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SYNTHESIS AND EMERGING IDEAS

Porewater biogeochemistry and soil metabolism in dwarf red mangrove habitats (Twin Cays, Belize)

Rosalynn Y. Lee · William P. Porubsky · Ilka C. Feller · Karen L. McKee · Samantha B. Joye

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Abstract Seasonal variability in biogeochemical signatures was used to elucidate the dominant pathways of soil microbial metabolism and elemental cycling in an oligotrophic mangrove system. Three interior dwarf mangrove habitats (Twin Cays, Belize) where surface soils were overlain by microbial mats were sampled during wet and dry periods of the year. Porewater equilibration meters and standard biogeochemical methods provided steady-state porewater profiles of pH, chloride, sulfate, sulfide, ammonium, nitrate/nitrite, phosphate, dissolved organic carbon, nitrogen, and phosphorus, reduced iron and manganese, dissolved inorganic carbon, methane and nitrous oxide. During the wet season, the salinity of overlying pond water and shallow porewaters decreased. Increased rainwater infiltration through soils combined with higher tidal heights appeared to result in increased organic carbon inventories and more reducing soil porewaters. During the dry season, evaporation increased both surface water and porewater salinities, while lower tidal heights resulted in less reduced soil porewaters. Rainfall strongly influenced inventories of dissolved organic carbon and nitrogen, possibly due to more rapid decay of mangrove litter during the wet season. During both times of year, high concentrations of reduced metabolites accumulated at depth, indicating substantial rates of organic matter mineralization coupled primarily to sulfate reduction. Nitrous oxide and methane concentrations were supersaturated indicating considerable rates of nitrification and/or incomplete denitrification and methanogenesis, respectively. More reducing soil conditions during the wet season promoted the production of reduced manganese. Contemporaneous activity of sulfate reduction and methanogenesis was likely fueled by the presence of noncompetitive substrates. The findings indicate that these interior dwarf areas are unique sites of nutrient and energy regeneration and may be critical to the overall persistence and productivity of mangrove-dominated islands in oligotrophic settings.

Keywords Dwarf mangrove · Nutrients · Porewater · Redox metabolites · Sulfate reduction · Methanogenesis

R. Y. Lee · W. P. Porubsky · S. B. Joye (✉)
Department of Marine Sciences, University of Georgia, Room 220 Marine, Sciences Building, Athens, GA 30602-3636, USA
e-mail: mjoye@uga.edu

Present Address:
R. Y. Lee
Institute of Marine and Coastal Sciences, Rutgers University, New Brunswick, NJ 08901-8521, USA

I. C. Feller
Smithsonian Environmental Research Center, Edgewater, MD 21037, USA

K. L. McKee
National Wetlands Research Center, U.S. Geological Survey, Layfayette, LA 70506, USA

Introduction

Microbial activity drives the mineralization of organic matter in intertidal soils and sediments and influences porewater nutrient availability and the speciation of redox-active compounds (Paerl and Pinckney 1996). Terminal metabolism couples organic matter oxidation to the reduction of an oxidant and produces a variety of end products, including dinitrogen and nitrous oxide gases, reduced iron and manganese, sulfide and methane which are indicative of denitrification, metal reduction, sulfate reduction and methanogenesis, respectively. Terminal metabolic processes recycle complex organic matter back to inorganic forms such as bicarbonate, ammonium, and phosphate, which are critical for maintaining ecosystem primary production in oligotrophic settings.

Mangrove soils are typically nutrient deficient (Alongi 1996; Alongi and Sasekumar 1992; Boto and Wellington 1984) despite being rich in organic matter, suggesting highly efficient recycling of the inorganic nutrients regenerated during mangrove litter decomposition (Holguin et al. 2001). In natural mangrove systems, nitrogen fixation is an important source of new nitrogen but this process is spatially and temporally variable (Lee and Joye 2006). The high productivity of mangroves is thus largely driven by internal nutrient recycling, which is coupled to organic matter mineralization.

Mangrove soils can be both hypersaline and biochemically reducing (Kathiresan and Bingham 2001). Increased rainfall during the wet season can affect porewater salinity, redox potential, and pH as well as soil biogeochemical processes (Alongi et al. 1999, 2004). Previous studies investigating benthic metabolism and nutrient transformations in mangrove soils fringing oceans or rivers have demonstrated a relationship between organic matter availability, sulfate reduction and mangrove density and/or species (Nedwell et al. 1994, Sherman et al. 1998). Comparable data from more spatially extensive dwarf or scrub mangrove zones are lacking.

On Twin Cays, the island edges are characterized by fringing mangroves while island interiors are characterized by dwarf mangroves. A similar shoreline-to-interior tree height gradient characterizes many offshore mangrove islands (Feller et al. 2003; Lovelock et al. 2005). Fringe mangrove forests occur along the exposed edges of coastal waters as well as along protected shorelines; fringe soils are well flushed daily by tides. Dwarf mangroves occur in areas where physiological stressors (e.g., nutrient limitation or hypersalinity) limit tree height (typically to 1 m or less). Dwarf mangrove forests are a dominant feature of Caribbean mangrove ecosystems, often accounting for up to 60% of the ecosystem area (Cintrón et al 1978; Feller and Mathis 1997; Feller et al. 2003; Rodriguez and Feller 2004; Lovelock et al. 2005; Lugo 1997; Spalding et al. 1997). Because dwarf mangrove soils experience distinct hydrology and biogeochemistry, these habitats serve as critical biogeochemical components of mangrove ecosystems and possibly valuable sources to adjacent reef and open ocean ecosystems.

Dwarf mangrove stands are characterized by trees $<$1.5 m tall that are sparsely distributed with limited canopy development (Rützler and Feller 1996). Interior lagoons and shallow ponds within dwarf mangrove zones may be important areas of nutrient regeneration and energy production for the broader ecosystem. More open canopies, lower elevations, extended hydroperiods, and differences in benthic communities that are characteristic of dwarf mangrove stands (McKee et al. 2002; Feller et al. 2003; Lee and Joye 2006) are features that may drive unique biogeochemical signatures or microbial processes compared with other forest types.

The objective of this study was to characterize steady-state porewater biogeochemical signatures of soils in dwarf mangrove stands and to use these data to evaluate pathways of benthic metabolism and nutrient regeneration. We quantified steady-state porewater profiles of dissolved chemical species during a wet and dry season using diffusion equilibration samplers. We hypothesized that wet–dry seasonality would strongly influence the flushing of soils, leading to changes in the inventories of porewater metabolic constituents and the redox status of the soils. These differences were in turn hypothesized to affect the rates of carbon mineralization and nutrient regeneration. This work was conducted at Twin Cays, an oceanic island range, which is the Smithsonian Institution's primary field site for mangrove research in Belize (Rützler and Feller 1996). Twin Cays has served as a model system for studying nutrient dynamics in oligotrophic settings (e.g., McKee et al. 2002; Feller et al. 2003; Joye and Lee 2004; Lee and Joye 2006).

Materials and methods

Twin Cays, a group of oceanic mangrove islands located 15.5 km off the coast of Belize at 16°50′ N, 88°06′ W (Feller et al. 2003; Lee and Joye 2006), is one of many island mangrove systems (Rützler and Feller 1996) that lie along the MesoAmerican Barrier Reef system. Island mangroves differ from mainland mangroves in that they have limited terrestrial influence; they are not impacted by river runoff except following extreme climate events such as hurricanes (Muller-Karger et al. 2005); and they are constantly bathed by full salinity ocean water. The Twin Cays archipelago is forested primarily by red mangrove (*Rhizophora mangle*) but black mangrove (*Avicennia germinans*) and white mangrove (*Laguncularia racemosa*) are also present in some areas. The islands are underlain by 9–10 m deep mangrove peat that accreted during the Holocene keeping pace with rising sea level (Macintyre and Toscano 2004). The Holocene peat lies atop Pleistocene limestone deposits (Macintyre and Toscano 2004; McKee et al. 2007). *Rhizophora mangle* exhibits a decreasing tree-height gradient from the seaward edges of the islands to the interior where dwarf trees surrounding treeless ponds dominate the landscape. Dwarf mangrove habitats account for approximately sixty percent of the surface cover on Twin Cays (Rodriguez and Feller 2004) and are, consequentially, a dominant feature of these and similar islands. Dwarf mangrove zones are waterlogged except during extremely low tides, which occur in late spring and early summer. A striking feature of this zone is the presence of mm- to cm-thick microbial mats on the sediment surface (Joye and Lee 2004; Lee and Joye 2006). The microbial composition of these mats varies but they are characterized by high rates of primary production (Joye and Lee 2004; Lee et al. in preparation) and nitrogen fixation (Lee and Joye 2006).

