Reactive-transport modeling of iron diagenesis and associated organic carbon remineralization in a Florida (USA) subterranean estuary

Moutusi Roy a,⁎, Jonathan B. Martin a, Christopher G. Smith b, Jaye E. Cable c

a Department of Geological Sciences, University of Florida, Gainesville, FL, USA
b United States Geological Survey, St. Petersburg, FL, USA
c Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA, USA

A R T I C L E   I N F O

Article history:
Received 24 August 2010
Received in revised form 12 January 2011
Accepted 1 February 2011
Available online 26 February 2011

Editor: P. DeMenocal

Keywords:
Iron flux
Submarine groundwater discharge
Reactive-transport model
Diagenesis
Subterranean estuary

A B S T R A C T

Iron oxides are important terminal electron acceptors for organic carbon (OC) remineralization in subterranean estuaries, particularly where oxygen and nitrate concentrations are low. In Indian River Lagoon, Florida, USA, terrestrial Fe-oxides dissolve at the seaward edge of the seepage face and flow upward into overlying marine sediments where they precipitate as Fe-sulfides. The dissolved Fe concentrations vary by over three orders of magnitude, but Fe-oxide dissolution rates are similar across the 25-m wide seepage face, averaging around 0.21 mg/cm²/yr. The constant dissolution rate, but differing concentrations, indicate Fe dissolution is controlled by a combination of increasing lability of dissolved organic carbon (DOC) and slower porewater flow velocities with distance offshore. In contrast, the average rate constants of Fe-sulfide precipitation decrease from 2.19×10⁻⁸ s⁻¹ to 6.4×10⁻⁸ s⁻¹ from the shoreline to the seaward edge of the seepage face as more oxygenated surface water circulates through the sediment. The amount of OC remineralized by Fe-oxides varies little across the seepage face, averaging 5.34×10⁻² mg/cm²/yr. These rates suggest about 3.4 kg of marine DOC was remineralized in a 1-m wide, shore-perpendicular strip of the seepage face as the terrestrial sediments were transgressed over the past 280 years. During this time, about 10 times more marine solid organic carbon (SOC) accumulated in marine sediments than were removed from the underlying terrestrial sediments. Indian River Lagoon thus appears to be a net sink for marine OC.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Subterranean estuaries are subsurface freshwater–saltwater mixing zones at the seaward end of coastal aquifers, where freshwater discharges to overlying coastal waters in a region referred to as the seepage face (Church, 1996; Moore, 1996, 1999; Moore and Church, 1996). Along with fresh groundwater, saline porewater from this mixing zone also discharges to the surface water. The combined discharge of fresh and saline water is known as submarine groundwater discharge (SGD) (e.g., Burnett et al., 2003; Taniguchi et al., 2003). Freshwater discharge (terrestrial SGD) originates from coastal aquifers and the saline water discharge (marine SGD) originates from the overlying saline water column, primarily driven by density differences (Cooper, 1959; Herzberg, 1901). This saline surface water recirculates across the sediment–water interface over a depth range of cm to meters. Recirculation results from various processes, including tidal pumping (Riedl et al., 1972), wave pumping (Shum, 1992), bioirrigation (Aller, 2001), and density-driven circulation (Bokuniewicz et al., 2004; Herzberg, 1901), all of which have previously been combined as ‘non-local exchange’ for modeling purposes (e.g., Meile et al., 2001; Smith et al., 2008a, b).

The chemical composition of SGD is influenced by reduction-oxidation (redox) conditions and redox-controlled diagenetic reactions. Redox conditions are particularly critical for precipitation and dissolution of Fe-oxides, which are important terminal electron acceptors in organic carbon (OC) remineralization. Other important terminal electron acceptors include oxygen (O₂) and nitrate (NO₃⁻), which provide a higher energy yield and thus are reduced before Fe-oxides, and sulfate (SO₄²⁻) and carbon dioxide (CO₂) (Froelich et al., 1979; Snyder et al., 2004). Iron-oxides may represent a primary terminal electron acceptor for OC remineralization where O₂ and NO₃⁻ concentrations are low and large amounts of Fe-oxide are present. Although redox reactions affect dissolved Fe concentrations, flow also can be an important control on its concentration in porewaters of subterranean estuaries (Charette et al., 2002; Charette et al., 2005; Windom et al., 2006). Iron dissolved during OC reduction of Fe-oxides can discharge from the sediment with SGD, and this flux may also be an important Fe source to coastal ecosystems, where it acts as a micronutrient affecting chlorophyll production and primary productivity (e.g., Martin, 1990). Iron precipitation or dissolution can also
influence distributions of other nutrients (e.g., phosphate) and metals in subterranean estuaries (Caetano and Vale, 2002; Charette et al., 2005; Ler and Stanforth, 2003).

Rates of Fe-oxide reduction and associated magnitudes of OC oxidation can be estimated in marine sediments using reactive-transport models (Burdige, 1991; Van Cappellen and Wang, 1995, 1996). These models typically are applied to sediment systems lacking SGD, although some recent models have considered the influence of freshwater discharge on Fe diagenesis (Spiteri et al., 2006, 2008a). Models are often based on mass exchange between dissolved and solid Fe phases and can be complicated by environmental changes in pH and the concentrations of electron donors other than OC (e.g., Postma, 1985; Spiteri et al., 2006). Similarly, estimates of OC remineralization by Fe oxides can be complicated if terminal electron acceptors other than Fe-oxides are involved in the reaction (e.g., Canfield et al., 1993a, b; Froelich et al., 1979; Van Cappellen et al., 1998).

