Sources and sinks of CO\textsubscript{2} and CH\textsubscript{4} in siliciclastic subterranean estuaries

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Abstract

Anthropogenic production of greenhouse gases (GHGs) has intensified the need to constrain estimates of natural atmospheric sources from both terrestrial and marine systems. Estuaries are known sources of carbon dioxide (CO\textsubscript{2}) and methane (CH\textsubscript{4}); however, less is known about GHG dynamics in subterranean estuaries (STEs). We evaluate CO\textsubscript{2} and CH\textsubscript{4} dynamics in three proximal STEs bordering Indian River Lagoon, Florida, where groundwater flows through siliciclastic sediments with minor carbonate mineral contents. Although the three STEs have similar mineralogical and flow characteristics, CO\textsubscript{2} and CH\textsubscript{4} concentrations vary by orders of magnitude. Nonconservative mixing of both gases is observed, and CH\textsubscript{4} is generally produced while CO\textsubscript{2} is sequestered. The extent of methanogenesis is linked to the redox potential of inflowing groundwater, as well as degree of CH\textsubscript{4} oxidation, which results mostly from anaerobic oxidation of methane. Methane concentrations vary by orders of magnitude, and stable isotopic signatures suggest differences in the microbial production pathway between sites. CO\textsubscript{2} is sequestered due to the production of alkalinity relative to dissolved inorganic carbon, which occurs both through rapid CaCO\textsubscript{3} dissolution at the shoreline as low-pH groundwater from the siliciclastic aquifer interacts with carbonate minerals in lagoon sediments, as well as redox reactions, particularly sulfate reduction and denitrification. These results demonstrate a high variability in CO\textsubscript{2} and CH\textsubscript{4} concentrations, and thus fluxes, even among geographically constrained and hydrogeologically similar STEs. Although STEs are sources of both CO\textsubscript{2} and CH\textsubscript{4} to surface waters, the variability of production and consumption complicates global estimates of GHG fluxes from STEs.

Estuaries represent the interface between freshwater and salt water and are sites of net remineralization of terrestrial organic carbon, which generates large fluxes of CO\textsubscript{2} from water to the atmosphere (Abril and Borges 2004; Cai 2011). Analogous freshwater–saltwater mixing zones exist at the interface between coastal aquifers and adjacent saline pore waters, known as subterranean estuaries (STEs; Moore 1999), which contribute both freshwater and solutes to the coastal zone via submarine groundwater discharge (SGD). Although the impact of SGD on surface water carbon budgets has received relatively little attention compared to nutrients and metals (e.g., Slomp and Van Cappellen 2004; Kroeger and Charette 2008; Spiteri et al. 2008; Roy et al. 2010; Whelan et al. 2011; Johannesson et al. 2011), several factors suggest that SGD may be an important source of greenhouse gases (GHGs). Similar to surface estuaries, STEs are net heterotrophic, but lack the CO\textsubscript{2} sink of photosynthesis that reduces CO\textsubscript{2} fluxes from surface estuaries. Additionally, isolation from the atmosphere allows the development of anaerobic conditions that may drive organic matter remineralization toward methanogenesis. Methanogenesis is the terminal remineralization reaction for organic matter and converts organic matter to CO\textsubscript{2} and methane (CH\textsubscript{4}). Like CO\textsubscript{2}, CH\textsubscript{4} is a GHG but has approximately 25 times the warming potential of CO\textsubscript{2} and thus relatively smaller CH\textsubscript{4} fluxes have disproportionate impacts on warming and C cycling.

Although GHG fluxes from STEs could be significant, gases may undergo additional chemical transformations due to enhanced biogeochemical processing in the freshwater–saltwater mixing zone (e.g., Moore 1999). Remineralization of organic carbon in fresh groundwater should generate CO\textsubscript{2} and CH\textsubscript{4}, but biogeochemical reactions within STEs may modify their concentrations. Several studies have found SGD to be a significant source of carbon to surface waters (Cai et al. 2003; Liu et al. 2012; Liu et al. 2017). However, little consensus exists as to whether STEs are sources or sinks of CO\textsubscript{2} because mineralogical control of remineralization reactions may alter pore-water buffering capacity, which controls the speciation of dissolved inorganic carbon (DIC) and hence CO\textsubscript{2} concentrations. Changes to the buffering capacity of water depends on the relative impacts of diagenetic reactions to DIC and alkalinity (Alk), and are expressed as difference between concentrations expected from

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CH₄ fluxes from STEs have received relatively more attention than CO₂ fluxes because CH₄ is used as a quasi-conservative tracer of SGD due to its typically high concentrations in groundwater compared to surface water (Cable et al. 1996; Corbett et al. 2000; Dulaiova et al. 2010). However, use of CH₄ as a tracer requires understanding of its sources and sinks within STEs, for example, methanogenesis and methanotrophy (e.g., Schutte et al. 2016). Furthermore, CH₄ production occurs via multiple microbial pathways (CO₂ reduction and acetoclastic methanogenesis; Whiticar and Schoell 1986), which produce distinct stable isotopic signatures of CH₄. Little is known of the microbial pathway by which CH₄ is produced in STEs, although current understanding suggests that CO₂ reduction is favored in settings with higher salinity and lower labile organic carbon availability (Whiticar and Schoell 1986; Megonigal et al. 2005). As both salinity and organic carbon quantity and quality vary within and among STEs and control redox gradients, both the quantity of CH₄ and pathway by which it is produced should vary in STE settings.

To evaluate potential ranges of GHG fluxes from STEs, we assess sources and sinks of CO₂ and CH₄ at three siliciclastic STEs bordering Indian River Lagoon, Florida. The sampling sites are within 50 km of one another and have similar environmental and hydrogeologic characteristics. These similarities thus allow us to assess GHG dynamics in STEs without confounding variables such as flow rates and flow paths. We use salinity-based conservative mixing models to evaluate impacts of reactions on CO₂ and CH₄ concentrations within the STEs. We first assess the controls of methanogenesis and methanotrophy to determine the role of STE biogeochemical processing on CH₄ budgets. We then assess CO₂ concentrations and evaluate mineralogical and redox controls on STE carbonate speciation (Table 1). We compare ΔAlk : ΔDIC ratios in the three sampled STEs with those expected from various reaction stoichiometries (Table 1) in order to evaluate which reactions could control CO₂ concentrations in siliciclastic STEs. These results allow us to evaluate the potential role of SGD on GHG production and sources from coastal systems.