We investigated the temporal and spatial variability of soil biogeochemical signatures at three sites inhabited by dwarf *R. mangle* between August and September 2002 and between April and May 2003. Seasonal variation in some microbial processes (e.g., nitrogen fixation) at Twin Cays results from variations in precipitation and tidal height rather than fluctuations in temperature (Lee and Joye 2006). Water temperatures at Carrie Bow Cay, a Smithsonian Institution field station located 2 km from Twin Cays, were similar in April–May and August–September, while tidal heights and rainfall were significantly lower in April–May (between −25 and +27 cm relative to mean sea level and 1.3 mm day^{-1}, respectively) than in August–September (between −11 and +30 cm relative to mean sea level and 4.6 mm day^{-1}, respectively) (Opishinski 2002–2003; Lee and Joye 2006). The spatial variability in Twin Cays dwarf *R. mangle* soil biogeochemistry was assessed at three distinct sites: the Weather Station, the Dock and the Lair. The microbial mat at the surface of each site sampled varied slightly in thickness (a few mm to 1 cm depth on average) and composition (commonly containing coccoidal and non-heterocystous cyanobacteria, and occasionally containing heterocystous cyanobacteria and/or a visible layer of purple sulfur bacteria; Joye and Lee 2004).

Steady state profiles of dissolved constituents in dwarf mangrove soils were obtained using porewater diffusion equilibration samplers (hereafter referred to as "peepers"; Hesslein 1976). Ultra high molecular weight polyethylene peepers with 30 (18-ml volume) chambers over a length of ~50 cm were assembled with 0.2 μm Biotrans™ nylon membranes and nylon screws while submerged in helium-purged deionized water (details provided in Weston et al. 2006). Peepers were transported to the field site in 0.15-mm thick polypropylene bags of helium-purged deionized water with no headspace. Peepers were inserted vertically in the peat soil no closer than 1.5 m to a dwarf mangrove tree approximately 6 months before collection. The dimensions of the peeper chambers (1 cm deep; membrane area = 18 cm^2) yield a diffusive equilibrium time between the oxygen-free deionized water inside the chambers with the surrounding porewater of at least 6, and optimally 8, weeks (Grigg et al. 1999). For simplicity, peepers collected in September 2002 will be referred to as from September (although they represent the biogeochemical signature of August through September), and peepers collected in May 2003 will be referred to as from May (although they represent the biogeochemical signature of April through May). Peepers were installed in the same general vicinity (within a 3 m^2 area) at each site on both sampling dates. Due to the intensive nature of peeper sampling, one peeper was inserted per season at each of the three sites, and the data were averaged to

characterize the biogeochemistry of dwarf *R. mangle* soils on Twin Cays (a sampling approach commonly employed with peeper studies, e.g., Koretsky et al. 2003; Weston et al. 2006).

Peepers were removed from the soil, placed in helium-purged 0.15-mm thick polypropylene bags, and transported to the Smithsonian Institution field station on Carrie Bow Cay for sampling; the time between retrieval and sampling was about 30 min. After transfer into helium-purged glove bags, porewater from each chamber was sampled through the nylon membrane using a gas-tight glass syringe fitted with an 18 gauge needle. Water from each peeper chamber was analyzed immediately for pH and subsampled for ammonium (NH_4^+), nitrate + nitrite (NO_x), phosphate (PO_4^{3-}), dissolved organic carbon (DOC), nitrogen (DON), and phosphorus (DOP), dissolved inorganic carbon (DIC), hydrogen sulfide (H_2S), sulfate (SO_4^{2-}), chloride (Cl^-), reduced iron (Fe^{2+}) and manganese (Mn^{2+}), methane (CH_4) and nitrous oxide (N_2O) concentration determination at the University of Georgia (UGA) laboratory. The pH was determined in 1 ml of unfiltered porewater from each chamber using a Sensorex® low volume flow-through pH electrode assembly. The pH sensor was calibrated using National Bureau of Standards pH 4 and 7 standards. Other sub-samples were stored in acid-washed, ultrapure deionized water rinsed, and combusted (500°C) glass vials. One ml of unfiltered porewater was injected into helium-purged, crimp-sealed 6-ml headspace vials and acidified with 0.1 ml of concentrated phosphoric acid (after removal from the glove bag) for analysis of DIC, CH_4, and N_2O. All other vials were sealed with Teflon®-lined screw caps.

An unfiltered water sample (0.1–0.5 ml) was pipetted into a vial containing 0.5 ml zinc acetate (20 weight %), as a preservative, for subsequent H_2S analysis. The remaining water from each chamber was filtered through a 0.2 μm Target® cellulose filter and further aliquotted. A sub-sample for NH_4^+ analysis (0.1–0.5 ml) was pipetted into a vial containing 0.2 ml phenol reagent (22 ml phenol, 198 ml ethanol, 8 ml deionized water) for preservation. Four ml of filtered water was placed in a 7-ml vial and preserved with 0.1 ml of concentrated nitric acid (after removal from the glove bag); this sample was stored at 4°C for subsequent analysis of DOC, PO_4^{3-}, DOP, Cl^-, SO_4^{2-}, Fe^{2+}, and Mn^{2+}. The remaining filtered porewater was stored at 4°C until analysis of NO_x and DON.

All samples were analyzed within 3 weeks of collection. Ammonium was analyzed colorimetrically via the phenol hypochlorite method (Solorzano 1969). Nitrate+nitrite was measured by vanadium reduction and nitric oxide detection on an Antek® model 745 Nitrate/Nitrite Reduction system inline with a chemiluminescent nitric oxide detector (Valderrama 1981; Garside 1982). Phosphate was analyzed colorimetrically using the molybdate blue method (Strickland and Parsons 1972). Dissolved organic carbon (DOC) was measured by high temperature combustion and infrared CO_2 detection on a Shimadzu® Total Organic Carbon (TOC) 5000 analyzer. Dissolved organic nitrogen (DON) was calculated as the difference between total dissolved nitrogen (TDN) and dissolved inorganic nitrogen (DIN = $NH_4^+ + NO_x$); TDN was measured by high temperature oxidation on a Shimadzu® TOC 5000 analyzer inline with an Antek® model 7050 chemiluminescent nitric oxide detector (Álvarez-Salgado and Miller 1998). Dissolved organic phosphorus (DOP) was calculated as the difference between total dissolved phosphorus (TDP) and dissolved inorganic phosphorus (DIP = PO_4^{3-}); TDP was measured colorimetrically as PO_4^{3-} after combustion and acid hydrolysis (Solorzano and Sharp 1980). Hydrogen sulfide (H_2S) was analyzed colorimetrically using the Cline method (Cline 1969). Sulfate (SO_4^{2-}) and chloride (Cl^-) were quantified using ion chromatography on a Dionex® system. Reduced iron (Fe^{2+}) and manganese (Mn^{2+}) were analyzed colorimetrically using the ferrozine and formaldoxime methods, respectively (Stookey 1970; Armstrong et al. 1979).

Dissolved inorganic carbon, CH_4, and N_2O concentrations were quantified by gas chromatography. Methane and DIC were measured on a Shimadzu® gas chromatograph fitted with an Alltech® Carbosphere™ column, a Shimadzu® methanizer, which converted DIC to CH_4, and a flame ionization detector; N_2O was measured on a Shimadzu® gas chromatograph fitted with a HayeSep® DB column and an electron capture detector. Concentrations of gases (DIC, CH_4 and N_2O) were determined by comparison of sample peak areas to the areas generated by certified gas standards from Scott Specialty Gases (a mix of 10% DIC and 10% CH_4 in a balance of ultrapure He and a mix of 500 ppm N_2O in a balance of ultrapure He).

