Methanotrophy controls groundwater methane export from a barrier island

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Abstract

Methane concentrations can be high in coastal groundwater, resulting in methane export driven by submarine groundwater discharge. However, the magnitude of this methane flux depends significantly on the rate of methanotrophy, the often overlooked process of microbial methane consumption that occurs within coastal aquifer sediments. Here we describe a zone of methanogenesis within the freshwater lens of a barrier island aquifer and investigate the methane source/sink behavior of the barrier island system as a whole. The median concentration of methane dissolved in fresh groundwater beneath the center of the island was 0.6 mM, supported by high rates of potential methanogenesis (22 mmol m⁻² day⁻¹). However, rates of microbial methane consumption were also elevated in surrounding sediments (18 mmol m⁻² day⁻¹). Groundwater flowing from the zone of methanogenesis to the point of discharge into the ocean had a long residence time within methanotrophic sediments (~195 days) such that the majority of the methane produced within the barrier island aquifer was likely consumed there.

1. Introduction

Methane (CH₄) accounts for 17% of the total radiative forcing of Earth's atmosphere, making it the third most important greenhouse gas behind water vapor and carbon dioxide (Myhre et al., 2013). Since the industrial revolution, the atmospheric concentration of CH₄ has risen by 150% to 1.8 ppm. This increase was driven by human activities such as agriculture, energy production, and waste management (Ciais et al., 2013). Methane is consumed in the atmosphere by chemical reaction with hydroxyl radicals (Myhre et al., 2013) and in marine and terrestrial waters, sediments, and soils by

41 microbial methanotrophy. Thus, CH₄ plays a critical role in the global heat budget and is
42 active in atmospheric chemistry. Understanding the atmospheric, terrestrial, aquatic, and
43 marine sources and sinks of CH₄ is therefore highly relevant in the context of climate
44 change.

45 Globally, the dominant CH₄ production mechanism is methanogenesis mediated
46 by members of the archaea. In the terrestrial realm, these microorganisms are active
47 primarily in anoxic, aquatic habitats (Cicerone and Oremland, 1988). Therefore, the most
48 important sites of CH₄ production are organic rich soils saturated with fresh water (e.g.
49 marshes, rice paddies, landfills) (Ciais et al., 2013). Coastal environments are often
50 overlooked as sites of methanogenesis because of the high sulfate content of seawater.
51 Under these conditions, sulfate reducing bacteria are expected to outcompete
52 methanogenic archaea for organic carbon substrates since sulfate reduction is a more
53 energetically favorable process. However, the coastal zone contributes substantially to the
54 total marine CH₄ flux to the atmosphere (Bange, 2006), and the groundwater flowing
55 through soils and sediments is a dominant source of CH₄ to the coastal ocean (Bugna et
56 al., 1996; Grunwald et al., 2009).

57 These interstitial fluids are enriched with dissolved CH₄ derived from
58 methanogenesis in aquifers containing freshwater and sufficient organic carbon substrate
59 (Bugna et al., 1996). Aquifers matching this description are not limited to inland
60 environments. Coastal uplands develop a lens of fresh groundwater floating above a layer
61 of denser, saline groundwater (Collins and Easley, 1999), thereby creating a zone with
62 the potential for CH₄ production. Barrier islands are globally important coastal landforms,
63 occupying 15,100 km (6.5%) of open ocean shorelines (Stutz and Pilkey, 2001) and an

64 additional 7,410 km of lower energy coastal environments (Pilkey et al., 2009).

65 Therefore, barrier island methanogenesis could make important contributions to coastal
66 CH₄ budgets.

67 Methane in coastal surface waters is often associated with submarine groundwater
68 discharge (SGD) and has been used as a tracer for SGD in numerous studies (Cable et al.,
69 1996; Kim and Hwang, 2002). However, before reaching the ocean, groundwater
70 traverses multiple zones of intense biogeochemical cycling within coastal aquifers. These
71 zones, where freshwater mixes with seawater and where rapid porewater advection is
72 driven by wave and tidal action, are referred to as the subterranean estuary (Moore,
73 1999). Brackish groundwater contains high concentrations of sulfate, and infiltrating
74 seawater carries oxygen into coastal aquifers. Therefore, the subterranean estuary has the
75 potential to host active CH₄ oxidation by both anaerobic and aerobic methanotrophic
76 microorganisms. The balance between CH₄ production, transport, and consumption rates
77 within the subterranean estuary will control the flux of CH₄ to the adjacent coastal ocean.