**Methods**

Indian River Lagoon is located on the Atlantic coast of central Florida and spans approximately 250 km of coastline in three hydrological subunits: Mosquito Lagoon, Indian River Lagoon, and Banana River Lagoon (BRL; Fig. 1). Three STEs in the Indian River and BRLs were included in this study, Eau Gallie North (EGN), BRL, and Riverwalk Park (RWP). Sediments in these STEs are siliciclastic ranging from fine sand to clays, which allow groundwater seepage to occur at rates

| Equation | Reaction                                                                 | ΔAlkalinity : ΔDIC                        |
|----------|--------------------------------------------------------------------------|------------------------------------------|
| 1        | Aerobic respiration (CH₃OH)₁₀₆(NH₃)₁₆H₂PO₄+138O₂→106CO₂+122H₂O            | (−16)(NO₃)/(106)(CO₂)=−0.15*             |
| 2        | Denitrification (CH₂O)₁₀₆(NH₃)₁₆H₃PO₄+84.8HNO₃→106CO₂+42.4N₂+148.4H₂O+16NH₃+H₃PO₄ | +(84.8)(NO₃)/(106)(CO₂)=0.8*             |
| 3        | Iron reduction (CH₂O)₁₀₆(NH₃)₁₆H₃PO₄+424FeOOH+848H⁺→106CO₂+742H₂O+424Fe²⁺+16NH₃+H₃PO₄ | +(848)(H⁺)/(106)(CO₂)=8*                  |
| 4        | Sulfate reduction (CH₂O)₁₀₆(NH₃)₁₆H₃PO₄+53SO₄²⁻→106H⁺+106CO₂+53H₂O+53H₂S+16NH₃+H₃PO₄ | +(53×2)(SO₄)/(106)(CO₂)=1*               |
| 5        | Methanogenesis (CH₂O)₁₀₆(NH₃)₁₆H₃PO₄→53CO₂                                   | 0/53(CO₂)=0                               |
| 6        | CaCO₃ precipitation/dissolution CaCO₃-CO₂⁻+Ca²⁺                             | Dissolution: (2×1)Ca²⁺/(1(CO₂⁻)=2         |
| 7        | Sulfide oxidation¹  H₂S+2O₂→SO₄²⁻+2H⁺                                       | Precipitation: 1(CO₂⁻)/(2×1)Ca²⁺=-2      |
| 8        | Fe oxidation¹  4Fe³⁺+6H₂O+4FeOOH+8H⁺                                        | −(2×1)(SO₄²⁻)/0=∞                       |
| 9        | AOM  CH₄+SO₄²⁻→HCO₃⁻+HS⁻+H₂O                                               | (2×1)(SO₄²⁻)+1(HCO₃⁻)/1(HCO₃⁻)=3       |

*Chen and Wang (1999).
²Anderson and Schiff (1987).
ranging from 0.02 to 0.9 m$^3$ d$^{-1}$ m$^{-1}$ of shoreline at EGN (Martin et al. 2007). This slow seepage makes STE salinity gradients static over timescales of days to weeks. Seasonal variation in lagoon water salinity and fresh groundwater head is known to cause fluctuations in seepage face width (Roy et al. 2013), and storm-driven saltwater intrusion events can alter seepage face salinity for several months (Smith et al. 2008).

We collected pore-water samples during three sampling campaigns: May and September of 2015 and May of 2016. Samples were collected from multilevel piezometers (Martin et al. 2007) that had previously been installed at EGN, RWP, and BRL sites (Fig. 1). Piezometers were installed in 2004 at EGN and during May 2014–September 2015 at RWP and BRL. At EGN, sampled piezometers were installed at 0, 10, and 20 m offshore (EGN-0, EGN-10, and EGN-20), at RWP were 10, 20, and 35 m offshore (RWP-10, RWP-20, and RWP-35), and at BRL were 1, 11, 21, and 45 m offshore (BRL-1, BRL-11, BRL-21, and BRL-45; piezometer schematic illustrated in Fig. 2).

**Sample collection**

Pore-water samples were pumped to the surface through 0.5 cm diameter flexible poly(vinyl chloride) tubing attached to multilevel piezometer ports. Piezometers are constructed with multiple (4 to 8) well screenings at depths ranging from 7 cm to 2.5 m below the sediment–water interface. Tubing leads from the screened intervals to the surface and is sampled by pumping water using a peristaltic pump which samples pore waters at increasing depths below the sediment–water interface (Fig. 2). The tubing was connected to an overflow cup in which a YSI Pro-Plus sensor was installed and used to monitor salinity, temperature, pH, oxidation–reduction potential (ORP), and dissolved oxygen (DO). DO was measured using a polarographic membrane that has an interference from hydrogen sulfide, which prohibited measurement of DO concentrations when hydrogen sulfide was present. Once all parameters were stable, water was filtered through 0.45 μmol L$^{-1}$ trace-metal grade Geotech medium capacity disposable canister filters into sample vials. Samples for cations and anions were collected in high-density polyethylene bottles; cation samples were preserved with trace-metal grade nitric acid (pH < 2), whereas no preservative was added to anion samples. Samples for nutrients were filtered into 15-mL polypropylene containers and frozen until analysis. DIC samples...
were filtered through 0.2 μmol L$^{-1}$ filters directly to the bottom of 20 mL Qorpac glass vials and allowed to overflow until sealed tightly with no headspace.

Redox-sensitive solutes, Fe(II) and hydrogen sulfide, were measured on 0.45-μmol L$^{-1}$ filtered water in the field immediately after pumping from the multisampler tubing using colorimetric methods. Fe(II) was measured in triplicate using the ferrozine method (Stookey 1970). Water was sampled from the flowing pore-water stream, and 1 mL of ferrozine was immediately added to 10 mL of sample and agitated to mix. The absorbance at 560 nm was measured immediately and was lower than 0.001 absorbance units. Measured absorbance values were converted to concentrations with a Hach DR 890 portable colorimeter. Blanks were subtracted from sample absorbance, and blanks of distilled water were subtracted from sample absorbance. Blanks were measured on 0.45-μmol L$^{-1}$ filtered water in the field. Sampling for hydrogen sulfide occurred simultaneously with the Fe sampling and $H_2S$ was measured immediately in triplicate using the methylene blue method according to U.S. EPA methods outlined in Hach (2013). Precision is reported at 0.1 mg L$^{-1}$.