The DIC produced by microbial respiration in soils, hereafter noted DIC_R, was calculated by

correcting porewater DIC concentrations for the DIC originating from the overlying seawater (Eq. 1):

$$DIC_R = [DIC]_{PW} - [DIC]_{OLW} \quad (1)$$

where $[DIC]_{PW}$ is the porewater DIC concentration and $[DIC]_{OLW}$ is the overlying water DIC concentration. Mangrove peat is organic rich (65–95% organic matter; Feller et al. 2003) and is comprised mainly of coarse and fine roots (~80%) plus leaves and wood (~20%) derived from mangrove trees. The carbonate content of surficial peat is insignificant (McKee and Faulkner 2000; Feller et al. 2003) and it is unlikely that carbonate dissolution contributed to the observed DIC_R values. Estimates of the calcium carbonate saturation index (SI), calculated for in situ pH and bicarbonate concentrations and assuming the calcium concentration of seawater (i.e., 10.53 mM), suggested that carbonate precipitation is unlikely (i.e., $SI \leq 1$; data not shown).

Net rates of SO_4^{2-} reduction were estimated from the observed depletion of SO_4^{2-} over the depth profile. Since the ratio of Cl^- to SO_4^{2-} in seawater does not vary (Pilson 1998), the expected concentration or inventory of SO_4^{2-} can be estimated from the measured concentration or inventory of Cl^-. Sulfate depletion was calculated using Eq. 2:

$$SO_{4\ dep}^{2-} = \left[Cl_M^- * R_{SW}^{-1}\right] - SO_{4\ M}^{2-} \quad (2)$$

where Cl^-_M and $SO_{4\ M}^{2-}$ are the measured concentrations of Cl^- and SO_4^{2-}, respectively, and R_{SW} is the molar ratio of Cl^- to SO_4^{2-} in surface seawater ($R_{SW} = 19.33$; Weston et al. 2006). Sulfate depletion reflects the net microbially mediated consumption of SO_4^{2-} (Weston et al. 2006). Inventories of DIC_R were compared to inventories of $SO_{4\ dep}^{2-}$ to estimate soil respiration coupled to SO_4^{2-} reduction, assuming a stoichiometry of 2 moles of DIC produced per mole of SO_4^{2-} reduced (Canfield et al. 1993a). Ratios of inorganic nutrient inventories to $SO_{4\ dep}^{2-}$ inventories were used to evaluate the magnitude of nutrient regeneration coupled to SO_4^{2-} reduction.

Porewater profiles from individual peepers equilibrated at the three different sites were averaged to account for between-site variability in porewater constituents at each sampling time. After averaging, total sediment inventories at four depth intervals (0–5, 5–10, 10–20, 20–40 cm) and over the entire depth range ('all', 0–40 cm) were calculated using a porosity-corrected trapezoidal integration of each porewater constituent. Porewater chemical inventories were then compared via a 2-tailed *t*-tests assuming unequal variance.

Data for the total carbon (C), nitrogen (N), and phosphorus (P) content of microbial mats, leaves (live and senescent), and roots from dwarf red mangrove trees were obtained from the literature or measured using a ThermoFinnigan FlashEA 1112 Elemental Analyzer (for C and N; Kristensen and Andersen 1987) or ashing/acid digestion (for P; Aspila et al. 1976). Samples were air-dried and ground using a mortar and pestle. For C and N analysis, both acidified (1 N HCl) and unacidified samples were analyzed on a ThermoFinnigan Flash EA 1112 Series NC analyzer to determine total C and N (unacidified = organic + inorganic) as well as organic (acidified = organic only). The carbonate content was calculated as the total C (unacidified sample C content) minus the organic C (acidified sample C content). Total P content was determined using an ashing-acid digestion method (adapted from Aspila et al. 1976). A known amount of sediment (ca. 15 mg) was ashed for 2 h at 550°C and then transferred into 50-ml plastic centrifuge tubes containing 25 ml of 2 M HCl. The sediment-acid mixture was then heated (95°C) in a water bath for 2 h. After cooling, an aliquot was then filtered (0.45 μm filter) and analyzed for phosphate using the molybdenum blue method (peat, mat, leaves; Strickland and Parsons 1972).

Results

Individual peepers from three different dwarf mangrove habitats on Twin Cays demonstrated substantial variability in constituent distribution over depth within each sampling period (Fig. 1). Microbial mats covered the soil surface to different extents at the three sites. For example, the site with the highest porewater concentration of DIC and depletion of SO_4^{2-} in the porewater at depth was an environment at the edge of an interior lagoon that was home to a more thicker microbial mat and a sparser distribution of dwarf mangroves than the other two sites, which contained thinner mats and higher densities of dwarf red mangroves.

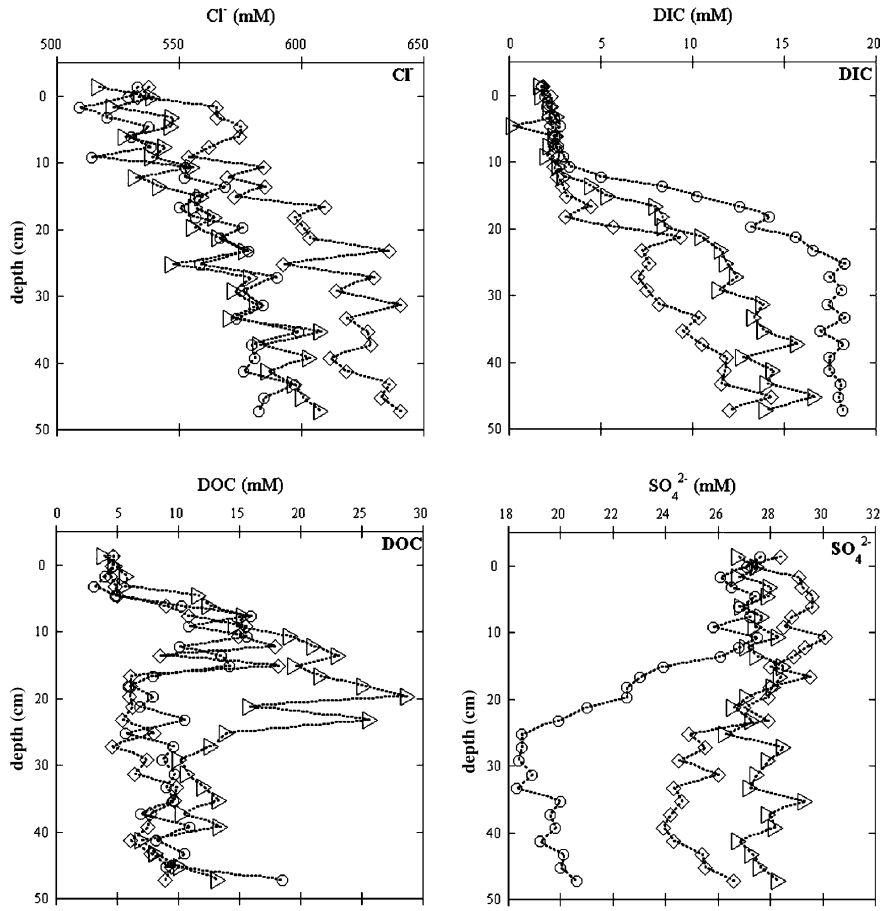

Fig. 1 Porewater steady-state profiles of Cl^-, DIC, DOC, and SO_4^{2-} from individual peepers in September. Three peepers were incubated in replicate dwarf mangrove zones on each sampling date. Symbols are consistent throughout the four panels and refer to peepers from Weather Station (○), Lair (◇) or Dock (▷) sites

During both wet (September) and dry (May) seasons, geochemical variability in the top 10 cm layer of soil was typically low (Fig. 2). The chlorinity below 13 cm depth in September and May was similar, being slightly elevated relative to surface seawater (surface seawater salinity was ~35‰ while the porewater salinity was 36.8‰) (Fig. 2). In contrast, the salinity in the upper 10 cm was higher in May ($p = 0.025$ for 5–10 cm and $p = 0.076$ for 0–10 cm; Fig. 2). Although pH was slightly more acidic in May than in September, soils were generally circumneutral, and pH tended to decrease with depth (Fig. 2). Sulfate concentrations decreased with depth in parallel to increased H_2S concentrations. Increases in reduced metabolite concentrations, including NH_4^+, Fe^{2+}, Mn^{2+}, and H_2S (~200, 10, 20, and 13 mM, respectively), with depth indicated reducing conditions, especially in September. Reduced manganese concentrations and inventories at depth were higher in September ($p = 0.035$) than in May. Orthophosphate, DIC, and CH_4 concentrations also increased with depth below the surface (Fig. 2). Dissolved organic carbon and DON concentrations increased with depth in September but comparably less in May ($p = 0.077$ for DOC and $p = 0.087$ for DON). Dissolved organic carbon inventories for all depths were significantly higher in September than in May ($p = 0.015$). Concentrations of NO_x were consistently low, but detectable, over the entire depth profile in both seasons.

