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Manganese, iron, and sulfur cycling in Louisiana continental shelf sediments



Richard Devereux*, John C. Lehrter, David L. Beddick Jr., Diane F. Yates, Brandon M. Jarvis

United States Environmental Protection Agency, National Health and Environmental Effects Research Laboratory, Gulf Ecology Division, 1 Sabine Island Drive, Gulf Breeze, FL 32561, USA

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ABSTRACT

Sulfate reduction is considered the primary pathway for organic carbon remineralization on the northern Gulf of Mexico Louisiana continental shelf (LCS) where bottom waters are seasonally hypoxic, yet limited information is available on the importance of iron and manganese cycling in the region. Sedimentary manganese, iron, and sulfur cycling were investigated on the LCS using a combined chemical analysis and sediment diagenesis modeling approach. Three stations situated 320 km across the LCS along the 20 m isobath were sampled up to five times between the spring of 2006 and summer of 2007. Bottom water oxygen levels at the stations ranged from 203 mmol m^{-3} in spring to 2.5 mmol m^{-3} in summer. Porewater Mn and Fe^{2+} concentrations (up to 275 and 300 $\mu\text{mol L}^{-1}$, respectively), sulfate reduction rates (1.0–8.4 $\text{mmol m}^{-2} \text{d}^{-1}$), and the fraction of total oxalate extracted iron obtained as Fe(II) (0.25–0.52) differed between station and season. Sediments at station Z02 on the eastern LCS, south of Terrebonne Bay, had higher organic matter content and sulfate reduction rates than sediments at Z03, 160 km further west. Sulfate reduction rates were higher in summer than spring at station Z02 but not at Z03 where porewater Mn and Fe concentrations were highest in summer. Porewater Fe^{2+} concentrations, solid phase oxalate-extractable Fe concentrations, and sediment incubation experiments suggested iron reduction at Z03 may account for 20% or more of organic carbon remineralization. LCS Fe(III) concentrations decreased and sulfate reduction rates increased in model simulations by lowering interfacial dissolved oxygen levels and increasing the rates of organic matter deposited on the sediment surface. Results from this study demonstrate that LCS sedimentary metal oxide cycling may be more important in organic carbon mineralization pathways than previously recognized.

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1. Introduction

Northern Gulf of Mexico bottom waters on the inner Louisiana continental shelf (LCS), where the water depth is < 50 m, are hypoxic (oxygen < 65 mmol m^{-3}) during the spring, summer, and fall with a hypoxic area that can extend over 20,000 km^2 (Rabalais et al., 2002). LCS sediment oxygen demand adds to the drawdown of oxygen in the water column (Dortch et al., 1994; Rowe et al., 2002; Morse and Eldridge, 2007; Bianchi et al., 2011) and can account for up to 25% of the oxygen consumed below the pycnocline (Murrell and Lehrter, 2011; McCarthy et al., 2013). In turn, reduction of O_2 in the benthic boundary layer overlying the sediments reduces the depth of O_2 diffusion into the sediments (Cai and Sayles, 1996). Thus, modeling studies have indicated that sulfate reduction rates (SRR) are the highest in LCS sediments

during hypoxia (Eldridge and Morse, 2008). Higher SRR could raise sediment sulfide concentrations to levels that are toxic to benthic infauna (Rabalais et al., 2002, 2007) and promote release of phosphorus from iron minerals transported onto the LCS thus stimulating increased phytoplankton production and prolonging the hypoxic event (Sutula et al., 2004; Morse and Eldridge, 2007; Reed et al., 2011). Further, the spatial expansion of LCS hypoxia per unit nutrient load delivered by the Mississippi River was suggested to be related in part to inhibition of coupled nitrification–denitrification because of impaired bioturbation by macrofauna during hypoxia (Liu et al., 2010). Although these studies provide valuable information on feedbacks between the water column and sediments, there is need for further study of LCS sediment biogeochemistry in relation to low bottom water oxygen concentrations to better elucidate the fate of carbon, nutrients, and metals delivered from the Mississippi River watershed (Dale et al., 2010).

Despite the apparent importance of Fe(III) and Mn(IV) reduction in the remineralization of terrestrial and marine organic matter in muddy, river-dominated continental shelf sediments

* Corresponding author.

E-mail address: devereux.richard@epa.gov (R. Devereux).

(Aller, 1998; McKee et al., 2004; Aller and Blair, 2006), relatively few studies to date have addressed carbon oxidation coupled to metal oxide reduction on the LCS where hypoxia occurs (Canfield, 1989; Morse and Rowe, 1999; Rowe et al., 2002; Sell and Morse, 2006; Reese et al., 2012). Organic matter is efficiently remineralized in meter-thick, iron-rich muddy sediments flowing from the outfall of large rivers, such as the Mississippi River, because mixing with the overlying oxygenated waters promotes active redox cycling of manganese and iron (Aller, 1998). Bacterial mediated iron reduction could be the most important source of porewater reduced iron near the Mississippi River outfall (Canfield, 1989). However, across the larger region of the inner shelf, where sediment deposition rates are low and the mud layer is thin (Xu et al., 2011), little is known of Fe and Mn cycling although these pathways could serve as an important buffer against increased sulfidogenesis and loss of benthic fauna that often accompany eutrophication and hypoxia in coastal systems (Howarth et al., 2011).