Linkages between Fe-oxide reduction, OC oxidation, and hydrogeology of the subterranean estuary raise the question of whether subterranean estuary sediments act to sequester OC or produce a net flux of oxidized carbon (e.g., CO2) from the sediments. Information regarding whether subterranean estuaries sequester OC through deposition or provide a source to overlying marine waters through SGD could prove beneficial to the overall understanding of global carbon cycling. In this paper we develop a reactive-transport model of Fe-oxide reduction, precipitation of dissolved Fe to solid Fe-sulfide, and flux of Fe from the subterranean estuary to the water column to estimate magnitudes and rates of OC remineralization.

2. Study site

The study site is a shore-normal transect that extends across the seepage face of Indian River Lagoon, Florida (Fig. 1). Details of hydrostratigraphy, hydrogeology, and non-local exchange are discussed elsewhere (Cable et al., 2004; Martin et al., 2004, 2006, 2007; Pandit and El-Khazen, 1990; Toth, 1988). The hydraulic conductivity of the upper several meters of sediment ranges from 10−2 to 10−8 cm/s but is more homogenous in the upper 70 cm sediments ranging from 10−2 to 10−4 cm/s (data based on 28 cores, Hartl, 2006). Flowpaths through our sampled area are oriented perpendicular to the sediment–water interface (Fig. 1b). Indian River Lagoon is a microtidal estuary with a tidal range of 10−3 to 10−2 cm throughout the year. Waves are wind

![Fig. 1. Description of the study site. a. Geographic location of the transect. b. Regional flowpaths in the study area. Considering the aspect ratio of flowpaths, vertical flows (cm scale) are faster than sluggish lateral flows (in m to km scale) in the seepage face. c. Hydrologic framework of the study site. The bold dashed line indicates the freshwater saltwater boundary of the subterranean estuary. Upper part of the subterranean estuary (area under orange dashed line) is the freshwater seepage face (area under solid orange line). Flowpaths of terrestrial fresh SGD (red arrows) and marine SGD at the freshwater–saltwater boundary (brown arrow) are shown. Marine SGD across the sediment–water interface, i.e. non-local exchange of brackish water, are shown by yellow arrows. Note: figure is vertically exaggerated and thus flowpaths of terrestrial SGD are nearly vertical in the seepage face. d. Location of the stations in the transect. Note: CIRL 39 is 250 m offshore.](image-url)
driven with maximum amplitudes of a few 10 s of cm (Smith, 1987, 1993; e.g., Martin et al., 2007).

The previous work on hydrogeology (Martin et al., 2007; Smith et al., 2006) allows us to define the freshwater–saltwater boundary of the subterranean estuary and thus the seaward edge of the seepage face at the 300 mmol chloride (Cl\textsuperscript{−}) isocountour (Roy et al., 2010). This boundary occurs approximately 22 m offshore during our sampling time in April, 2007. Although storms and variations in aquifer recharge shift the location of the freshwater–saltwater boundary over week to month long periods (e.g., Smith et al., 2008a), depth profiles of dissolved Cl\textsuperscript{−} at the freshwater–saltwater boundary do not change from November 2004 to September 2005 (Martin et al., 2007). Consequently, we assume the freshwater–saltwater boundary is pseudo steady state during the week long time period of sampling.

About 90% of the total SGD has a marine origin but within the freshwater seepage face non-local exchange is limited but increases in strength with distance offshore (Martin et al., 2007). Non-local exchange process is primarily bioirrigation in Indian River Lagoon because of the small wave and tidal amplitudes. Non-local exchange processes are greatest outside the seepage face of the subterranean estuary where is no upward freshwater flow for limiting downward flow of non-local exchange (Roy et al., 2010; Smith et al., 2008b). Total SGD was measured by seepage meters and the fraction of terrestrial SGD was calculated by multiplying the total SGD with the Cl\textsuperscript{−} ratio of seepage water and lagoon water column (Martin et al., 2007). Calculations showed flow velocity of terrestrial SGD decreases from 0.079 m/day at the shoreline to 0.007 m/day at 20 m offshore and the magnitude of terrestrial SGD integrated over the seepage face is

![Fig. 2. Distribution of Fe in dissolved and solid phases. a. Distribution of dissolved Fe. The bold dashed line (red color in online version) represents the freshwater–saltwater boundary. Dashed lines are dissolved Fe concentration contours at 1 \( \mu \)mol, 10 \( \mu \)mol, 100 \( \mu \)mol. Note: values of x axes are different. b. Distribution of Fe-oxides, and total sulfur in sediments along with the description of corresponding lithostratigraphic units.](image-url)
0.9 m³/day/m of shoreline (Martin et al., 2007). Residence time of recirculated brackish water decreases from a few days at the shoreline to less than a day 250 m offshore (Martin et al., 2004, 2006). The depth of bioirrigation (i.e., non-local exchange) increases from about 10 cm at the shoreline to around 70 cm 250 m offshore. Consequently, flow is dominated by terrestrial SGD in the seepage face. This offshore increase in the rate and depth of non-local exchange reflects decreasing strength of terrestrial SGD with distance from shore (Martin et al., 2004, 2007; Smith et al., 2008b).

2.1. Sampling methodology and locations

Detailed information on sampling techniques, sampling locations, and analytical protocols are described in Martin et al. (2007), Smith et al. (2008a,b), and Roy et al. (2010). Briefly, samples were collected from seven sites forming a shore-perpendicular transect from the mainland edge to 22.5 m offshore in the lagoon. These sites are designated EGN0 to EGN22.5, with the numbers representing the distance from the shoreline in meters (Fig. 1d). Porewater samples were collected using multilevel piezometers (“multisamplers” ; Martin et al., 2003) in April 2007, at eight depths ranging from the sediment–water interface to 115 cm below the sediment–water interface for stations EGN0 to EGN20, and to 185 cm below the sediment–water interface (cmbsf) at EGN22.5. Samples were separated by 7 to 30 cm intervals. Sediment cores were collected at EGN0, EGN10, EGN20, and EGN22.5 using standard vibracoring techniques.