Gas samples were collected via headspace extractions according to methods outlined in Repo et al. (2007). Unfiltered water was pumped into the bottom of 500 mL bottles until they overflowed and immediately capped with rubber stoppers fitted with two 3-way inlet valves. Sixty milliliters of water was extracted from one inlet and replaced with 60 mL of ultrapure N$_2$ gas. Bottles were shaken for 2 min to equilibrate headspace gas with water, and headspace gas was extracted and immediately injected into 60-mL glass serum bottles that were evacuated immediately before the sample introduction. Samples were stored at room temperature until analysis within 1 week of collection. Method check standards were collected by injecting samples of known concentrations of CO$_2$ and CH$_4$ into evacuated vials and treated identically to samples.

**Laboratory methods**

Gas samples were analyzed for CO$_2$ and CH$_4$ concentrations and $\delta^{13}$C-CO$_2$ and $\delta^{13}$C-CH$_4$ on a Picarro cavity ring-down spectrometer. Carbon isotopic compositions are reported in reference to Vienna Pee Dee Belemnite. We report $\delta^{13}$C-CO$_2$ values from the May 2016 sampling trip only because $\delta^{13}$C-CO$_2$ values from previous sampling trips were impacted by an interference from hydrogen sulfide. To remove this interference, sample gas from the May 2016 sampling trip was passed through an in-line elemental copper scrubber before analysis (Malowany et al. 2015).

Anion and cation concentrations were measured on an automated Dionex ICS-2100 and ICS-1600 Ion Chromatograph, respectively. Error on replicate analyses was less than 5%. DIC concentrations were measured on a UIC (Coulometrics) 5011 CO$_2$ coulometer coupled with an AutoMate Preparation Device. Samples were acidified, and the evolved CO$_2$ was carried through a silver nitrate scrubber to the coulometer where total C was measured. Accuracy was calculated to be ±0.1 mg L$^{-1}$ based on measurement of check standards. Dissolved Si concentrations were analyzed on a Dionex ICS-2100 and ICS-1600 Ion Chromatograph, respectively. Error on replicate analyses was less than 10%.

**Data processing—dissolved gas concentrations and isotope ratios**

Conversion to molar units from the headspace concentrations followed the methods outlined in Bastviken et al. (2004). To solve for the moles of gas originally dissolved in solution, we first converted measured gas concentration (ppm) in the headspace to moles:

$$ n_g = \frac{P_x \times V_g}{R \times T} $$

where $n_g$ equals the moles ($n$) of gas in the gaseous phase, $P_x$ is the measured partial pressure of CH$_4$ or CO$_2$ (atm), $V_g$ is the volume of headspace gas (liter), $R$ is the common gas constant (0.0821 L atm K$^{-1}$ mol$^{-1}$), and $T$ is the temperature (K) of water at the time of collection. The number of moles of gas dissolved in the aqueous phase ($n_{aq}$) is calculated by:

$$ n_{aq} = C_{aq} \times V_{aq} = P_x \times K_{H_2} \times V_{aq} $$

where $C_{aq}$ is aqueous concentration, $V_{aq}$ is aqueous volume (500 mL minus 60 mL replaced by headspace gas to give a total volume of 440 mL), and $K_H$ is Henry’s Law constant (mol L$^{-1}$ atm$^{-1}$). The value of $K_H$ depends on temperature according to Sander et al. (2011). We used this relationship to calculate $K_H$ of CO$_2$ and CH$_4$ for each water sample based on the water temperature at the time of sampling. The concentration of dissolved gas in water samples ($C_{aq}$) was then calculated as the sum of the number of moles of gas in aqueous and gaseous phases divided by the aqueous volume:

$$ C_{aq} = \frac{n_g + n_{aq}}{V_{aq}} $$

CH$_4$ oxidation was calculated using the isotopic method outlined in Mahieu et al. (2008) and Preuss et al. (2013). The fraction of oxidized methane ($f_{ox}$) in an open system is given by:

$$ f_{ox} = \frac{\delta_f - \delta_p}{1000(\alpha_{ox} - \alpha_{trans})} $$

where $\delta_f$ is the measured $\delta^{13}$C-CH$_4$ value for each pore-water sample, $\delta_p$ is $\delta^{13}$C-CH$_4$ of produced methane, $\alpha_{ox}$ is the oxidation fractionation factor, and $\alpha_{trans}$ is a fractionation factor resulting from transportation of CH$_4$. While the exact value of
δp is unknown, diagenetic alteration of δ13C-CH4 values through oxidation or transport only enrich δ13C-CH4 signatures, therefore the value of δp is take as the most depleted δ13C-CH4 signature per STE site, assuming it has little or no diagenetic alteration. Literature-reported values for αox range between 1.003 and 1.049. We calculate the fraction of oxidized methane with the largest fraction factor (αox = 1.049; Mahieu et al. 2008), which yields the minimum amount of CH4 oxidation required to explain the observed variations in δ13CH4 and thus is a conservative estimate for CH4 oxidation. Literature-reported values for αtrans vary from 1 for advection-dominated systems to 1.0178 for diffusion-dominated porous media (de Visscher et al. 2004; Mahieu et al. 2008; Preuss et al. 2013). Based on Roy et al. (2011), we assume that transport is advection dominated and thus assume αtrans = 1.

The concentration of oxidized methane (CH4(ox)) is derived by solving the set of equations:

\[
\text{CH}_4\text{(produced)} = \text{CH}_4\text{(measured)} + \text{CH}_4\text{(ox)} \tag{14}
\]

\[
\text{CH}_4\text{(ox)} = \alpha_{\text{ox}} \times \text{CH}_4\text{(produced)} \tag{15}
\]

and substituting Eq. 14 into Eq. 15 to eliminate CH4-produced yields.

\[
\text{CH}_4\text{(ox)} = \left( f_{\text{ox}} \times \text{CH}_4\text{(measured)} \right) / \left( 1 - f_{\text{ox}} \right) \tag{16}
\]

**Modeling**

We used concentrations of major cations and anions, pH, temperature, and DIC concentrations to model the alkalinity and speciation of carbonate ions in PHREEQC using the PHREEQC database (Parkhurst 1995). Alkalinity was estimated from the charge balance of the model input (Parkhurst 1997). We also used major elemental composition, pH, temperature, and Si concentrations to model saturation indices of calcite and quartz. The saturation index (SI) is calculated as SI = log (IAP/Ksp), where IAP is the ion activity product and Ksp is the solubility product for calcite and quartz minerals.