Below the upper 10 cm layer of soil, concentrations of biologically produced trace gases were extremely high. Concentrations of N_2O (up to 375 nM) greatly exceeded the concentrations predicted from equilibrium with atmospheric N_2O (~6 nM). Similarly, porewater CH_4 concentrations (up to 80 μM) exceeded concentrations predicted from equilibrium with atmospheric CH_4 (~1.2 nM) (Fig. 2). Concentrations of N_2O and CH_4 did not exceed saturation values (3 mM for N_2O or 1.9 mM

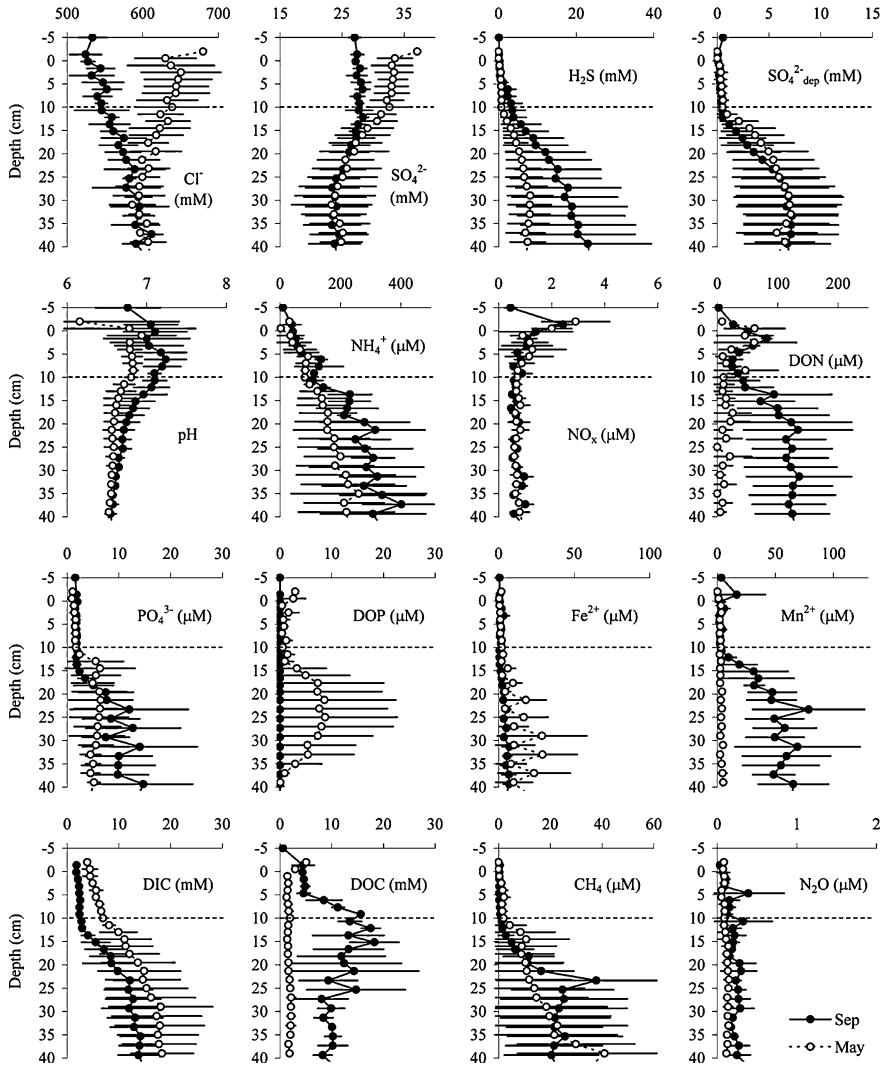

Fig. 2 Average steady-state porewater profiles of Cl^-, SO_4^{2-}, H_2S, $SO_{4\,dep}^{2-}$, pH, NH_4^+, NO_x, DON, PO_4^{3-}, DOP, Fe^{2+}, Mn^{2+}, DIC, DOC, CH_4 and N_2O from September (●) and May (○). CH_4 and N_2O are also expressed in units of % saturation relative to the atmosphere. Dotted lines indicate base of homogenous surface soil layer at 10 cm. Error bars = one standard deviation of the mean

for CH_4 calculated from solubility data presented in Weiss and Price (1980) and Yamamoto et al. (1976), respectively; data not shown) indicating that bubble formation and ebullition are not likely important mechanisms for trace gas release from these soils.

Total dissolved nitrogen was comprised primarily of NH_4^+ and secondarily of DON, but only concentrations of DON at depth were higher in September than in May ($p = 0.042$; Fig. 2). Though concentrations of TDP were comparable, differences in the proportions of PO_4^{3-} and DOP over depth were noted. We compared the observed porewater inorganic C:N:P molar ratios to the Redfield ratio (106:16:1; Redfield 1958) and to potential soil organic matter sources in dwarf mangrove zones, including microbial mats, green and senescent *R. mangle* leaves, and fine and coarse roots of *R. mangle* (Table 1). Porewater DIN:DIP ratios were similar between seasons (Figs. 2, 4, Table 1), and consistently indicated P limitation with respect to the Redfield ratio. DIC_R:DIN molar ratios were greater in May than in September (31:1 and 59:1 in surface and deep May samples versus 6:1 and 37:1 in surface and deep September samples; $p = 0.022$ for surface samples and $p = 0.036$ for deep samples; Table 1). The DIC_R:DIP ratios followed a similar pattern with higher values in May than in September ($p = 0.100$) and consistent increases in the ratio with depth (Table 1).

Dissolved organic C, N, and P contributed significantly to the porewater C–N–P pools (Figs. 2–4). Similar to the DIN:DIP ratios, the TDN:TDP ratios

Table 1 Porewater inorganic C:N:P ratios and C:N:P content and ratios of major organic matter (OM) sources in Twin Cays dwarf red mangrove habitats

	n	C% (se)	N% (se)	P% (se)	C:N:P (molar)
Porewater					
May					
Porewater, 0–10	3				3693:47:1
Porewater, 20–40	3				2979:36:1
September					
Porewater, 0–10	3				1293:45:1
Porewater, 20–40	3				1198:29:1
OM sources					
Microbial mat	20	29.5 (1.2)	2.9 (0.5)	0.094 (0.017)	809:68:1
Green leaf[ab]	3	48.6 (4.1)	1.13 (0.02)	0.038 (0.001)	3298:66:1
Senescent leaf[b]	9	46.2 (2.8)	0.49 (0.05)	0.007 (0.000)	15568:141:1
Fine root	10	41.8 (0.5)	0.75 (0.04)	__ (__)	65:1:__
Coarse root	10	38.1 (0.3)	0.43 (0.02)	__ (__)	103:1:__

[a] Smallwood et al. (2003); [b] Feller et al. (2003)

indicated P limitation relative to the Redfield ratio (Fig. 3). The DOC:DON:DOP molar ratios demonstrated little variability over season or depth (average ratio = 3033:26:1). DOC:DON ratios were insignificantly higher in September than May (Fig. 3).

Porewater constituent inventories integrated over various depths (0–5, 5–10, 10–20, and 20–40 cm) as well as over all depths (0–40 cm) were compared to examine seasonal variability (Figs. 3, 4). Although Cl^-, SO_4^{2-}, H_2S, DIC, NH_4^+, PO_4^{3-}, and DOP exhibited differences at specific depths, inventories over all depths were not significantly different between seasons. Only DOC, DON, and Mn^{2+} inventories over all depths differed significantly by season, ranging from 5–10 times higher over all depths in September than in May ($p = 0.015$, 0.067 and 0.035, respectively; Fig. 3). Inventories of $SO_4^{2-}{}_{dep}$ and CH_4 were not significantly different between September and May (Fig. 3).