78 In this work, we tested the hypotheses that: 1) barrier island aquifers support
79 zones of microbial CH₄ production, 2) a fraction of this CH₄ is exported to the
80 atmosphere or ocean, and 3) the dominant fate for CH₄ is microbial consumption within
81 the barrier island system. The ratio of CH₄ export from the barrier island aquifer to total
82 CH₄ production within the aquifer is controlled by the CH₄ consumption rate in sediments
83 along the groundwater flow path and the residence time of CH₄-bearing groundwater
84 within those methanotrophic sediments. We investigated these processes on a barrier
85 island in Georgia, USA by surveying groundwater CH₄ concentrations, CH₄ production

and consumption rates, and CH₄ efflux to the atmosphere across the island, and by modeling groundwater flow paths and rates.

2. Methods

2.1. Site description

Sapelo Island is located on the coast of Georgia, USA (Fig. 1a). The study site, Cabretta Island, is a small (~250 m wide), Holocene barrier island on the seaward side of Sapelo Island (Fig. 1b). The mean annual rainfall on Cabretta Island is 130 cm and the mean tidal range is 2.5 m (Fig. 1c). Trees and shrubs grow on the upland of the island, which is flanked by a small tidal creek and salt marsh on one side and a dune and beach system on the other. A transect of groundwater monitoring wells spanning this range in environment type was installed across the island in 2008 (Fig. 1b,c). Wells were placed in 7 clusters with 1-3 wells per cluster. Within each cluster, wells with 30 cm screened intervals were installed from 1–5 meters below the sediment surface. Each well was capped and contained a tightly fitting internal casing to minimize the internal storage volume of the well and prevent contamination of the aquifer with materials from the surface.

Cabretta Island is a transgressive barrier island composed of alternating layers of mud and sand. A simplified version of the island stratigraphy described by Wilson et al. (2011) is provided in Figure 1c. Surficial salt marsh sediments were composed of mud and silt on the leeward side of the island. This stratum was connected with older marsh sediment buried beneath the island upland and beach, outcrops of which could be seen near the low tide line on some portions of the beach (Fig. 1d). An unconfined sandy

aquifer overlaid the buried marsh platform on the island upland and beach, and a confined sandy aquifer was located beneath the marsh mud. The particulate organic carbon content of the mud found in the marsh platform buried beneath the island center was $0.64\% \pm 0.17\%$ (n=3) and $0.05\% \pm 0.01\%$ (n=6) in the unconfined sandy aquifer. Rain falling on the island upland percolated through the sediment creating a freshwater lens within the sediment of the unconfined sandy and buried marsh platform aquifers (Fig 1c). This freshwater mixed with infiltrating seawater, creating a salinity gradient that is not represented in the figure.

2.2. Groundwater and surface water geochemistry

An initial survey of Cabretta Island groundwater and surface water geochemistry was carried out with samples collected every other month from August 2008 – August 2010. Salinity, temperature, and dissolved oxygen (DO) concentrations were measured in the field, while samples were preserved and returned to the laboratory to measure the concentrations of sulfide (H_2S), CH_4 , dissolved organic carbon (DOC), chloride, and sulfate. Prior to sample collection, the stagnant groundwater was purged from each monitoring well using a peristaltic pump. The salinity and temperature of each sample was determined using a handheld conductivity meter (YSI Model 30) with an accuracy of $\pm 2\%$, and the DO concentration was measured using a polarographic DO probe connected to a handheld meter (Thermo Fisher Orion 5-Star portable DO meter). When the scent of H_2S was present in a sample, the DO concentration was assumed to be zero and was not measured to prevent poisoning the DO probe. Freshly recharged groundwater was pulled into a disposable syringe using tygon tubing. Surface water

samples were collected directly from the adjacent tidal creek and ocean surf zone using the same syringe and tubing. The syringe and tubing was rinsed with ~30 mL of fresh well water prior to collection of an actual sample.