To assess the impacts due to mixing vs. reactions in the STE, we constructed salinity-based conservative mixing models. Surface saltwater compositions were used for the saline end member. Freshwater end members for conservative mixing models are taken as the average of the freshest samples collected at shoreline piezometers interacting with lagoonal sediments, which likely differ in composition from solid aquifer material. The use of freshest samples also minimizes mixing between inflowing fresh groundwater and marine salt water, which will impact water chemistry and likely dissolved gas concentrations. The choice of a freshwater end member for each STE site (rather than a common end member for all STEs) also minimizes the impact of heterogeneity in the freshwater aquifer on mixing model results. For instance, the dissolved gas concentration of fresh groundwater may vary based on catchment land cover and heterogeneity in aquifer composition, which may impact infiltration rates and the degree of interaction between groundwater and organic soil layers, as well as the terminal electron acceptor concentrations in groundwater (for instance nitrate).

At BRL, the freshwater values were averaged for all sampling campaigns (n = 3; Table 2) For EGN, the freshwater end member was derived from samples collected during the September 2015 and May 2016, because in May 2015, only two water samples were available at the shoreline, and both were more diagenetically altered and saltier than the freshest water samples from the other two sampling times. For RWP, the freshwater end member was the average of the freshest samples collected in May and September 2015, because the shoreline piezometer was damaged and not available to sample after the September 2015 campaign.

**Results**

**Mixing model results**

Freshwater end members have lower pH and ORP values compared to saltwater end members for BRL and RWP, but for EGN, the freshwater end member has a higher ORP value than the EGN saltwater end member (Table 2). All freshwater end members have higher concentrations of CO2 and CH4, as well as higher concentrations of DIC compared to saltwater end members. BRL and RWP freshwater end members have higher

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Table 2. Chemical composition (average ± 1 SD) of freshwater and saltwater end members used in salinity-based conservative mixing models. Freshwater end members are the average of freshest and least diagenetically altered samples from shoreline piezometers at each seepage face at each sampling time. Saltwater end members are the average of lagoon surface water collected at each seepage face at each sampling time.

| Site | n | End member | Salinity | pH | ORP | CH4 (μmol L⁻¹) | CO2 (μmol L⁻¹) | DIC (mmol L⁻¹) | Alk (meq L⁻¹) |
|------|---|------------|----------|----|-----|---------------|---------------|---------------|--------------|
| BRL  | 3 | Fresh      | 2.3±0.67 | 6.3±0.22 | -192±100 | 51±54 | 1950±1695 | 8.7±0.8 | 4.8±0.8 |
|      | 3 | Salt       | 21.98±0.44 | 8.04±0.12 | -36±20 | 0.2±0.1 | 32±13 | 2.1±0.1 | 2.2±0.2 |
| EGN  | 2 | Fresh      | 0.62±0.20 | 6.2±0.04 | 83±34 | 0.3±0.1 | 1149±987 | 3.2±0.5 | 1.5±0.3 |
|      | 3 | Salt       | 21.84±2.68 | 7.77±0.30 | -27±60 | 0.1±0.1 | 53±30 | 1.9±0.1 | 2.0±0.0 |
| RWP  | 3 | Fresh      | 0.55±0.11 | 6.93±0.13 | -82±13 | 62±49 | 509±269 | 7.7±0.1 | 6.4±0.1 |
|      | 3 | Salt       | 23.28±1.4 | 7.94±0.44 | 20±43 | 0.1±0.1 | 49±38 | 1.9±0.2 | 2.1±0.2 |
concentrations of alkalinity, but EGN freshwater end members have lower alkalinity than the saltwater end member.

Freshwater end members vary in their concentration of CH$_4$ and CO$_2$: BRL and RWP have similar concentrations of CH$_4$ (51 ± 54 and 62 ± 49 μmol L$^{-1}$, respectively), whereas EGN contains 0.3 ± 0.1 μmol L$^{-1}$ CH$_4$. CO$_2$ concentrations are similar between BRL and EGN freshwater end members (1950 ± 1695 and 1149 ± 987 μmol L$^{-1}$, respectively), whereas RWP concentrations are lower (509 ± 269 μmol L$^{-1}$; Table 2).

CO$_2$ and CH$_4$ are nonconservative with salinity at all STE sites (Fig. 3a,b). CO$_2$ concentrations are generally lower than those predicted by conservative mixing, while CH$_4$ concentrations are generally higher. Maximum CH$_4$ concentrations reach 200 μmol L$^{-1}$ at BRL and 400 μmol L$^{-1}$ at RWP and
occur in low-salinity portions of the STE, whereas maximum CH₄ concentrations reach 7 μmol L⁻¹ at EGN and occur near a salinity of 20. pH increases with salinity at all STE sites (Fig. 3c). DIC and alkalinity mix nonconservatively, and measured concentrations are generally higher than those predicted by conservative mixing although some alkalinity concentrations are lower than those predicted by conservative mixing, particularly at RWP (Fig. 3d,e). Both the ratios of Alk : DIC and proportion of DIC speciated as CO₂ decrease with salinity at all sites (Fig. 3f,g).

δ¹³C-CO₂ and δ¹³C-CH₄

Cross plots of δ¹³C-CO₂ and δ¹³C-CH₄ signatures indicate production pathways of CH₄ as well as extent of oxidation, because each process fractionates carbon between the two species within a range of fractionation factors (εc; Whiticar and Schoell 1986; Whiticar 1999). Here, isotopic compositions of CO₂ and CH₄ indicate that methanogenesis at RWP is consistent with CO₂ reduction, while that produced at BRL and EGN is consistent with acetoclastic methanogenesis, as well as CH₄ oxidation (Fig. 4a). The asymptotes of cross plots of CH₄ concentrations vs. δ¹³C-CH₄ values indicate that the δ¹³C signature of CH₄ produced by microbial methanogenesis (δ₀; Eq. 13) is similar for BRL and EGN at −53‰ and −54‰, but lower at RWP at −78‰ (Fig. 4b).