Eldridge and Morse (2008) modeled dissolved inorganic carbon (DIC) fluxes and SRR over a season of hypoxia and recognized that Fe(III) reduction rates could be as high as SRR. Even as sulfate reduction was identified as the most important electron acceptor for organic carbon mineralization in LCS sediments, the need for further investigation of Mn and Fe reduction pathways was noted (Morse and Rowe, 1999; Rowe et al., 2002; Morse and Eldridge, 2007; Eldridge and Morse, 2008). Major uncertainties included spatially and temporally limited sample sizes. LCS sediment studies with measurements relative to understanding Mn and Fe cycling have only taken place at stations under or near the Mississippi River plume or outside the hypoxic zone altogether (Canfield, 1989; Sell and Morse, 2006; Trefry and Presley, 1982). In addition, SRR have been measured several times on the LCS yet only once at the same station during both hypoxic and normoxic conditions, and not in successive seasons (Morse and Lin, 1991; Morse and Rowe, 1999; Rowe et al., 2002; Morse and Eldridge, 2007).

Although it is well understood that low water column oxygen levels can lead to depletion of metal oxides in sediments and increased sulfidogenesis (Kristiansen et al., 2002; Kastev et al., 2007; Middelburg and Levin, 2009) spatial distributions and temporal interactions among LCS sedimentary iron pools, organic carbon content, and SRR remain insufficiently described. We anticipated the relative importance of metal oxide cycling and SRR would vary across the LCS because of differences in the rates of sediment and organic matter delivered to the seafloor (Corbett et al., 2004, 2007). Results of this study, from five cruises to three LCS regions over two years, revealed spatial variation in sediment iron concentrations, active Mn and Fe cycling, and seasonal variations in porewater chemistry and SRR relative to bottom water O₂ concentrations and location on the LCS.

2. Methods

2.1. Sampling stations and sediment collection

Five cruises were taken aboard the US EPA OSV *Bold* during spring and summer of 2006 and 2007. Stations were established at three sites spanning 320 km along the LCS at the 20 m isobath (Table 1 and Fig. 1). Stations were selected to represent zones where contributions of benthic respiration to bottom water hypoxia were proposed to differ with riverine influence (Rowe et al., 2002). Station Z01 was located just west of the Mississippi River delta (29°0.117'N, 89°32.258'W), station Z02 was south of Terrebonne Bay (28°52.292'N, 90°27.712'W) and station Z03 was located on the central LCS, west of Vermilion Bay (29°2.037'N, 92°23.007'W). For the June 2006 cruise, station Z02 was relocated

Table 1

Station water depths (m), temperatures (°C), bottom water dissolved oxygen levels (mmol m⁻³), and salinities.

Station and date	Bottom depth	Bottom temp.	Dissolved oxygen	Surface salinity	Bottom salinity
Z01					
April 06	18.2	21.3	90	13.8	35.8
June 06	18.8	26.7	168	24.7	36.1
Sept. 06	19.1	30.4	149	23.1	35.7
Z02					
April 06	19.6	21.6	113	29.7	33.0
June 06 2b	19.7	24.0	2.5	27.6	36.0
Sept 06	19.3	29.6	20	30.0	35.5
April 07	18.5	22.0	145	32.1	36.1
August 07	19.7	28.8	7.8	31.6	33.4
Z03					
April 06	23.1	21.7	170	34.3	36.2
June 06	21.4	25.7	143	29.7	35.9
Sept 06	20.7	29.1	58	30.1	32.7
April 07	22.0	21.7	193	33.8	35.9
August 07	22.8	28.3	3.8	32.0	35.3

eastward (station Z02b; 29°1.571'N, 90°3.298'W) where bottom water was hypoxic.

Sediment cores (10 cm dia. and up to 40 cm deep) with overlying water were taken with an Ocean Instruments multi-corer. Cores displaying minimal disturbance at the sediment–water interface and overall depth were retained for study. In 2006, depth profiles of geochemical parameters were determined on five cores collected at each station. In 2007, sulfate and potential Mn and Fe (III) oxide reduction rate measurements were emphasized and supporting chemistry data were obtained from one 10 cm dia. core at each station. Station Z01 was not sampled in 2007. Temperature, salinity, and dissolved oxygen (DO) concentration profiles of the water column were obtained at each site with a Sea-bird 911 CTD (reported in Lehrter et al. (2012)).

The cores with overlying water were held loosely capped at room temperature and processed ship board within a day of collection inside a nitrogen-filled glove bag to minimize exposure of sediment samples to oxygen. The cores were sliced at 2 cm intervals to a depth of 18 cm and each slice was tightly closed inside a polypropylene centrifuge bottle. The bottles were removed from the glove bag, centrifuged at 2500g for 10 min at 10 °C, and then returned to a nitrogen-filled glove bag where they were opened and the porewater above the sediment was collected. The porewater was passed through 0.22 μm pore size nylon membrane filters (Corning Life Sciences) into vials and then samples of sediment, after having been mixed inside the centrifuge bottle, were transferred into polypropylene tubes or combusted scintillation vials. The vials and tubes were tightly closed, taken from the glove bag, and stored for later analyses. Sediment porosity was determined gravimetrically after drying 2.0 cm fractions from parallel 2.5 cm diameter cores in a 60 °C vacuum oven. Grain size particle distribution was determined using the hydrometer method (Eaton et al., 2005).

Porewater samples for dissolved inorganic carbon DIC, NH₄⁺, SO₄²⁻, Fe²⁺, Mn, and total Fe determinations were stored at 4 °C. The samples used for porewater Fe and Mn analyses were acidified immediately after collection with 20 μl concentrated hydrochloric acid ml⁻¹ sample. Sediments for solid phase Fe concentration measurements were kept at -70 °C, and sediments for particulate organic carbon (OC), particulate organic nitrogen (ON), inorganic

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