2.2. Analytical methods

Iron concentrations in the porewater samples were measured using an Element-II Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the Department of Geological Science, University of Florida. An estimate of measurement error was derived by measuring SLRS-4, a certified reference material from National Research Council of Canada. We obtained a value of 0.110 ppm ± 0.004 (n = 36; 2σ), 7% higher than the reported value of 0.103 ppm ± 0.005 (2σ), but within the range of errors. Corrections have not been made for this offset. Dissolved sulfide concentrations were measured a few hours after collection using a Milton Roy Spectronic 401 spectrophotometer (method modified from Cline, 1969). Samples and set of standards were treated by the mixed diamin reagent immediately after sample collection and were allowed the same time for color development prior to analyzing in spectrophotometer (Roy et al., 2010).

Sediment samples from the cores were sequentially leached using a technique described in Hall et al. (1996). Leachates of the sediment collection using a Milton Roy Spectronic 401 spectrophotometer used as an internal standard. Precision of repeated measurements (n=10) of atropine, which was used as an internal standard.

3. Analytical results

All porewater Fe concentration profiles show maxima that increase from less than 1 μmol at the shoreline to about 300 μmol at the seepage face boundary (Fig. 2a). The depths of Fe maxima increase from 35 cm below the seafloor (cmbsf) at EGN5 to 186 cmbsf at EGN22.5. Dissolved sulfide concentrations also show maxima, but at shallower depths than the Fe maxima, around 7 cmbsf at EGN5 to around 15 cmbsf at EGN20. In between Fe and sulfate maxima, dissolved Fe concentrations decrease upward but no physical and geochemical modeling evidence of Fe-sulfide precipitation is present (Roy et al., 2010). This intermediate decrease in dissolved Fe concentrations most likely have resulted from dissolved Fe adsorption onto Fe-oxides or from partial oxidation of dissolved Fe-oxides during dissimilatory Fe-oxide reduction (Iкопini et al., 2004).

Sediments from the seepage face show three distinct lithostratigraphic units based on their colors, which include black, grayish-white, and orange sediments from top to bottom (Fig. 2b). Based on the fossil association and facies distribution analyses, Hartl (2006) suggested black sediments have marine and orange sediments have terrestrial origin. Roy et al. (2010) showed these black sediments are Fe-sulfide rich and orange sediments are Fe-oxide coated quartzitic sands. This transition of depositional conditions from terrestrial Fe-oxides to marine Fe-sulfides indicates sea level rise. The calculated sea level rise is 3 mm/yr based on the 14C age (500 years) of the wood debris found at 150 cm below mean sea level (for details see Roy et al., 2010). At this rate of sea level rise, sediments currently at the freshwater–saltwater boundary would have been flooded about 280 years back (Roy et al., 2010). Because of sea level rise, there is a continuous landward migration of the seepage face and new Fe-oxides are continuously brought to the seepage face. Consequently, Fe-oxides never get exhausted in the seepage face. Thickness of Fe-sulfide rich sediments increases from about 15 cm at EGN0 to about 60 cm at the freshwater–saltwater boundary (EGN22.5). However Fe-sulfide and OC contents remain similar from EGN0 to EGN22.5 (~0.16 wt% and 0.34 wt%, respectively), suggesting thickening mainly resulted from longer time of accumulation rather than faster burial process offshore. Here we have developed a porewater and sediment Fe mass balance model at sites EGN0, EGN10, EGN15, EGN17.5, EGN20, and EGN22.5. However solid phase Fe-oxide content data was only available from EGN0, EGN10, EGN20 and EGN22.5. Roy et al. (2010) showed Fe-oxide content varies little across the seepage face, thus we assumed Fe-oxide contents for sites EGN15 and EGN17.5, are similar to those at EGN20.
term $K_2$, for both $K_{2a}$ and $K_{2b}$, and $R_2$, for both $R_{2a}$ and $R_{2b}$, thus the corresponding equation for the Fe sink is

$$R_2 = K_{2a}[\text{Fe}]$$

(5)

Although $K_2$ is assumed to be constant with depth at any one location, $R_2$ may vary because of the changes in dissolved Fe concentrations (Fig. 2). Rate constants are often called pseudo-rate constants for early diagenetic models (see Berner, 1980) because they are controlled by variations in activity coefficients, chemical potentials, and ionic strength. These characteristics vary across the seepage face because of freshwater and saltwater mixing altering $K_1$ and $K_2$ values.

Based on porewater ion activity data and PHREEQC modeling of the porewater concentration data, neither Fe-oxide dissolution nor Fe-sulfide precipitation reaches equilibrium (Roy et al., 2010), and thus Eqs. (1), (2), and (3) are assumed to be kinetically controlled. The kinetic control indicates reaction (1) is a forward and continuous reaction, and supplies a sufficient amount of dissolved Fe for continuous adsorption of dissolved Fe and precipitation of Fe-sulfide (reactions (2) and (3)). This continuous supply of Fe indicates reactions (2) and (3) are also forward and continuous.