Estimates of CH₄ oxidation are reported as both a fraction of total dissolved CH₄ (fₐx; Eq. 13) as well as mass of CH₄ oxidized (CH₄(ox); Eqs. 14–16). Values of fₐx show little relationship with salinity (Fig. 5a), and CH₄(ox) concentrations are highest in low-salinity samples of all sites (Fig. 5b). Values of fₐx and CH₄(ox) concentrations reach maxima at negative ORP values (Fig. 6a,b).

**Fig. 4.** δ¹³C-CH₄ compared to δ¹³C-CO₂ (a) and CH₄ concentrations (b). Zones of CO₂ reduction and acetoclastic methanogenesis, and expected change in isotopic compositions due to oxidation are taken from Whiticar (1999). Fields are defined by fractionation factors between CO₂ and CH₄, εc, where εc ≡ δ¹³C-CO₂ − δ¹³C-CH₄.

**Fig. 5.** Cross plots of salinity and CH₄ oxidation reported as a (a) fraction of total CH₄ per sample (fₐx) and (b) mass of CH₄ oxidized (CH₄(ox)).

**Mineral saturation indices**

Freshwater end members are at equilibrium or slightly supersaturated with respect to quartz at all sites, while saltwater end members are undersaturated. SIquartz of STE samples are variable with salinity (Fig. 7a). Freshwater end members...
are undersaturated with respect to calcite for both BRL and EGN sites, but supersaturated for RWP, while saltwater end members are supersaturated for all sites (Fig. 7b). SI\textsubscript{cal} values decrease to below the freshwater end member for some STE samples at BRL and RWP, but are consistently higher than the freshwater end member for EGN (Fig. 7b). Ca concentrations display nonconservative mixing with salinity, and measured concentrations are lower than conservative mixing lines in low-salinity STE samples from BRL and RWP and higher than conservative mixing lines for mid- to high-salinity samples. Ca concentrations of STE samples are consistently higher than the conservative mixing line for EGN at all salinities (Fig. 7c).

**Redox gradients**

ORP decreases with salinity at all sites, and steepest decreases are observed in samples with a salinity less than 5 (Fig. 8a). Dissolved organic carbon (DOC) concentrations decrease with salinity for BRL, but increase with salinity for EGN, and remain relatively constant with salinity for RWP (Fig. 8b). Nitrate concentrations are below detection limit for most samples, but several low-salinity samples have elevated concentrations at BRL (up to 55 \(\mu\text{mol L}^{-1}\)), EGN (up to 200 \(\mu\text{mol L}^{-1}\)), and RWP (4 \(\mu\text{mol L}^{-1}\); Fig. 8c). Fe(II) concentrations are highest in low-salinity samples of BRL (up to 40 \(\mu\text{mol L}^{-1}\)) and RWP (up to 15 \(\mu\text{mol L}^{-1}\)) but in saline STE samples of EGN (up to 40 \(\mu\text{mol L}^{-1}\); Fig. 8d). Sulfide (HS\textsuperscript{-}) concentrations are elevated at all salinities at BRL (up to 150 \(\mu\text{mol L}^{-1}\) with one outlier at 250 \(\mu\text{mol L}^{-1}\)) and RWP (up to 100 \(\mu\text{mol L}^{-1}\)). HS\textsuperscript{-} concentrations at EGN are elevated in saline STE samples.

**Fig. 6.** Cross plots of ORP and CH\textsubscript{4} oxidation reported as a (a) fraction of total CH\textsubscript{4} per sample (\(f_{\text{ox}}\)) and (b) mass of CH\textsubscript{4} oxidized (CH\textsubscript{4(ox)}).

**Fig. 7.** Saturation indices of STE samples with respect to (a) quartz and (b) calcite, and concentrations of Ca (c). Freshwater and saltwater end members are depicted with open-square symbols, and conservative mixing lines are drawn between freshwater and saltwater end members. Samples from shoreline piezometers (BRL-1, EGN-0, and RWP-0) are depicted with filled gray circles.
samples and reach maximum concentrations of 100 \( \mu \text{mol L}^{-1} \) (Fig. 8e).

**\( \Delta \text{Alk} : \Delta \text{DIC} \) ratios**

Deviations between measured concentrations of DIC and alkalinity and conservative mixing lines between freshwater and saltwater end members are expressed as \( \Delta \text{DIC} \) and \( \Delta \text{Alk} \). We show cross plots of samples at each STE site, which are grouped by salinity: low (< 5), mid (between 5 and 20), and high salinity (> 20). Low to mid-salinity samples at BRL are depleted in DIC relative to conservative mixing lines, although \( \Delta \text{Alk} \) values are near 0 (Fig. 9a). With a few exceptions, other data points, ranging from low to high salinity, plot between the \( \Delta \text{Alk} : \Delta \text{DIC} \) lines of sulfate reduction and methanogenesis. Low-salinity STE samples at EGN plot between the \( \Delta \text{Alk} : \Delta \text{DIC} \) lines of CaCO\(_3\) dissolution and sulfate reduction. Other samples plot the \( \Delta \text{Alk} : \Delta \text{DIC} \) lines of sulfate reduction and denitrification (Fig. 9b). At RWP, fresh STE samples plot near the \( \Delta \text{Alk} : \Delta \text{DIC} \) line of CaCO\(_3\) precipitation (Fig. 9c). Other samples (low to high salinity) plot near the \( \Delta \text{Alk} : \Delta \text{DIC} \) line of sulfate reduction.

**Discussion**

Observed concentrations of CO\(_2\) and CH\(_4\) in Indian River Lagoon STEs vary by orders of magnitude between sites, as well as along salinity gradients within individual study sites (Fig. 3a,b). The variability observed in freshwater end members (Table 2) is small compared to differences between sites and with salinity (Fig. 3a,b), which indicates that biogeochemical processing within these STEs is the major control on these GHG concentrations and would have a larger impact on CO\(_2\) and CH\(_4\) fluxes from STEs than variability in fresh groundwater composition. Despite differences in concentrations, we observe that measured CH\(_4\) concentrations in STEs are consistently greater than those predicted from conservative mixing and indicate net production, while measured CO\(_2\) concentrations are consistently lower and indicate net consumption.
The similarity in chemical changes between sites suggests that processes controlling CO₂ and CH₄ production and consumption are related between sites, but vary in magnitude. We discuss controls of these processes below, followed by implications of these findings for fluxes of CO₂ and CH₄ in SGD.