Molar ratios of H_2S, DIC_R, NH_4^+, and PO_4^{3-} to $SO_4^{2-}{}_{dep}$ were comparable in May and September over all depths and at deep depths (10–40 cm; Fig. 5). In May, H_2S and $SO_4^{2-}{}_{dep}$ inventories were not significantly different, suggesting that H_2S accumulated in direct proportion to the SO_4^{2-} consumed by sulfate reduction. In September, H_2S accumulations significantly exceeded ($p = 0.04$) the expected inventories due to SO_4^{2-} depletion. Assuming a reaction stoichiometry of 2 moles of CO_2 produced per mole of SO_4^{2-} reduced, DIC_R ratios indicated that SO_4^{2-} reduction dominated organic carbon mineralization. Oxidation of Redfield ratio organic matter coupled to SO_4^{2-} reduction would yield ratios of 0.3 NH_4^+:$SO_4^{2-}{}_{dep}$ and 0.019 PO_4^{3-}:$SO_4^{2-}{}_{dep}$, respectively, but such ratios were rarely achieved in the porewater. If SO_4^{2-} reduction was coupled solely to remineralization of senescent *R. mangle* leaf organic matter, 0.018 mol NH_4^+ and 0.00013 mol PO_4^{3-} would be produced per mol of SO_4^{2-} reduced.

Discussion

Hydrologic forcing

The lack of strong geochemical gradients observed in the upper 10 cm of soils can be attributed to porewater flushing by physical and biological processes, such as precipitation, tidal drainage, or root activities (Alongi et al. 1999, 2004). Wet–dry seasonality significantly affects water levels and salinities in tropical mangrove soils (Alongi et al. 2004). Variation in precipitation and tidal height may drive significant exchange of pore fluids in mangrove soils (Ridd and Sam 1996; Ridd et al. 1997; Sam and Ridd 1998). However, in most systems, hydrological forcing functions are poorly constrained (Lee 1995; Twilley and Chen 1998). Porewater advection through mangrove soils, caused by changes in hydraulic head, varies daily and seasonally as a function of tidal height (Ridd et al. 1997). Tides often alleviate mangrove soil saturation deficits, and the lower frequency of tidal inundation can make higher

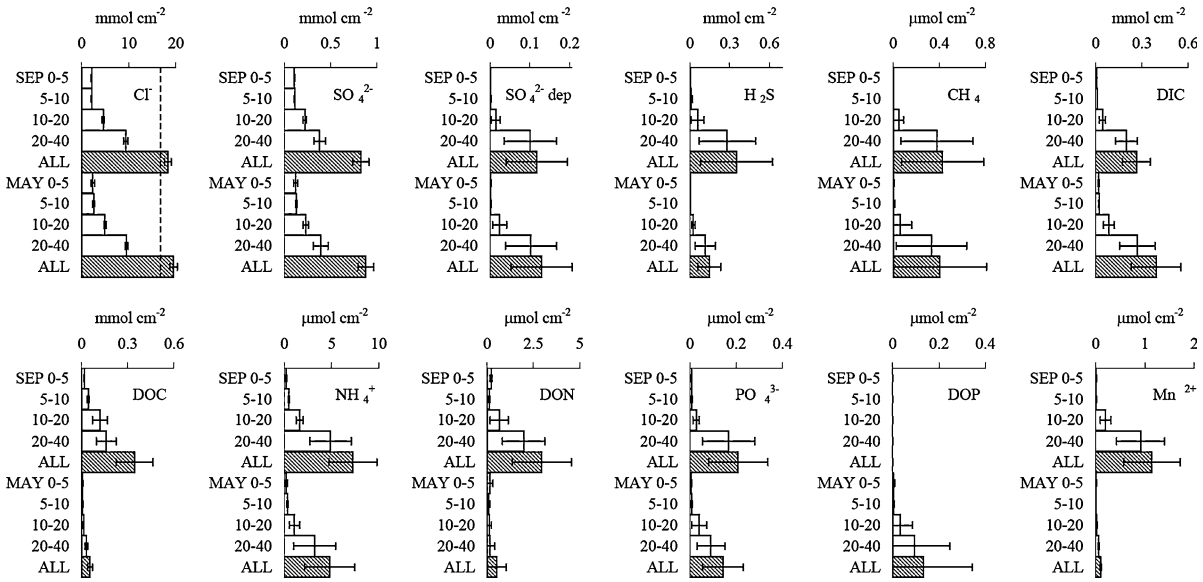

Fig. 3 Porewater inventories of Cl^-, SO_4^{2-}, $SO_{4\ dep}^{2-}$, H_2S, CH_4, DIC, DOC, NH_4^+, DON, DIP, DOP and Mn^{2+} over 0–5, 5–10, 10–20, 20–40 cm and 'ALL' (0–40 cm) depths in September and May. Dotted line indicates background Cl^- inventory of seawater over 'ALL' (0–40 cm) depths. Error bars = one standard deviation of the mean

elevation soils more sensitive to changes in precipitation (Twilley and Chen 1998). In Rookery Bay (FL, USA), for example, the cumulative tidally driven water inputs and effluxes were of similar magnitude, around 12,000 mm $year^{-1}$ (Twilley and Chen 1998), suggesting that tidal fluctuations efficiently flushed the peat soils.

Daily and seasonal variations in both precipitation and tidal height at Twin Cays (Lee and Joye 2006) likely resulted in negligible gradients in porewater constituent concentrations in the 10-cm upper soil stratum (Fig. 2). Although the average tidal range at Twin Cays is ~20 cm (Rützler and Feller 1996), substantial variation in tidal forcing occurs between seasons. During spring and early summer, tidal elevations below mean sea level at all tidal stages are common and precipitation is low, leading to extremely dry conditions in dwarf mangrove zones (Lee and Joye 2006). During the dry season, low precipitation and high evaporation rates increased shallow porewater salinity and lower tidal heights increased soil exposure to the atmosphere. Dry season soils were thus more oxidized and contained lower concentrations of reduced species such as H_2S and NH_4^+ (Fig. 2).

The spring-early summer hydrological regime contrasted markedly with that of the fall-winter. During the wet fall-winter season, dwarf mangrove stands were inundated continuously because of higher tidal heights. Increased precipitation decreased shallow porewater salinity and may have stimulated pond water infiltration through the soils. Wet season soils were characterized by higher inventories of dissolved organic matter (DOM) and elevated rates of anaerobic microbial metabolism (see below). Differences in hydrology thus appear to be important drivers of porewater geochemical signatures of soils at Twin Cays in the dwarf mangrove zone.

Biogeochemistry: organic matter

Dissolved organic matter (DOM) in the soil porewater is derived mainly from the decay of mangrove litter and roots (Alongi et al. 2005). Soils from dwarf mangrove zones in this study exhibited high DOC:-DON and DOC:DOP ratios. During decomposition, soluble, reactive litter leachates (e.g., sugars, carbohydrates, and amino acids) are quickly consumed by microorganisms (Benner et al. 1986), while refractory litter components, e.g., lignins, decay an order of magnitude more slowly (Robertson 1998). Soluble phenolic tannins represent a significant fraction of *R. mangle* litter leachate and can inhibit microbial