Sulfide concentrations were determined in samples that were filtered, fixed with 20% (w/v) zinc acetate, and stored at 4°C for subsequent colorimetric analysis (Cline, 1969). The detection limit for this method was 0.5 μM H_2S . A 10 mL subsample of unfiltered water for CH_4 analysis was injected into a 20 mL headspace vial sealed with a butyl rubber septum that contained a sodium hydroxide pellet (for sample fixation) and had previously been purged with helium (to minimize the background CH_4 concentration). This sample was stored upside down prior to measurement via gas chromatography (Shimadzu GC-2010 with flame ionization detector and Carbosphere column). The detection limit for this method was determined to be 0.5 μM from field blanks. This high detection limit (relative to water at equilibrium with the atmosphere) was likely due to CH_4 carryover from high concentration samples within the sampling syringe. DOC samples were filtered into an acid-washed Nalgene bottle and stored frozen until analysis using a Shimadzu TOC-5000 analyzer. Samples for analysis of chloride and sulfate were filtered, fixed with concentrated nitric acid, and stored in an acid-washed glass scintillation vial before measurement by ion chromatography (Dionex ICS-2000). The sulfate depletion ($[\text{SO}_4^{2-}]_{\text{DEP}}$, Table 1) was calculated as the difference between the expected sulfate concentration (the measured chloride concentration divided by the chloride to sulfate ratio of seawater, 19.33) and the observed sulfate concentration (Weston et al., 2006). Positive values indicate the depletion of sulfate relative to chloride, presumably due to sulfate reduction.

2.3. CH_4 concentration depth profiles

A more detailed investigation of CH_4 cycling within the barrier island aquifer was conducted during the winter (February-March) and summer (July-August) of 2012. Equilibration chambers were used to measure CH_4 concentrations in the pore space of barrier island sediment (Fig. 2a). These watertight chambers were constructed from PVC pipes with an inner diameter of ~4 cm, an outer diameter of ~4.8 cm, a length of ~40 cm, and a volume of ~500 mL. Large holes were drilled through the sides of each pipe, which was capped with a PVC cap on one end and a thick, butyl rubber stopper on the other such that the total length of the chamber was ~45 cm. The pipe was covered with a CH_4 -permeable silicone rubber (Grunwald et al., 2009) tubing with an inner diameter of ~5 cm and a wall thickness of 1.59 mm. The tubing was secured to the PVC body of the equilibration chamber using waterproof tape, creating a watertight but gas-permeable chamber. Chambers were connected to a photoacoustic field gas monitor (Innova 1412, LumaSense Technologies Inc., Santa Clara, CA) via two lengths of gas-tight, FEP-lined polyethylene tubing that penetrated the rubber stopper. The concentration of CH_4 within the chamber was measured by recirculating the gas between the equilibration chamber and field gas monitor in a closed loop.

CH_4 equilibration across the silicone rubber tubing was tested in the laboratory by spiking five equilibration chambers with CH_4 to a final concentration of ~2000 ppm. The concentration of CH_4 within each chamber was tracked through time using the field gas monitor. CH_4 concentrations within the chamber returned to near atmospheric concentrations within two days (Fig. 2b), indicating that the CH_4 concentration measured

within an equilibration chamber represented the running average of the CH₄ concentration within the sediment over approximately a two day window. To measure a depth profile of CH₄ concentration, four equilibration chambers were stacked inside a PVC housing with an internal diameter of ~7.6 cm and 2.5 mm wide slits cut along its entire length to allow infiltration of pore water or gas (Fig. 2c). Equilibration chambers were separated from one another in the housing by thick, butyl rubber stoppers to prevent vertical gas or water exchange. These profilers covered a 2-meter depth range, with individual chambers measuring average CH₄ concentrations over 0.5-meter intervals. Average concentrations and associated measurements are discussed and displayed as being located at the middle of the depth range covered by each chamber.

