; Cable bacteria

## 1. INTRODUCTION

Coastal sediments and continental shelves represent less than 20% of the seafloor surface, but account for more than 60% of the total organic matter mineralization in marine sediments (Burdige, 2006; Dunne et al., 2007). In coastal

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and shelf sediments, sulfate reduction forms the dominant degradation pathway of organic matter, which results in the release of free sulfide in the pore water (Jorgensen, 1982; Aller, 2014). Despite a high production rate, little free sulfide is transferred across the sediment–water interface, due to efficient sulfide oxidation mechanisms, thus stimulating intense sulfur cycling within the sediment. It has been estimated that 75–90% of the free sulfide is reoxidized by various electron acceptors, such as oxygen, nitrate, and iron and manganese (hydr)oxides, while only a minor part of the free sulfide that is produced will precipitate as iron sulfides and becomes ultimately buried as pyrite (Bottrell and Newton, 2006).

Recently, a new mechanism of sulfide oxidation has been discovered in coastal sediments, in which the two half-reactions of sulfide oxidation are coupled by electrical currents that run over centimeter-scale distances (Nielsen et al., 2010). This process is referred to as electrogenic sulfur oxidation, abbreviated as e-SOx (Meysman et al., 2015), and couples the cathodic reduction of oxygen (COR) near the sediment–water interface to anodic sulfide oxidation (ASO) in deeper sediment layers (Nielsen et al., 2010; see schematic in Fig. 1d). Although conventional mechanisms for microbially induced electron transport, such as the use of redox shuttles, conductive pili (Gorby et al., 2006; Lovley, 2008; Logan and Rabaey, 2012) or conductance within the mineral matrix (Ntarlagiannis et al., 2007; Kato et al., 2010) cannot be completely excluded based on the observed sediment pore water chemistry in electro-active sediments, perturbation experiments (placing filters in the sediment, passing a tungsten wire through the suboxic zone) have provided strong evidence that long filamentous bacteria, so-called cable bacteria, are the most likely mediators of the observed long-distance electron transport (Pfeffer et al., 2012; Trojan et al., 2016). In laboratory incubation experiments, the depth distribution of these cable bacteria closely follows the development of the suboxic zone, thus providing additional evidence that cable bacteria are responsible for e-SOx (Schauer et al., 2014).

An electro-active sediment is a deposit that is subject to long-distance electron transport. This transport of electrons over centimeter-scale distances generates a charge separation, which will induce an electrical field in the pore water (Risgaard-Petersen et al., 2012). This electrical field will exert a force on the ions in the pore water, thus generating an additional advective solute transport termed “ionic drift” (Risgaard-Petersen et al., 2012). Recently, a new micro-electrode has been developed which senses the electrical potential that accompanies the electrical field and current (Damgaard et al., 2014). These measurements reveal that the current density can amount up to  $400 \text{ mA m}^{-2}$  (Risgaard-Petersen et al., 2014), which then generates substantial fluxes due to ionic drift in the electro-active zone of the sediment (i.e. the zone where cable bacteria are active).

The discovery that sediments can be electro-active has the potential to radically change our view of redox pathways and geochemical cycling in coastal sediments. Laboratory incubation experiments have shown that e-SOx has the capacity to exert a strong influence on the carbon, iron and

sulfur cycling in marine sediments (Risgaard-Petersen et al., 2012; Rao et al., 2016). This strong effect is particularly induced by the spatial separation of strong proton production and strong proton consumption, respectively associated with the ASO half-reaction at depth (Fig. 1d) and the COR half-reaction near the sediment surface (Fig. 1d). The release of protons in the suboxic zone promotes the dissolution of iron sulfide, which makes free sulfide available for oxidation by e-SOx, which again releases more protons, thus creating a positive feedback mechanism (Risgaard-Petersen et al., 2012; Meysman et al., 2015). Similarly,  $\text{Ca}^{2+}$  is liberated from carbonate minerals by acidic dissolution at depth, and upon upward diffusion, these  $\text{Ca}^{2+}$  ions re-precipitate as calcium carbonate near the sediment–water interface (SWI), where alkaline conditions prevail (Risgaard-Petersen et al., 2012). Moreover, a recent study has shown that the development of e-SOx strongly stimulates solute fluxes across the sediment–water interface, and is capable of releasing large amounts of alkalinity in the overlying water (Rao et al., 2016).

Originally discovered within laboratory incubations, it has been recently demonstrated that e-SOx occurs in a variety of natural environments like coastal mud plains, salt marshes, seasonally hypoxic basins, and mangroves (Malkin et al., 2014; Burdorf et al., 2016). However, until now, the geochemical impact of e-SOx on the geochemistry of *in situ* sediments has not been documented. In this study, we examined the effect of e-SOx on the cycling of carbon, nutrients, metals and sulfur in muddy sediment of the Belgian Coastal Zone.

## 2. MATERIALS AND METHODS

### 2.1. Field site location

Sediment biogeochemistry was investigated at Station 130 ( $51^{\circ}16.3'N$ ,  $2^{\circ}54.3'E$ ), a subtidal mud accumulation site located in the Belgian Coastal Zone (BCZ) of the southern North Sea (Fig. 1a and b), located  $\sim 5$  km offshore from the coastal city of Oostende (Belgium). This site is characterized by an average water depth of  $\sim 12$  m, a tidal amplitude of  $\sim 4.5$  m and strong tidal currents parallel to the coast (Vlaamse Hydrografie, 2012). The sediment at the field site predominantly consists of cohesive clay and mud, sometimes covered by a thin (0–2 cm) sand layer. The sediment is rich in organic matter and carbonate (Van Lancker et al., 2004), has a shallow oxygen penetration depth (1–3 mm) (Gao et al., 2009) and large bioturbating fauna are largely absent (Braeckman et al., 2014). A previous study has documented the geochemical fingerprint of e-SOx as well as the presence of cable bacteria on two separate occasions at this site (October 2011 and March 2013; Malkin et al., 2014), but no detailed pore water investigations were carried out.

### 2.2. Sediment sampling

Bottom water samples and sediment cores were collected in January, March and May 2014. Temperature (T), salinity (S) and oxygen ( $\text{O}_2$ ) saturation were measured in the bot-

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