4.2. Reactive-transport model

Offshore variations in the rates of Fe-oxide dissolution and Fe-sulfide precipitation were estimated based on one-dimensional reactive-transport models with a model domain equal to the sampling domain. Within the model domain terrestrial SGD flows upward from the lower most sampled region. The model domain is divided into three zones based on sediment and porewater compositions. The uppermost zone extends from the sediment–water interface to the bottom of the black sediments. The intermediate zone extends from bottom of the black sediments to the depth of the dissolved Fe maxima. The lowermost zone extends from the depth of the dissolved Fe maxima to the bottom of the sampling and model domains. In the upper zone, dissolved Fe concentrations decrease upward as a result of Fe precipitation as Fe-sulfides. In the intermediate zone, Fe concentrations decrease upward due to adsorption of dissolved Fe onto Fe-oxides (e.g., Icopeni et al., 2004; Lovley et al., 1987). In the bottom most zone, dissolved Fe concentrations increase upward as a result of Fe-oxide dissolution. The reaction constants for Fe-oxide dissolution, Fe-sulfide precipitation, or dissolved Fe adsorption ($K_1$, $K_{2a}$, or $K_{2b}$) are assumed to be constant with depth at the “average rate constant” (e.g., Wang and Van Cappellen, 1996) at any site, although their values vary from one sample site to another.

In the zone where Fe-oxide dissolution occurs, the early diagenetic equation for $\text{Fe}^{2+}$ production can be represented by

$$\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial z^2} - \omega \frac{\partial C}{\partial z} + K_1 C_{\text{solid}}$$

(Berner, 1980). Similarly, in the upper and intermediate zones where Fe is removed from porewaters, its consumption can be represented by

$$\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial z^2} - \omega \frac{\partial C}{\partial z} - K_2 C$$

(7)

where $C$ is the dissolved Fe concentration (µmol) to be modeled; $C_{\text{solid}}$ is the measured Fe-oxide concentration in sediment leachates, corrected for porosity ($\Phi$); $t$ is time in non-steady state models; $K_1$ is the pseudo first-order Fe-oxide dissolution rate constant; $K_2$ is the pseudo first-order Fe-removal rate constant; $z$ is depth below the sediment–water interface (positive downward); $\omega$ is the advection rate of terrestrial SGD (negative downward); and $D_s$ is the molecular diffusion (D) of dissolved Fe at infinite dilution, which has been corrected for tortuosity. The value of $D$ for Fe is 7.2 $10^{-6}$ cm$^2$/s (Li and Gregory, 1974), and the correction for tortuosity is

$$D_s = \frac{D}{(1 - 2^9 \log(\phi))}$$

(8)

(Berner, 1980; Boudreau, 1996). The porosity and sediment density for Indian River Lagoon sediments are 0.45 and 2.67 gm/cm$^3$, respectively (Hartl, 2006), yielding a value of $D_s$ of 2.77 $10^{-6}$ cm$^2$/s and bulk density of 1.92 gm/cm$^3$, which we assume remain constant throughout the subterranean estuary. Flow of terrestrial SGD decreases offshore and is approximated by (Martin et al., 2007) as:

$$\omega = 0.16 - 0.0064x$$

(9)

where $x$ is the offshore distance in meters and $\omega$ is the seepage rate in cm/day. We assumed the freshwater–saltwater boundary is pseudo steady state during the week of sampling. Thus we used

$$\frac{\partial C}{\partial t} = 0$$

Eqs. (6) and (7) were solved numerically by a two point boundary solving technique (Glover et al., 1998; Press et al., 1992). The modeled domain extends from the sediment–water interface to 115 cmbsf at sites EGN0 to EGN20, and to 186 cmbsf at EGN22.5. The model domain was divided into N number of 1-cm long cells. The upper and lower boundary conditions follow Dirichlet boundary conditions and use the measured dissolved Fe concentrations at the sediment–water interface and bottom of the sampling domain, respectively. The only model
parameters are $K_1$, $K_{2a}$, and $K_{2b}$, which were adjusted to minimize the difference between measured and modeled dissolved Fe concentrations. We used the Nelder–Mead optimization technique (Nelder and Mead, 1965) to find values of $K_1$, $K_{2a}$, and $K_{2b}$ in their corresponding zones.

The values obtained for $K_1$, $K_{2a}$, and $K_{2b}$ for reaction rates were used to estimate the rates of Fe-oxide dissolution ($R_1$) and adsorption of dissolved Fe and precipitation of Fe-sulfides ($R_{2a}$ and $R_{2b}$ respectively) using Eqs. (4) and (5). Summing the $R$ values for each cell provides the mass per unit volume of dissolved Fe-oxides, adsorption of the dissolved Fe, and sulfide precipitation for the model domain at each site (mg/cm$^3$/yr). Thicknesses of the reaction zones vary from one site to another and the entire thickness of the Fe-oxide dissolution zone is unknown. Consequently, total values for mass transfers cannot be estimated for individual sites. Consequently, average fluxes per unit cross sectional area (i.e., the depth integrated flux values; Wang and Van Cappellen, 1996) of Fe-oxide dissolution and Fe-sulfide precipitation (mg/cm$^2$/yr) were obtained by multiplying the summed value of total reactions by the observed thickness, $l$, of the corresponding zones. No porewater data are available with a sharp increase by a factor of about 10 times to 2.46 mg/cm$^2$/yr at EGN22.5. The value of $K_{2b}$ is lower than $K_{2a}$, decreasing from 8.90 $10^{-12}$ s$^{-1}$ at EGN0 to 8.90 $10^{-12}$ s$^{-1}$ at EGN22.5 (Fig. 5a). The rate decreases slightly from EGN0 to EGN10 and then increases monotonically to EGN22.5. In general, $K_2$ from the upper two zones decreases offshore, particularly in the black sediments, where $K_{2a}$ decreases from a value of 21.9 $10^{-8}$ s$^{-1}$ at EGN0 to 0.64 $10^{-8}$ s$^{-1}$ at EGN22.5. The value of $K_{2b}$ is lower than $K_{2a}$ decreasing from 5.74 $10^{-8}$ s$^{-1}$ at EGN0 to 0.76 $10^{-8}$ s$^{-1}$ at EGN22.5.