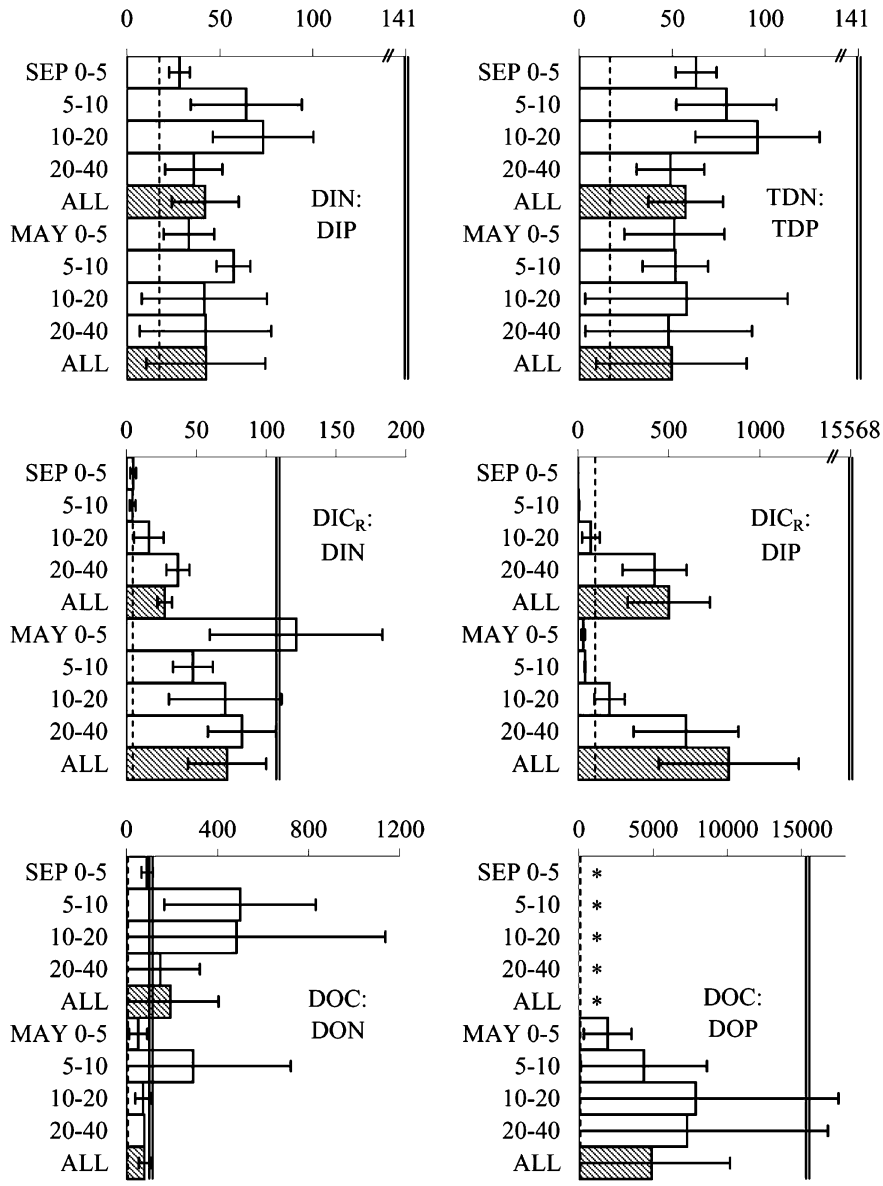

Fig. 4 Molar ratios of porewater DIN:DIP, TDN:TDP, DIC_R:DIN, DIC_R:DIP, DOC:DON and DOC:DOP over 0–5, 5–10, 10–20, 20–40 cm and 'ALL' (0–40 cm) depths in September and May. Dotted lines indicate Redfield C:N:P ratios of 106:16:1; double solid lines indicate senescent *R. mangle* leaf C:N:P ratios (Table 1). * = DOP below detection; error bars = one standard deviation of the mean

degradation of DOM if present at high concentrations (g l^{-1}; Benner et al. 1986). Mineralization and/or leakage of labile DOM from productive (carbon and nitrogen fixing) cyanobacteria-dominated microbial mats (Joye and Lee 2004; Lee and Joye 2006) may have also contributed to the observed sediment–water interface peaks in DON (Fig. 2; Joye et al. in preparation). Autochthonous microbial mat N-inputs via nitrogen fixation may have also contributed to the high DIN:DIP ratios observed in both seasons (Fig. 2, Table 1; Lee and Joye 2006).

DON and DOC concentrations exhibited no gradient with depth in May, but in September concentrations increased 10- and 5-fold, respectively, at depth. Litter fall from Twin Cays dwarf mangroves is twice as high in the fall as in spring (Koltes et al. 1998). We hypothesize that increased litterfall, combined with increased inundation during the wet season, resulted in greater DOC and DON inputs to the soils by leaching of mangrove and microbial mat derived DOM and microbial and/or invertebrate breakdown of mangrove leaves and detritus to

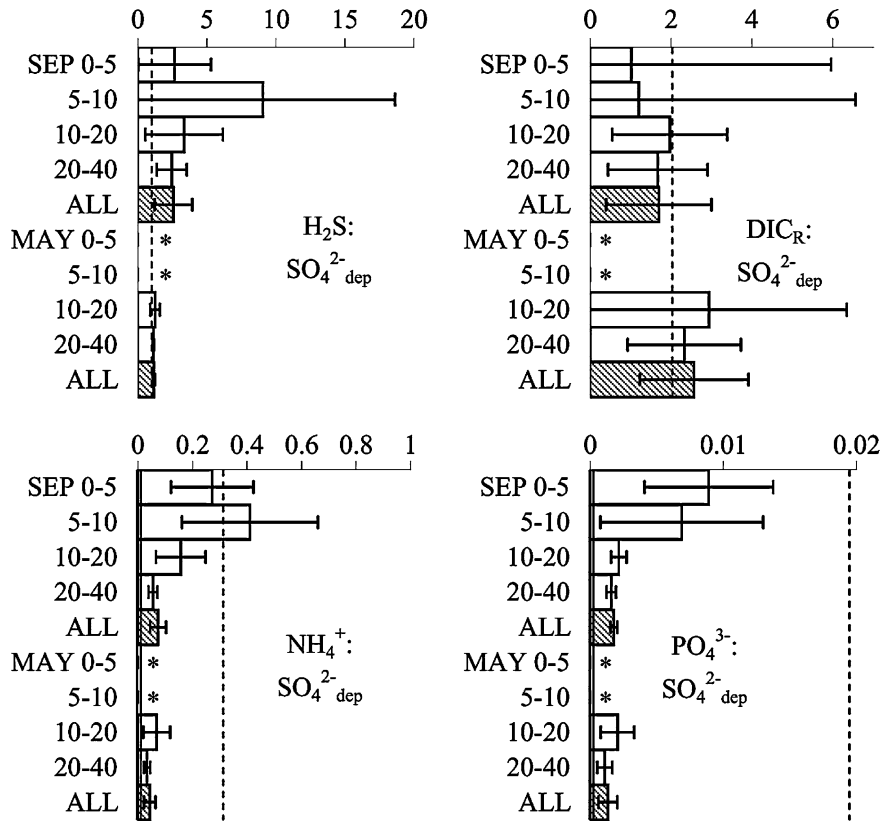

Fig. 5 Molar ratios of porewater H_2S, DIC_R, NH_4^+ and PO_4^{3-} to $SO_{4\,dep}^{2-}$ over 0–5, 5–10, 10–20, 20–40 cm and 'ALL' (0–40 cm) depths in September and May. Dotted lines indicate stoichiometric ratios of SO_4^{2-} reduction coupled to oxidation of Redfield organic matter; double solid lines indicate N:P:SO_4^{2-} reduction ratios of 0.018:0.00013:1 when coupled to oxidation of senescent *R. mangle* leaves (see text for details). * = no $SO_{4\,dep}^{2-}$; error bars = one standard deviation of the mean

DOM (Figs. 2, 3). We cannot rule out, however, the possibility that seasonal variation in root-derived organic leachates also contributed to this pattern.

Biogeochemistry: microbially mediated redox processes

Twin Cays soils were anoxic below the surface 1–2 cm (Joye and Lee 2004); therefore anaerobic metabolic processes, including denitrification, iron and manganese reduction, sulfate reduction, and methanogenesis, dominated organic carbon turnover in the 40 cm depth profile examined. High denitrification rates in mangrove soils can be fueled by in situ (e.g., nitrification) or external (e.g., tidal) inputs of NO_x (Alongi et al. 1999). Offshore oceanic waters are usually characterized by low NO_x concentrations. However, dense communities of sponges live on the submerged roots of fringing mangrove trees and are host to a variety of microbial symbionts, including nitrogen fixing and nitrifying bacteria (Diaz and Ward 1997; Corredor et al. 1988; Diaz et al. 2004; Rützler et al. 2000, 2004). These porous sponges may be hot spots of N cycling on coral reefs and in mangrove habitats, but linkages between the sponge-supported microbial N cycling and the surrounding ecosystem are poorly understood. Sponges are an important N source to associated algae on coral reefs (Davy et al. 2002), and in mangrove environments, incoming tidal waters may transfer prop root-sponge-derived NO_x to fringing mangrove trees and/or to the microorganisms inhabiting mangrove soils (Rützler et al. 2000, 2004).

Previously reported rates of denitrification in Twin Cays soils show the highest in situ denitrification rates occurred in the fringing mangrove zone, with the lowest rates observed in dwarf mangrove soils (Lee and Joye 2006). However, potential denitrification rates (i.e., with NO_3^- added) were high in both zones, indicating that most surficial mangrove soils possess a high potential for denitrification when NO_x is available (Lee and Joye 2006). Rates of potential denitrification in deeper (<40 cm) soils from dwarf or fringe habitats were much lower than rates observed in surficial layers, but rates were still measurable ($\sim$1 nmol N $cm^{-3}\,h^{-1}$ or $\sim$1 μM h^{-1}; Porubsky

and Joye, unpublished data). Clearly, dissimilatory sinks for NO_x exist in these soils.