CH₄ sources and sinks

Sources of methane to Indian River Lagoon STEs include inland fresh groundwater, as shown by elevated CH₄ concentrations in freshwater end members of both BRL and RWP (Table 2), as well as methanogenesis within the STEs. Concentrations of CH₄ in fresh groundwater end members (51 ± 54 and 62 ± 49 μmol L⁻¹, respectively) are similar to groundwater concentrations in other studies where CH₄ is used as a tracer of SGD (Cable et al. 1996; Corbett et al. 2000; Dulaiova et al. 2010). However, methanogenesis within BRL and RWP STEs increases CH₄ concentrations by 5- to 10-fold. The low freshwater CH₄ concentrations at EGN (<1 μmol L⁻¹) are also enhanced by 5- to 10-fold by methanogenesis within the STE, but the maximum concentration (7 μmol L⁻¹) is orders of magnitude lower than the other sites (hundreds of micromol per liter at BRL and RWP; Fig. 3b). Therefore, although the majority of CH₄ in STEs is produced within the STEs at each site, the magnitudes of CH₄ sources and sinks vary substantially and result in orders of magnitude variability in STE CH₄ concentrations. These findings challenge the underlying assumptions of studies using CH₄ as a conservative tracer of fresh groundwater inputs via SGD and imply that current estimates of SGD volumes, if based on relatively lower inland groundwater CH₄ concentrations, may be overestimated if additional CH₄ is generated when groundwater flows through STEs. CH₄ may still be useful as a qualitative indicator of SGD if combined with other tracers such as Rn and Ra, which do not undergo biogeochemical modification in sediments or the water column and instead reflect the degree of interaction between sediments and saline or fresh pore waters isolated from direct contact with the atmosphere (Cable et al. 1996; Corbett et al. 2000; Dulaiova et al. 2010). However, because SGD fluxes of Rn and Ra to surface waters may result from either fresh SGD or recirculated seawater, while CH₄ concentrations are typically elevated in fresh groundwater only and predominantly reflect fresh SGD, SGD estimates using Rn and Ra are not directly comparable to those using CH₄, and knowledge of the sources and sinks of CH₄ in STEs is needed to evaluate the role of CH₄ as a tracer of SGD as well as the role of SGD in coastal CH₄ and carbon budgets.

As the terminal metabolic process of organic matter remineralization, methanogenesis occurs when other terminal electron acceptors have been depleted (Froelich et al. 1979). It is therefore more likely to occur in freshwater than salt water, which contains high concentrations of sulfate, because methanogens are readily out-competed for chemical substrates by sulfate-reducing microbes (Whiticar 1999). The redox potential of flowing fresh groundwater should therefore exert an initial control on CH₄ fluxes in SGD, because methanogenesis may only occur if organic carbon supplies in freshwater are high compared to terminal electron acceptor abundances. While the fresh groundwater end members at BRL and RWP are reducing and support methanogenesis, potentially due to factors such as land use or aquifer solid composition that...
would impact the redox potential of inflowing groundwater, fresh groundwater at EGN has positive ORP values (Table 2) and low organic carbon content (Fig. 8b), leading to lower CH4 concentrations compared to BRL and RWP (Table 2). Despite limited methanogenesis in the freshwater end member of EGN, additional CH4 is generated in more saline portions of the STE (Fig. 3b) but is likely inhibited by relatively high concentrations of sulfate. In contrast, the majority of methanogenesis occurs in fresher portions of the BRL and RWP sites, and likely results from the initial low redox potential of groundwater combined with higher availability of organic carbon in freshwater portions to drive further remineralization reactions. Additional methanogenesis within STEs at BRL and RWP may result from more intense microbial activity driven by increases in the availability of dissolved organic carbon, as has been shown to occur in other STE sites (Suryaputra et al. 2015) and in particular at Indian River Lagoon (Pain et al., In press).

In addition to variability in the concentrations of CH4 produced in Indian River Lagoon STEs, stable isotopic signatures of CH4 suggest that its microbial production pathway may differ between sites. Cross plots of $\delta^{13}$C-C-CH4 and $\delta^{13}$C-CO2 provide evidence of a difference in methanogenesis pathway because data from RWP plot predominantly in the region typical of CO2 reduction, whereas data from BRL and EGN plot in the acetoclastic region, as well as that produced by CH4 oxidation (Fig. 4a). Acetoclastic methanogenesis at BRL and EGN is supported by similarity in their $\delta^{13}$C signatures: $\delta^{13}$C-CH4 at BRL and EGN are at $-53^\circ$ and $-54^\circ$, respectively, whereas the $\delta^{13}$C-CH4 of CH4 produced at RWP is $-78^\circ$ and may reflect a greater proportion of CO2 reduction (Fig. 4b; Whiticar 1999).

Variations in the predominant methanogenesis pathways are often attributed to salinity or organic carbon quality, and acetoclastic methanogenesis is more typically observed in freshwater environments with greater availabilities of labile organic carbon substrates (Whiticar and Schoell 1986; Megonigal et al. 2005). Salinity is not likely the driver of the differences in pathways between sites here, because although $\delta^{13}$C-CH4 signatures suggest different methanogenesis pathways at BRL and RWP, both occur in fresh portions of STEs (Fig. 3b). Organic carbon substrates may vary in quality, although previous assessment of dissolved organic carbon quality at these sites indicates similar shifts in organic matter quality along STE salinity gradients (Pain et al., In press). The observed difference in methanogenesis pathway may therefore be related to other factors, such as the structure of the microbial community or nutrient availability (Megonigal et al. 2005). While further investigation of methanogenesis pathways is beyond the scope of this study, our findings highlight that both the concentrations as well as methanogenesis pathway in STEs may be more variable than previously considered and may complicate estimates of fluxes and stable isotopic compositions of CH4 derived from SGD. However, the ubiquitous production of CH4 at STE sites suggests that current estimates of fluxes of CH4 via SGD may be underestimates if based on inland groundwater CH4 concentrations.