Depth integrated flux values for Fe-oxide dissolution, OC remineralization, and dissolved Fe precipitation show little variation across the seepage face. The depth integrated flux values of Fe-oxide dissolution ranges from 0.054 mg/cm$^2$/yr at EGN0 to 0.242 mg/cm$^2$/yr at EGN22.5 (Fig. 5b). Depth integrated flux values for OC remineralization resulting from Fe-oxide dissolution range from 0.014 mg/cm$^2$/yr at EGN0 to 0.061 mg/cm$^2$/yr at EGN22.5 (Fig. 5b). Despite the offshore decrease in $K_{2a}$ and $K_{2b}$, the depth integrated flux values of dissolved Fe precipitation in the upper two zones increase across the seepage face, ranging from 0.05 mg/cm$^2$/yr at EGN0 to 0.33 mg/cm$^2$/yr at EGN20, with a sharp increase by a factor of about 10 times to 2.46 mg/cm$^2$/yr at the seaward edge of the seepage face (Table 1).

6. Discussion

6.1. Model validation

The reactive-transport model was validated by comparing measured and model-estimated concentrations of sedimentary Fe-sulfides. The rate of Fe-sulfide precipitation varies offshore (Fig. 5a), and thus we assume Fe-sulfide precipitation also varied through time as EGN22.5 was transgressed (e.g., Roy et al., 2010). Consequently, site EGN22.5 was chosen for validation because it occurs at the seepage face boundary and provides a complete record of sulfide precipitation during transgression of the modern seepage face. The total accumulation of Fe-sulfide at EGN22.5 can be estimated by plotting the amount of Fe-sulfide precipitated at each site versus the time since the site became flooded and integrating the area under the curve (Fig. 6a). The Fe-sulfide precipitation rates are divided into five segments, with each segment representing a linear change in the rate of Fe-sulfide precipitation.

![Fig. 4. Dissolved Fe model. Solid dark circles represent measured dissolved Fe concentrations at discrete depths, and dark gray curved lines represent dissolved Fe models. The straight dashed lines represent the boundary between upper and intermediate zones used in the model, and the straight solid lines represent the boundary between intermediate and bottom zones. The bold dashed line (red color in online version) represents the upper part of the freshwater–saltwater boundary of the subterranean estuary, the seepage face boundary.](image-url)
between two adjacent sampling sites. The time since sediments were onshore was estimated from the local relative rate of sea level rise, 3 mm/yr (Hartl, 2006; Penland and Ramsey, 1990; Roy et al., 2010).

The average concentration of Fe-sulfide is estimated to be 0.13 wt.% at EGN22.5 similar to the measured average of Fe-sulfides of 0.16 wt.%. Although the estimate and measured amounts are similar, their depths in the sediment differ. The model estimates show Fe-sulfide concentrations increase continuously with depth to around 60 cmbsf, but measured Fe-sulfide concentrations reach a maximum around 25 cmbsf (Fig. 6b). This difference reflects the assumption in the model that once Fe-sulfides form, they continue to be accumulated over time and thus the model predicts the highest concentration of Fe-sulfide should be in the lowermost black sediments.

Field measurements of dissolved oxygen (DO) concentrations show the water column has about nine times higher average DO (averaging about 9 mg/L) than the shallow porewaters. By forcing water with elevated DO concentrations into the sediment, non-local exchange supplies oxygen from the water column to the porewaters at depths of about 15 cmbsf to 50 cmbsf dipping downward from the shoreline to the seepage face boundary. The exchange rates range from about 95.7 cm/day near shore to about 6.9 cm/day offshore (e.g. Smith et al., 2008b). This exchange forces approximately 0.1 mg/day oxygen into nearshore sediments and about 0.4 mg/day offshore. Elevated fluxes of DO into the sediments would decrease Fe-sul de offshore by inhibiting the amount of sulfide that can react with the dissolved Fe. Additionally, the increased flux of DO would also flush dissolved Fe from the sediment.

The difference in distributions of Fe-sulfide between the modeled and measured values could have multiple explanations. One is Fe-sulfide precipitates only at the dissolved sulfide maximum, where it is likely to be the most supersaturated. Alternatively, Fe-sulfides could be re-mobilized at the base of black sediments and re-deposited near the sediment–water interface, creating the observed sulfide maxima there. Remobilization could be linked to the reduction of Fe-oxides at the interface of the orange and black sediments and the Fe-sulfide maxima could relate to the depth of bioirrigation. Regardless of the difference in distribution of Fe-sulfides, similarity between the model estimate and observed Fe-sulfide mass in the sediment suggests the model calculations are a good approximation of mass flux between the solid and dissolved phases.

### 6.2. Comparison of diffusion, advection and reaction rates

We calculated the dimensionless Peclet number ($P_e$), to check whether mass transport is advection or diffusion dominated in each site. This value is the ratio of advection and diffusion, across the model domain given by

$$P_e = \frac{(L^* \omega_s)}{D_i}$$

(Berner, 1980; Lerman, 1975), where $L$ is the length of the model domain. The Peclet number ranges between 1.74 $10^{12}$ at EGN0 and 1.25 $10^{13}$ at EGN22.5, indicating the system is advection dominated. This result supports our assumption that reactions (1), (2) and (3) are not in thermodynamic equilibrium and instead are kinetically controlled.

### Table 1

Model results are reported for the average Fe-oxide dissolution and associated average OC remineralization. Fe-oxide compartments were truncated at most of the stations along with total Fe-oxide dissolution.