The concentrations of N_2O observed in these mangrove soils (Fig. 2) were 2 to 65 times greater than the concentrations expected if the soil pore fluids were in equilibrium with atmospheric N_2O concentration (i.e., about 6 nM). N_2O can be produced during both nitrification and denitrification; it is unclear whether N_2O is produced during dissimilatory nitrate reduction to ammonium or anammox (Joye and Anderson 2008). Previous studies of N_2O dynamics in mangrove habitats observed strong correlations between N_2O fluxes and DIN (mainly NH_4^+) concentration and attributed N_2O production to nitrification (Corredor et al. 1999; Bauza et al. 2002). However, the high sulfide concentrations present in these soils (0.5–20 mM, Fig. 2) probably inhibit nitrification (Joye and Hollibaugh 1995). Hydrogen sulfide may also block the terminal enzymatic step of denitrification, i.e., the reduction of N_2O to N_2 (Sørensen et al. 1978; Joye 2002), resulting in incomplete denitrification where NO_x is reduced only to N_2O rather than N_2 (Brundet and Garcia-Gil 1996). It is tempting to speculate that H_2S short-circuited denitrification, thus generating the extremely supersaturated N_2O concentrations observed in these mangrove soils. However, N_2O concentrations were elevated in surface sediments as well as in deeper sulfidic sediments, suggesting that multiple processes, including nitrification and denitrification, were involved in N_2O production. Understanding the processes regulating N_2O dynamics in these habitats requires further study, but given the extremely high porewater N_2O concentrations, we conclude that these soils likely support a significant flux of N_2O to the atmosphere, as observed in other mangrove soils (Corredor et al. 1999, Alongi et al. 2005).

On mangrove islands, soil iron and manganese oxide concentrations depend on allochthonous inputs, i.e., from the ocean (in seawater delivery), land (in terrestrial runoff), or atmosphere (in volcanic or dust inputs). Concentrations of iron and manganese in seawater are extremely low; therefore, it is unlikely that seawater infiltration provides a substantial iron and manganese source to such islands. Terrestrial runoff is a temporally limited input that reaches Twin Cays only following anomalous weather events, such as hurricanes or tropical storms. For example, in October 1998, the flood waters from Hurricane Mitch carried dissolved nutrients and particulates more than 40 km offshore from Belize (Muller-Karger et al. 2005). Periodic delivery of nutrient and particle-laden runoff waters to mangrove islands could serve as an important source of bioactive materials to these habitats. Finally, atmospheric inputs of Saharan dust are known to be an important source of metals to offshore islands in the Atlantic and Caribbean (Muhs et al. 1990; Hayes et al. 2001). Despite abundant iron and manganese oxides in some mangrove soils, rates of iron and manganese reduction to Fe^{2+} and Mn^{2+}, respectively, are often low (Alongi et al. 1999, 2005), and the reasons for this are not clear (Alongi et al. 1999).

Twin Cays soil porewaters contained substantial concentrations of dissolved, reduced Fe^{2+} (<10 μM) and Mn^{2+} (<50 μM), suggesting active cycling of metal oxides (Fig. 2). Comparable Fe^{2+} and Mn^{2+} concentrations (i.e., 9–53 μM and 6–69 μM, respectively) occur in Thailand mangrove soils with substantial rates of both iron and manganese reduction (about 1.5 mmol m^{-2} day^{-1}; Alongi et al. 2001). Twin Cays peat soils contained substantial concentrations of total iron and manganese (7–100 μmol Fe and 1–5 μmol Mn (g dry weight)$^{-1}$, respectively) (K.L. McKee, unpublished data). Terrestrial mangrove environments contain similar concentrations of total iron (~81 μmol Fe (g dry weight)$^{-1}$), but greater concentrations of total manganese (36 μmol Mn (g dry weight)$^{-1}$; Alongi et al. 2005). Despite the lower abundance of manganese oxides in Twin Cays soils, high concentrations of dissolved Mn^{2+} in the porewater suggest that the available manganese oxides present are reactive, while the change in dissolved Mn^{2+} concentrations over time suggests that the factors driving metal reduction vary seasonally (Figs. 2, 3). The higher dissolved Mn^{2+} concentrations observed in the wet season suggest more active manganese cycling during this time by either direct biological manganese oxide reduction (Burdige 1993) or by reductive dissolution of manganese oxides associated with the anaerobic oxidation of H_2S (Canfield et al. 1993b). In contrast, during the dry season, more oxidized soil conditions may have retained Mn^{2+} on the solid phase metal oxides (Canfield et al. 1993b).

Although Fe and Mn reduction typically account for only a small fraction of total organic carbon

mineralization in mangrove soils, metal reduction is consistently observed (Alongi et al. 1999). Coarse and fine roots comprise a large part (up to 80%) of Belizean and other mangrove peats (McKee and Faulkner 2000) and iron and manganese cycling may be stimulated by the presence and activity of mangrove roots (Alongi et al. 1999, 2001, 2005). The production of dissolved Fe^{2+} and Mn^{2+} has been correlated strongly with the density of live roots, leading Alongi et al. (1999, 2001, 2005) to speculate that root organic exudates stimulated metal reduction. The importance of plant roots in metal cycling has also been documented in salt marsh environments (Lacerda et al. 1993), where metal oxides precipitate as plaques on roots (Sundby et al. 1998). While rates of anaerobic microbial metabolism sometimes correlate positively with root density, rates do not correlate with soil organic carbon content (Alongi et al. 2001), suggesting that live roots enhance microbial metal cycling by providing dissolved organic carbon substrate(s). However, given the placement of peepers $\sim$1.5m from mangrove trees, it is not clear whether live root carbon excretion contributed to the observed patterns of metabolism.

Seasonality also appeared to influence metal cycling in Twin Cays soils: Mn^{2+} concentrations were substantially higher during the wet season than during the dry season (Figs. 2, 3). In Thailand mangrove soils, rates of anaerobic microbial terminal metabolism, including sulfate, iron and manganese reduction, were 2 to 4 times higher during the wet season than during the dry season (Alongi et al. 2001). At Twin Cays, dwarf mangrove litterfall is highest in the fall (Koltes et al. 1998), and during this season we documented significantly higher porewater DOC concentrations. While increased litterfall and subsequent degradation of detritus may have contributed to increases in labile DOC and stimulated higher rates of metal reduction, especially manganese reduction, as well as other anaerobic processes, it is also possible that the increased DOC concentrations were a by-product of metabolism and breakdown of organic matter derived from the abundant microbial mats present in the dwarf zone. Additional work is necessary to determine the contributing source(s).

The dominant pathway for organic matter oxidation in Twin Cays soils appeared to be SO_4^{2-} reduction, as reported for other coastal marine environments (Kristensen et al. 1991, 1995; Canfield et al. 1993a; Alongi et al. 1999). Sulfate depletion profiles indicated fairly similar SO_4^{2-} reduction rates in the wet and dry seasons ($\sim$120 and 130 μmol cm^{-2} of SO_4^{2-} depletion, respectively; Figs. 2, 5). During the wet season, however, H_2S inventories (352 μmol cm^{-2}; Fig. 3) exceeded net SO_4^{2-} reduction, as estimated from $SO_{4\ dep}^{2-}$ (120 μmol cm^{-2}; Figs. 4, 5), suggesting an additional H_2S source. Green *R. mangle* leaves consist of 0.31% sulfur by weight, while senescent leaves consist of 0.67% sulfur by weight (Fry and Smith 2002). The decomposition of sulfur rich mangrove detritus may offer a biogenic source of sulfur, such as amino acids or fulvic and humic acids, whose mineralization could contribute to porewater H_2S pools. Organic sulfur is a significant component of the sulfur pool in other mangrove soils and sediments (Altschuler et al. 1983; Holmer et al. 1994), where the mineralization of mangrove-derived organic sulfur compounds was postulated to lead to H_2S accumulation.

Since root exudation of labile organic carbon stimulates SO_4^{2-} reduction and metal reduction in mangrove soils (Alongi et al. 2001, 2005; Kristensen and Alongi 2006), we examined the relationship between sulfate reduction rates estimated from SO_4^{2-} depletion ($SO_{4\ dep}^{2-}$) and DOC concentrations, but found no correlation (data not shown). Weston et al. (2006) also found no correlation between $SO_{4\ dep}^{2-}$–derived SO_4^{2-} reduction rates and porewater DOC concentrations in temperate intertidal sediments from Georgia and South Carolina and concluded that the bulk DOC pool consisted of largely refractory organic matter. The refractory nature of the DOC pool could result in carbon limitation of the sediment microbial community (Weston et al. 2006; Weston and Joye 2005) and suggests that labile organic carbon inputs are consumed rapidly and efficiently by the resident microbial community (Weston and Joye 2005).