Once produced, CH4 may be consumed through microbial oxidation to CO2 through both aerobic and anaerobic pathways (e.g., anaerobic oxidation of methane [AOM]). Here, CH4 oxidation appears to decrease CH4 concentrations across the entire range of salinity (Fig. 5a). The impact of this oxidation on CH4 concentrations, and therefore on SGD fluxes, can be examined by converting $F_{ox}$ to mass of CH4 oxidized (Eqs. 14–16). The magnitude of the CH4 oxidation sink is greater in low-salinity samples of BRL and RWP, where CH4 concentrations are highest (Fig. 5b). Additionally, the greatest extent of CH4 oxidation, both in terms of $F_{ox}$ and CH4($\delta^{15}$N), is greatest at negative ORP values (Fig. 6a,b), indicating that oxidation is likely anaerobic.

Both the production of CH4 via methanogenesis and consumption via methane oxidation alter concentrations of CH4 in STEs and therefore will alter fluxes via SGD. The magnitude of CH4 sources is greater than sinks in the STEs sampled here, leading to measured CH4 concentrations that are greater than that expected by conservative mixing (Fig. 3b). Our results suggest that several generalizations may be made about the controls of CH4 sources and sinks in STEs. The magnitude of the CH4 source is likely related to groundwater redox potential. Methanogenesis may be a dominant organic matter remineralization pathway as reducing water flows through fresher portions of STEs where inhibition from seawater sulfate is minimized. The magnitude of the CH4 oxidation sink may be limited by groundwater residence time, or sulfate and oxygen gradients. Specifically, long groundwater residence times (~ 195 d) between the zones of methanogenesis and discharge at the sediment–water interface have led to near-complete consumption of groundwater-derived CH4 in other settings, implying that increases in groundwater residence time may be associated with lower CH4 fluxes via SGD (Schutte et al. 2016). CH4 oxidation may also be chemically limited because $O_2$ is required for aerobic CH4 oxidation while AOM is frequently coupled to sulfate reduction (Megonigal et al. 2005). The rate of delivery of $O_2$ to STE sediments may therefore control the extent of aerobic CH4 oxidation and would be limited in these STEs, because oxygen is rapidly reduced within the first few millimeters of the sediment–water interface. AOM would vary across the salinity gradient, because seawater is the principal source of sulfate in STEs (Megonigal et al. 2005). Consequently, this and other work (e.g., Schutte et al. 2016) suggest that oxidation modifies CH4 fluxes via SGD.

**CO2 sources and sinks**

Contrasting with observations of CH4 production at all Indian River Lagoon STE sites, CO2 concentrations are consistently lower than those predicted by conservative mixing models (Fig. 3a) and indicate net consumption. These changes are accompanied by increases in pH (Fig. 3c), increases in alkalinity above conservative mixing values (Fig. 3e), increases in
ratios of Alk : DIC (Fig. 3f), and decreases in the proportion of DIC speciated as CO₂ (Fig. 3g). The ratio of Alk : DIC determines the CO₂ buffering capacity of water, and higher ratios of Alk : DIC correspond with lower proportions of DIC speciated as CO₂ (Denman et al. 2007). Changes to Alk : DIC ratios result from reactions that produce and consume DIC and Alk in different proportions, and the stoichiometries of these reactions are well-known (Table 1). Here, increases in Alk : DIC with salinity (Fig. 3f) suggest that in situ reactions in STEs cause alkalinity to be generated in greater quantities than DIC as water flows through STE sediments. These changes alter the carbonate speciation of pore waters and leads to the net sequestration of CO₂ as HCO₃⁻, thus decreasing SGD fluxes of CO₂.

Reactions that alter carbonate chemistry may occur in STEs due to both changes in the solid-phase materials available to drive reactions as water flows from terrestrial aquifers through mixed marine and terrestrial sediments, as well as shifts in terminal electron acceptors that may be used to remineralize organic matter. In sediments containing calcium carbonate minerals, CaCO₃ dissolution is frequently the dominant reaction that sequesters CO₂ as HCO₃⁻. In the STEs sampled here, changes in mineral saturation indices and nonconservative mixing of Ca suggest that CaCO₃ dissolution occurs and produces alkalinity. This production reflects an increase in CaCO₃ mineral availability between predominantly siliciclastic inland aquifer material (Berndt and Katz 1992) and mixed terrestrial and marine lagoon sediments (Dorsett et al. 2011). Fresh groundwater end members are in equilibrium with siliciclastic inland aquifer material (SIquartz ≥ 0; Fig. 7a), whereas SIcal ≤ 0, reflecting limited interaction with CaCO₃ minerals (Fig. 7b). However, SIcal values increase in STE samples compared to fresh groundwater end members, particularly at shoreline piezometers of BRL and EGN, and Ca concentrations above conservative mixing lines suggest that CaCO₃ dissolution occurs (Fig. 7b,c). These changes suggest that rapid CaCO₃ dissolution occurs when groundwater that is undersaturated with respect to CaCO₃ begins to interact with lagoon sediments. This interaction generates alkalinity in greater proportions than DIC (Eq. 6) thus increasing Alk : DIC ratios (Fig. 3g) and leads to net CO₂ sequestration (Fig. 3a). ΔAlk : ΔDIC ratios of EGN freshwater are consistent with CaCO₃ dissolution as the primary reaction altering carbonate speciation and plot near the ΔAlk : ΔDIC line produced by CaCO₃ dissolution (Fig. 9b).

Although CaCO₃ dissolution may alter carbonate chemistry, particularly at the shoreline piezometers of EGN and BRL, the role of CaCO₃ dissolution should be limited when waters are supersaturated or approach equilibrium with respect to CaCO₃. This is the case for most STE samples apart from shoreline piezometers of BRL and EGN. In some cases, SIcal values near or above 0 and Ca concentrations lower than conservative mixing suggests that some CaCO₃ precipitation occurs, particularly in fresh portions of BRL and RWP (Fig. 7b, c). Additional reactions are therefore necessary to cause the increases in Alk : DIC ratios observed with increasing salinity, because CaCO₃ precipitation would decrease Alk : DIC ratios (Eq. 6). These reactions may include sulfate reduction, denitrification, and iron reduction, which play an important role in the generation of alkalinity in siliciclastic settings with limited CaCO₃ availability (Table 1; Berner et al. 1970). The alkalinity generated by redox reactions should vary with salinity, because freshwater-saltwater mixing in STEs leads to sharp gradients in redox potential, and each redox reaction produces DIC and alkalinity at distinct ratios (Table 1).