<table>
<thead>
<tr>
<th>Offshore distance (m)</th>
<th>0</th>
<th>10**</th>
<th>15</th>
<th>17.5</th>
<th>20</th>
<th>22.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_0$ (s$^{-1}$)</td>
<td>3.78 $10^{-12}$</td>
<td>1.81 $10^{-12}$</td>
<td>†</td>
<td>4.99 $10^{-12}$</td>
<td>†</td>
<td>8.90 $10^{-12}$</td>
</tr>
<tr>
<td>$D_0$ (from $K_0$)</td>
<td>4.09 $10^{-5}$</td>
<td>1.30 $10^{-4}$</td>
<td>†</td>
<td>1.80 $10^{-4}$</td>
<td>†</td>
<td>3.42 $10^{-5}$</td>
</tr>
<tr>
<td>$K_1$ (s$^{-1}$)</td>
<td>21.9 $10^{-8}$</td>
<td>2.80 $10^{-8}$</td>
<td>3.63 $10^{-8}$</td>
<td>3.91 $10^{-8}$</td>
<td>0.27 $10^{-8}$</td>
<td>0.64 $10^{-8}$</td>
</tr>
<tr>
<td>$D_1$ (from $K_1$)</td>
<td>1.78</td>
<td>0.63</td>
<td>1.72</td>
<td>3.87</td>
<td>0.40</td>
<td>2.25</td>
</tr>
<tr>
<td>$K_2$ (s$^{-1}$)</td>
<td>5.74 $10^{-8}$</td>
<td>5.36 $10^{-8}$</td>
<td>0.29 $10^{-8}$</td>
<td>1.39 $10^{-8}$</td>
<td>0.48 $10^{-8}$</td>
<td>0.76 $10^{-8}$</td>
</tr>
<tr>
<td>$D_2$ (from $K_2$)</td>
<td>2.48</td>
<td>0.48</td>
<td>3.14</td>
<td>1.00</td>
<td>0.78</td>
<td>2.05</td>
</tr>
<tr>
<td>Fe-oxide dissolution, $R_0$ (mg/cm$^2$/yr)</td>
<td>0.054</td>
<td>0.483</td>
<td>†</td>
<td>0.073</td>
<td>†</td>
<td>0.242</td>
</tr>
<tr>
<td>Fe-sulfide precipitation, $R_{K_0}$ (mg/cm$^2$/yr)</td>
<td>0.00076</td>
<td>0.0327</td>
<td>0.094</td>
<td>0.0757</td>
<td>0.0163</td>
<td>0.207</td>
</tr>
<tr>
<td>Fe-adsorption, $R_{K_1}$ (mg/cm$^2$/yr)</td>
<td>0.1796</td>
<td>0.0195</td>
<td>0.128</td>
<td>0.2230</td>
<td>0.3140</td>
<td>2.249</td>
</tr>
<tr>
<td>Total Fe removal, $R_0$ (mg/cm$^2$/yr)</td>
<td>0.050</td>
<td>0.052</td>
<td>0.222</td>
<td>0.299</td>
<td>0.330</td>
<td>2.456</td>
</tr>
<tr>
<td>OC remineralization (mg/cm$^2$/yr)</td>
<td>0.0135</td>
<td>0.121</td>
<td>†</td>
<td>0.018</td>
<td>†</td>
<td>0.061</td>
</tr>
</tbody>
</table>

† Dissolved Fe production zones were not sampled and thus not included in the modeled domain.

**At station 10 m offshore the intermediate compartment is missing.

![Fig. 5](image_url)

Variation in rate constants of Fe-oxide dissolution and associated average OC remineralization across the seepage face. a. Variation in first order kinetic rates of Fe-sulfide precipitation from upper and intermediate zones, and Fe-oxide dissolution from bottom zone. b. Variation in Fe-oxide dissolution rates (mg/yr), and total OC remineralization rates (mg/yr) from zone 3 at each site with distance offshore.
The Damköhler number (Da) can be used to assess the relative roles of advection to the kinetic reactions rates in a reactive flow system. This value is estimated by

\[ Da = \frac{K \cdot e^{n \cdot t}}{\omega} \]  \hspace{1cm} (11)

(Fogler, 2006), where K is the modeled pseudo reaction rate constant in each zone, C0 is the initial concentration of dissolved Fe, n is the order of the reaction, and t is the flow time. Because our system is advection dominated, t in each reaction zone equals

\[ t = \frac{1}{\omega} \]  \hspace{1cm} (12)

(e.g., Domenico and Schwartz, 1997), where I is the length of the individual reaction zones conceptualized in the modeled domain. For first-order reactions, \( C_0^{-1} = 1 \), and substituting this value and t from Eq. (12) into Eq. (11) we get

\[ Da = \frac{(K^*)}{\omega} \]  \hspace{1cm} (13)

(Lasaga, 1998), where K is the modeled pseudo rate constant (K1, K2a or K2b).

6.3. Hydrogeological controls on Fe-diagenesis

Previously, reactive-transport models have been used to estimate the reaction rates of Fe diagenesis in Waquoit Bay, Massachusetts (Spiteri et al., 2008a, b). In Waquoit Bay, Fe-oxides precipitate from dissolved Fe carried into the subterranean estuary with terrestrial SGD, depleting the porewater in Fe. In Indian River Lagoon, however, Fe-oxides dissolve to enrich the porewater in dissolve Fe (Roy et al., 2010). In the Spiteri et al. (2008a) model, a single value of \( 8.8 \times 10^{-5} \text{ mmol}^{-1} \text{s}^{-1} \) (from Canavan et al., 2006) was used for the first-order rate constant for Fe-oxide precipitation throughout the subterranean estuary regardless of location, variations in flow rates, or the distribution of OC. We expand on this approach here by estimating pseudo first-order rate constants for Fe-oxide reduction at each sampling site. We assume the rate constants vary at each site because of variability in sources and potential reactivity of OC and because reaction rates may depend on the variation in OC and because reaction rates may depend on the variation in OC.