Integrated rates of SO_4^{2-} reduction, estimated from $SO_{4\ dep}^{2-}$ and confirmed using $^{35}SO_4^{2-}$ radiotracer experiments (Weston et al. 2006), in temperate sediments (10–400 μmol cm^{-2}) were comparable to our estimates for Twin Cays mangrove soils ($\sim$100 μmol cm^{-2}; Fig. 5). At the sites studied by Weston et al. (2006), porewater SO_4^{2-} concentrations were depleted completely well above 40 cm. However, SO_4^{2-} concentrations at Twin Cays never reached zero (Fig. 2). Thus, the estimates of

integrated SO_4^{2-} reduction rates obtained from our peeper deployments likely underestimates the total activity of SO_4^{2-} reduction in the sediment column. In fact, substantial microbial activity may persist to the depths where live roots cease to exist (1–2 m deep; Alongi et al. 2005).

Methane inventories (0.45 μmol cm^{-2}) were small relative to SO_4^{2-} depletion inventories (100 μmol cm^{-2}; Fig. 3), suggesting that methanogensis was not a dominant pathway for organic matter oxidation in Twin Cays soils. However, CH_4 concentrations were high (up to 80 μM) during both seasons, suggesting that methanogenesis rates were significant and consistent over time. Methane is not commonly detected in the porewater from mangrove soils (Alongi et al. 1999, 2001, 2004), either because methanogenesis does not occur or because CH_4 does not accumulate due to efficient consumption by aerobic and/or anaerobic oxidation (Giani et al. 1996). A few studies have reported CH_4 efflux from mangrove soils (Harris et al. 1988; Barber et al. 1988; Sotomayor et al. 1994; Lu et al. 1999; Alongi et al. 2005), but the fluxes were typically below 100 μmol m^{-2} day^{-1}. These rates are extremely low compared to the fluxes observed from a sewage impacted site in Puerto Rico (up to 5 mmol m^{-2} day^{-1}; Sotomayor et al. 1994).

One of the most intriguing aspects of porewater CH_4 biogeochemistry at Twin Cays was accumulation of CH_4 in the presence of SO_4^{2-} (Fig. 2). Methanogenesis and SO_4^{2-} reduction do not typically occur contemporaneously because SO_4^{2-} reduction is more energetically favorable than methanogenesis (Capone and Kiene 1988). Furthermore, sulfate-dependent anaerobic oxidation of CH_4 occurs in SO_4^{2-} containing environments (Valentine and Reeburgh 2000), so CH_4 would not be expected to accumulate in SO_4^{2-} rich soil layers. Methanogens and SO_4^{2-} reducers compete for some substrates, such as acetate or hydrogen, and methanogens are typically outcompeted by SO_4^{2-} reducing bacteria. However, simultaneous activity of these microbial functional groups can occur in SO_4^{2-} rich sediments if methanogens use noncompetitive substrates such as methylated amines or if competitive substrates are abundant, thereby relieving competition (Oremland and Polcin 1982). Noncompetitive substrates, including methanol, trimethylamines and dimethylsulfide, can fuel methanogenesis in SO_4^{2-} containing mangrove sediments (Mohanraju et al. 1997; Lyimo et al. 2000; Purvaja and Ramesh 2001). These substrates are produced through a variety of pathways: methanol by anaerobic bacterial metabolism; methylated amines from the decomposition of organic osmolytes, e.g., choline or glycine betaine; and dimethylsulfide by the catabolism of dimethylsulfoniopropionate or amino acids (Lyimo et al. 2002). The distribution of methanogenic microorganisms and patterns of methanogenesis in these and other dwarf mangrove soils are worthy subjects for future investigations as such soils may prove to be an important source of atmospheric CH_4.

Nutrients released from the organic matter remineralization, including NH_4^+, PO_4^{3-}, DON, and DOP, increased with depth and were present at slightly greater concentrations during the wet season than in the dry season (Figs. 2, 5). Soils were more reducing during the wet season, as has been documented in other mangrove soils (Alongi et al. 2004). Orthophosphate and DOP concentrations were low but similar to concentrations of dissolved P in a variety of other mangrove soils, while dissolved N concentrations were high compared to other mangrove soils (Alongi et al. 1992; Middelburg et al. 1996; Sherman et al. 1998). The greater N inventories here may be the result of high rates of nitrogen fixation observed in soils from Twin Cays dwarf mangrove habitats (Lee and Joye 2006). Porewater DIN:DIP and TDN:TDP ratios were higher than the Redfield ratio (Table 1 and Fig. 4) but were lower than expected from mineralization of mangrove leaf litter only. The DIC_R:DIN and DIC_R:DIP ratios were higher in May than in September (Fig. 4). Inorganic and organic nutrient concentration data and ratios suggest that nutrients, particularly P, are efficiently immobilized by soil microbial communities and that different organic matter sources fuel soil microbial activity during different times of year.

The same peeper designs and analytical methods used in this study were used to evaluate porewater stoichiometry in estuarine creek bank sediments from Georgia and South Carolina (Weston et al. 2006), which allows direct comparisons of these data sets. Sulfate was present throughout the soil profile in this study, while it was consumed completely at shallow depths ($\sim$15 cm in summer) in estuarine sediments from Sapelo Island (coastal Georgia) and the Okatee estuary (South Carolina). In the temperate estuarine

sediments, H_2S concentrations were generally related to SO_4^{2-} reduction rates, but reoxidation and/or pyritization depleted H_2S inventories to some extent (Weston et al. 2006). Dissolved Fe^{2+} concentrations were an order of magnitude lower in Twin Cays soils than in temperate estuarine sediments, indicating that H_2S was inefficiently sequestered into the solid phase (as FeS or FeS_2). Therefore H_2S inventories either equaled (May) or exceeded (September) SO_4^{2-} depletion inventories, with excess H_2S in pore fluids is potentially resulting from the diagenesis of sulfur-rich mangrove organic matter. Methane inventories in mangrove soils were similar to those observed in saline estuarine sediments. Dissolved organic carbon inventories from temperate estuarine and Twin Cays sites were similar, and DOC pools at both sites appeared to be recalcitrant. Denitrification played a minor role in organic matter oxidation in both mangrove soils and estuarine sediments and was limited by low NO_x concentrations. Georgia salt marsh sediments also contained lower H_2S inventories than Twin Cays peat (Koretsky et al. 2003; Weston et al. 2006) while Fe^{2+} inventories in temperate estuarine sediments were much greater, suggesting a more significant role of iron reduction in the temperate marsh sediments than in Twin Cays soils.

Importance of dwarf mangrove environment

Dwarf forests are often targeted for conversion to other uses such as aquaculture (Primavera 1998; Murray et al. 2003) based on the assumption that they are unproductive, and thus, unimportant. However, the microbial mats that inhabit dwarf mangrove zones on Twin Cays and other similar mangrove islands exhibit high rates of carbon and nitrogen fixation (Joye and Lee 2004; Lee and Joye 2006). These mats contribute significantly to C and N cycling at local and ecosystem scales (Lee et al. in preparation), and mat-derived labile organic matter supports fish and crustacean production (McIvor et al. 2006).

As documented here, soils in dwarf mangrove habitats serve as chemical factories by recycling organic carbon and nutrients. Although available data are limited, soils from various mangrove forest types appear to have significantly different porewater biogeochemical signatures. On Twin Cays, Belize, soils from dwarf mangrove forests had significantly ($p \leq 0.05$) higher concentrations of H_2S, NH_4^+, DOC, DON, PO_4^{3-}, and Fe^{2+} than did soils from nearby fringing mangrove forests (Lee and Joye 2006). Concentrations of metabolites, such as NO_3^- and NH_4^+, in soils from dwarf mangrove forests in Belize (Lee and Joye 2006) exceeded those observed in soils from tropical (Alongi et al. 2000) or temperate (Clarke 1985) coastal fringing mangrove forests. Thus, the unique biogeochemical signatures present in soils from dwarf mangrove zones may make them important sources of nutrients and organic matter to adjacent, hydrologically linked ecosystems.

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