ΔAlk : ΔDIC ratios indicate that redox reactions control carbonate chemistry to a greater extent than CaCO₃ dissolution in mid- to high-salinity samples, but reactions differ between STE sites. At EGN, where CaCO₃ dissolution is an important process for the water composition at the shoreline, mid- and high-salinity samples reflect a greater importance of sulfate reduction or denitrification (Fig. 9b). Denitrification likely occurs in freshwater samples of EGN, because nitrate concentrations reach 200 μmol L⁻¹ (Fig. 8c), but consumption of all nitrate via denitrification would only yield up to 250 μmol L⁻¹ DIC (Eq. 2). Because ΔDIC values are in the millimol per liter range in the low-salinity samples that contain high nitrate concentrations (Fig. 9b), denitrification likely plays only a limited role in generating excess DIC and alkalinity because of low nitrate concentrations. While maximum HS⁻ concentrations reach 100 μmol L⁻¹ (Fig. 8e), which would only yield a ΔDIC of 200 μmol L⁻¹ according to reaction stoichiometry (Eq. 4), measured concentrations do not reflect the full extent of sulfate reduction, because iron sulfide mineral precipitation is known to occur and may consume nearly all free Fe(II) and HS⁻ (Roy et al. 2011). The close proximity of EGN mid- and high-salinity data points to the ΔAlk : ΔDIC line produced by sulfate reduction suggests that it is the predominant redox reaction altering carbonate speciation in higher salinity waters where pore waters are close to equilibrium with respect to CaCO₃ minerals (Fig. 7b).

ΔAlk : ΔDIC ratios at BRL and RWP cluster between the lines produced by sulfate reduction and methanogenesis in the upper right-hand and lower left-hand quadrant of the ΔAlk : ΔDIC plot, indicating net DIC consumption (Fig. 9a,c). Data points between the ΔAlk : ΔDIC ratios of sulfate reduction and methanogenesis may result from the co-occurrence of these processes. Co-occurrence is supported by elevated sulfide concentrations (up to 150 μmol L⁻¹ at BRL and 100 μmol L⁻¹ at RWP) across the observed salinity range, coinciding with elevated CH₄ concentrations in low (< 5) to mid (5–20) salinity samples at both sites.

A number of fresh to mid-salinity samples of BRL and RWP are depleted in DIC relative to conservative mixing (Fig. 9a,c). Some of this DIC consumption may be related to CaCO₃ precipitation, which is supported by some positive SIcal values and Ca concentrations lower than conservative mixing values in freshwater portions of both sites (Fig. 7b,c). For BRL in particular, additional reactions such as Fe reduction would be...
necessary to produce alkalinity, as data points are disproportionately depleted in DIC compared to alkalinity if DIC consumption is due to CaCO₃ precipitation alone (Fig. 9a). While further investigation is needed to determine the cause of the DIC sink in these waters, our results indicate that both redox reactions as well as shifts in CaCO₃ availability and mineral saturation state drive net CO₂ sequestration in STEs and serve to decrease CO₂ fluxes via SGD. However, despite the CO₂ sequestration in STEs, most of our STE samples have CO₂ concentrations elevated above surface water concentrations, indicating that SGD is a source of CO₂ to the Indian River Lagoon. Exports of alkalinity via SGD may additionally impact surface water CO₂ dynamics by altering surface water DIC : Alk ratios, which determines dissolved carbonate speciation. Here, non-conservative behavior and production of alkalinity in STEs may provide additional alkalinity to surface waters, which may enhance surface water buffering capacity and sequestration of CO₂ as HCO₃⁻, as was observed in Liu et al. (2017).

Implications for GHG fluxes via SGD

We observe that reactions in STEs significantly modify the GHG composition of SGD, and lead to net production of CH₄ coinciding with net sequestration of CO₂. These findings highlight challenges in the estimation of GHG fluxes of SGD, because despite relatively low variation in the concentration of CO₂ and CH₄ in inflowing groundwater, STE reactions lead to orders of magnitude differences in the concentrations of both gases. Extrapolation of SGD GHG fluxes even within the hydrogeologically homogenous and geographically constrained setting of this study therefore must account for a high degree of uncertainty in the estimation of SGD GHG concentrations. Despite differences in concentrations between sites, STE samples contain higher concentrations of both CO₂ and CH₄ compared to saltwater end members (Fig. 3a,b), and SGD is therefore a source of GHGs to coastal zones. The observed variability in CO₂ and CH₄ concentrations resulting from STE biogeochemical processing may preclude large-scale estimates of SGD on the coastal carbon budget.

Although STEs examined in this study are likely similar in hydrogeological characteristics such as groundwater flow rate, residence time in the STE, and composition of sediments, variations in these parameters are likely to impact STE processing of CO₂ and CH₄ concentrations and thus fluxes due to SGD. Residence time may be related to STE hydrogeology, and should be greater when SGD flows through fine grained sediments compared to coarse sand or karstic conduits (Pain et al., In press). Temporal variability due to changes in temperature or STE end member composition may also occur, as well as variation in groundwater residence times due to seasonal differences in recharge and groundwater flow rates (Michael et al. 2005). In the case of CH₄, increasing STE residence time would likely lead to greater consumption of CH₄ via methanotrophy, and greater residence times may therefore reduce groundwater fluxes of CH₄. Land use may play an additional role by altering the organic carbon and terminal electron acceptor concentrations and thus the redox potential of inflowing groundwater. The magnitude of the CO₂ sink within STEs should depend on the mineralogical composition of sediments as alkalinity may be produced via calcium carbonate mineral dissolution as well as Fe oxide reduction, and would thus depend on the availability of these mineral phases to generate alkalinity and sequester CO₂. Given the likely impacts of sediment composition, groundwater flow rates, and residence times of STEs on CO₂ and CH₄ concentrations, CO₂ and CH₄ fluxes due to SGD are likely highly variable but could have important impacts on coastal carbon budgets due to their elevated concentrations with respect to surface waters and nonconservative behavior in STEs.

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