Table 2

<table>
<thead>
<tr>
<th>Offshore distance (m)</th>
<th>( \omega ) (cm/s)</th>
<th>( K_1 ) (s(^{-1}))</th>
<th>( K_{2a} ) (s(^{-1}))</th>
<th>( K_{2b} ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \omega_1 )</td>
<td>2.67E-11</td>
<td>1.80E-06</td>
<td>8.819E-07</td>
</tr>
<tr>
<td></td>
<td>( \omega_2 )</td>
<td>3.78E-12</td>
<td>2.19E-07</td>
<td>5.744E-08</td>
</tr>
<tr>
<td></td>
<td>( \omega_3 )</td>
<td>7.19E-13</td>
<td>5.16E-08</td>
<td>7.829E-09</td>
</tr>
<tr>
<td>20</td>
<td>( \omega_1 )</td>
<td>( \dagger )</td>
<td>4.68E-08</td>
<td>4.84E-09</td>
</tr>
<tr>
<td></td>
<td>( \omega_2 )</td>
<td>( \dagger )</td>
<td>2.74E-09</td>
<td>5.81E-08</td>
</tr>
<tr>
<td></td>
<td>( \omega_3 )</td>
<td>( \dagger )</td>
<td>( \dagger )</td>
<td>( \dagger )</td>
</tr>
<tr>
<td>22.5</td>
<td>( \omega_1 )</td>
<td>7.33E-11</td>
<td>5.25E-08</td>
<td>7.27E-08</td>
</tr>
<tr>
<td></td>
<td>( \omega_2 )</td>
<td>8.90E-12</td>
<td>6.41E-09</td>
<td>7.63E-09</td>
</tr>
<tr>
<td></td>
<td>( \omega_3 )</td>
<td>2.92E-12</td>
<td>1.49E-09</td>
<td>4.15E-08</td>
</tr>
</tbody>
</table>

† Dissolved Fe production zones were not sampled and thus not included in the modeled domain.
‡ Model did not match with measured Fe data at this flow rate.

Flow rates from Martin et al. (2007) and estimated reaction rates yield Da values within the Fe-oxide reduction zone of roughly \( 10^{-5} \) to \( 10^{-3} \) (Table 1). These values indicate porewater advection is orders of magnitude larger than reaction rates for Fe-oxide dissolution and demonstrate dissolved Fe is flushed from the orange sediments where this Fe-oxide is reduced. In contrast, these flow rates indicate Da values are several orders of magnitude higher (roughly 0.5 to 2) in the black sediments. Because reaction rates and flow rates are approximately equal, precipitation of Fe-sulfides occurs in black sediments. Although the Da values indicate zones where advection or reaction rates dominate, they do not quantify the magnitudes of mass transfer by these reactions. In the following section, we estimate the magnitudes of these mass transfers through our reactive-transport models.
dissolution, thereby limiting variations in average rates of Fe-oxide reduction across the subterranean estuary (Table 1).

Coastal marine sediments typically contain more than 1 wt.% OC and reduce on average about 7.8 mg/cm²/yr of Fe-oxide when unaffected by SGD (e.g., Van Cappellen and Wang, 1995). In Indian River Lagoon, the orange terrestrial sediments contain on average about 0.04 wt.% OC and reduce on average about 0.2 mg/cm²/yr Fe-oxide (Table 1), about 15 times less than the average. This low Fe-oxide dissolution rate may reflect the terrestrial origin of the OC in the orange sediments. Terrestrial OC commonly is less labile than marine OC. Organic carbon in the black sediments is of marine origin, but without the presence of Fe-oxides Fe dissolution does not occur.

6.4. Fe Diagenesis and the organic carbon budget

Our model results can be used to estimate an OC budget in the seepage face of Indian River Lagoon. Surface estuaries are believed to limit terrestrial OC input to open oceans, thereby accumulating marine OC (Fontugne and Jouanneau, 1987; Middledburg and Herman, 2007), but it is unclear if subterranean estuaries similarly limit input of terrestrial OC to the open ocean. The total amount of OC remineralized by Fe-oxides during transgression across the seepage face can be estimated from the modeled OC remineralization rate, which varies little offshore (Fig. 6b), averaging around 5.34 × 10⁻² mg/cm²/yr (Table 1). Transgression of the modern seepage face during Holocene sea level rise took around 280 years (Roy et al., 2010). These data indicate the amount of OC remineralized by Fe-oxide alone is 3.74 kg for a 1 m shore-parallel length of the 25-m wide seepage face during the transgression of the current seepage face. The average dissolved oxygen (DO) concentration is 11.37 mg/L and the maximum DO concentration is 14.08 mg/L (see DO data in the Supplementary materials). The mean irradiation rate is 35.5 cm/day (Smith et al., 2008b). The average value of oxygen exchange across the sediment–water interface is thus 0.0126 mmol/(cm²·day) and using maximum DO concentration DO exchange is 0.0156 mmol/(cm²·day). Using the 1:1 stoichiometric ratio for the oxygenation of OC (Berner, 1980), the amount of OC remineralized by oxygen is ~2.8 mg/day, i.e. 0.28 kg in 280 years of sea level rise. Dissolved NO₃⁻ got exhausted at the shoreline (29 μmol at EGNO2 and 0.2 μmol from EGN10 to EGN22.5) and did not contribute much in the OC remineralization at the freshwater–saltwater boundary (Martin and Cable, 2008). These calculations suggest Fe-oxides are most likely the primary electron acceptor for OC remineralization in the Indian River Lagoon subterranean estuary.

The thickness of Fe-sulfide rich organic sediments, and thus the amount of solid marine OC, increases offshore from 15 cm at EGNO2 to 60 cm at EGN22.5. These Fe-sulfide rich organic sediments have an average of 0.34 wt.% of OC. Therefore, the average amount of marine solid OC buried in a 1-m long shore-parallel strip of the 25-m-wide sediment-wedge is about 35 kg. Consequently, the amount of marine OC remained in the sediments after oxygenation is about 34.72 kg. This value is about 10 times greater than the amount of OC that was removed by reduction of Fe-oxides. In the Indian River Lagoon subterranean estuary, apparently net accumulation of solid marine OC occurs when compared with the amount of OC remineralized by Fe-oxides. These estimates neglect oxidation of OC by other terminal electron acceptors, but because the porewaters contain little oxygen or nitrate, and sulfate reduction is minimal (Roy et al., 2010), Fe-oxides are likely to be the primary oxidant of OC. These estimates need to be verified through observations of the lithostratigraphy in the deep portion of the lagoon, but overall they suggest the Indian River Lagoon represents a net sink for OC.

The choice of major electron acceptor for OC remineralization depends on local geochemical conditions specific to a subterranean estuary. In the North Inlet (South Carolina) subterranean estuary SO₄²⁻ is the major electron acceptor in the high salinity zone and produces DIC, but in the low salinity zone DIC is from carbonate dissolution (Cai et al., 2003). In the Indian River Lagoon DIC and pH profiles are similar across the seepage face and sediments are mainly siliciclastic (Roy et al., 2010). There is no OC remineralization by Fe-oxides within the subterranean estuary of Waquoit Bay (Massachusetts), rather dissolved Fe in freshwater precipitates as Fe-oxides because of increase in pH (Charette et al., 2005; Spiteri et al. 2006, 2008a, b). A portion of these Fe-oxides remineralizes DIC at the freshwater–saltwater boundary of Waquoit Bay (Rouxel et al., 2008; Spiteri et al., 2008a). Unlike Waquoit Bay, Indian River Lagoon subterranean estuary never gets exposed to the oxic atmosphere during low tides and remains anoxic thus Fe-diagenesis is different (Roy et al., 2010). In the Turkey Point subterranean estuary DO and NO₃⁻ are the major electron-acceptors for OC remineralization (Santos et al., 2009). In contrast to Indian River Lagoon, the subterranean estuary at Turkey Point (north-eastern Gulf of Mexico, Florida) is a DOC production system and produces about 64 kg/m²/yr DOC (984 mmol/m²/day in 10 m wide subterranean estuary, Santos et al., 2009). This OC production value is orders of magnitude higher than OC accumulation in Fe-sulfide rich sediments at Indian River Lagoon. Flow rates of terrestrial SGD at Turkey point (0.2 to 2.2 m³/m²/day) are faster than freshwater flow at Indian River Lagoon (0.02 to 0.9 m³/m²/day), and the tidal range (1.02 m) is an order of magnitude higher at Turkey Point. Consequently, the Turkey point subterranean estuary is a tidal pumping dominated system and nutrients are supplied by non-local exchange. Unlike limited non-local exchange at Indian River Lagoon limits nutrient supply from water column. Roy et al. (2010) suggested dissolved Fe in water column (0.3 μmol) could not be the source of elevated porewater Fe (~300 μmol) at the freshwater–saltwater boundary. Dissolved oxygen and NO₃⁻ concentrations at Turkey Point (2.6 mg/L and 30 μmol, respectively) are also an order of magnitude higher than the same at Indian River Lagoon (0.9 mg/L and 0.2 μmol, respectively). These differences in local hydrology and redox conditions were reflected in OC diagenesis at both sites. Nonetheless, simultaneous OC remineralization and deposition at Indian River Lagoon and other subterranean estuaries suggest subterranean estuaries could be important sources and sinks in the OC budget. The global significance of these fluxes requires observations for OC fluxes to and from subterranean estuaries with a range of physical and chemical characteristics.

7. Conclusions

The reduction rate of Fe-oxide and associated DOC remineralization are approximately constant across the 25-m wide seepage face of the Indian River Lagoon with magnitudes of 0.213 mg/cm²/yr and 5.34 × 10⁻² mg/cm²/yr, respectively. In contrast, the pseudo rate constant for Fe-oxide reduction (Kₑ) increases from 3.78 × 10⁻¹² at the shoreline to 8.90 × 10⁻¹² at the seaward edge of the seepage face. The increase in Kₑ results from increasing availability of marine DOC as increasing amounts of lagoon water become entrained in pore-water of the seepage face. The Damköhler number indicates advection dominates kinetics of Fe-oxide reduction throughout the subterranean estuary. Unlike Fe-oxide reduction, the pseudo rate constant of Fe-sulfide precipitation (Kₛ) decreases offshore as a result of increasing amounts of oxygen supplied to the sediment via non-local exchange processes. However, the precipitation rate of Fe-sulfide increases offshore from 0.00076 mg/cm²/yr at the shoreline to 0.207 mg/cm²/yr at the seepage face boundary because of elevated dissolved Fe and sulfide concentrations. During the transgression of the current seepage face, approximately 3.74 kg of OC was oxidized by Fe-oxides. This amount of OC is approximately 10 times less than the amount of solid marine OC that was buried in the sediments during the transgression, suggesting net accumulation of OC in the sediment of our study site. These results suggest that subterranean estuaries may be important to global carbon budgets as both sources and sinks of OC depending upon the source of OC and the local hydrogeology. In our case, the subterranean estuary in eastern Florida primarily acts as a sink for marine OC.