Based on observed CH₄ concentration distributions (Fig. 3), an intensive study of sediment CH₄ cycling was carried out at the center of Cabretta Island and near the spring high tide line on the beach. Three depth profilers were installed at each location spaced one meter apart in a line parallel to the shoreline of Cabretta Island. During installation, it was observed that the top ~1.5 m of sediment at each location was composed of sand while the bottom 0.5 m was a mix of sand, mud, and silt that represented the transition into the buried marsh platform. CH₄ concentration profiles were measured from the island center twice during the winter (February-March) and the summer (July-August) of 2012. On the beach, profiles were measured six times in the winter and twelve times in the summer across multiple spring/neap tidal cycles. In October 2012, another four small equilibration chamber profiles (0-0.5 and 0.5-1.0 meter depth intervals) were installed in a transect down the beach at Cabretta Island, spaced approximately evenly from the high

to the low tide line. CH₄ concentrations were only measured in these chambers once because profilers were rapidly destroyed by waves.

2.4. Potential rates of CH₄ production and consumption

Potential CH₄ production and consumption rates were measured in laboratory bottle incubations. During winter and summer 2012, sediment was collected from triplicate profiles at the island center and on the beach with individual samples taken from the midpoint of each 0.5 m depth interval represented by an equilibration chamber. These samples were returned to the lab and 120 cm³ of sediment was placed in 500 mL Schott bottles. Bottles were split into oxic and anoxic treatments and their headspaces were purged with air and nitrogen, respectively, and then spiked with CH₄ to approximate *in situ* concentrations. Each treatment was carried out in triplicate at all four depths at both locations. After a 24-hour pre-incubation at *in situ* temperature (17°C winter, 27°C summer), the headspace of each bottle was reset by purging with air or nitrogen and spiking with CH₄. Headspace CH₄ concentrations were measured approximately 0, 3, 6, 12, 24, and 48 hours following the headspace reset using the field gas monitor. The linear rate of change in concentration was used to calculate the rate of CH₄ production or consumption in 120 cm³ of sediment. This rate was then scaled up to the 0.5 m³ of sediment represented by a 0.5 m depth interval (the length of one equilibration chamber) in a sediment column with a cross-sectional area of 1 m². The volumetric rate was converted to an areal rate by dividing by the height of the sediment layer represented by the equilibration chamber (0.5 m) for ease of comparison with transport fluxes.

2.5. *CH₄ efflux*

The flux of CH₄ from the sediment surface to the atmosphere was measured using triplicate flux chambers. These chambers were Plexiglas cylinders with a surface area of 0.047 m² and a volume of ~8 L. One chamber was placed next to each of the equilibration chamber profilers immediately before or after concentration profiles were measured. Flux chambers were covered throughout the measurement period such that fluxes were quantified in the dark. Two pieces of gas impermeable tubing entered each chamber through a septum in the top and were connected to the field gas monitor such that gas was circulated between the chamber and detector during measurement. Triplicate CH₄ concentration measurements within each flux chamber were recorded every 20-30 minutes over a 1-2 hour period using the field gas monitor. The CH₄ flux was calculated as the linear increase or decrease in CH₄ concentration within the flux chamber over time. The flux was quantified by linear regression of this time series (Samarkin et al., 2010). The slope of each linear regression was tested to ensure that it was significantly different from zero ($p < 0.025$).

2.6. *Groundwater flow velocity*

A groundwater flow model was constructed to estimate tidally driven groundwater flow rates on Cabretta Island along the flow path from the center of the island upland towards the low water line on the beach. The numerical model was developed using SUTRA (Voss and Provost, 2002), a finite element, saturated-unsaturated, variable-density, groundwater flow and solute transport program. SUTRA

solves a modified form of the Richards equation (Gardner and Wilson, 2006; Wilson and Gardner, 2006):

$$\nabla \cdot [K(\Psi)\nabla h] = S_w S_s \frac{\partial h}{\partial t} + \phi \frac{\partial S_w}{\partial t} - \alpha_s S_w \frac{\partial \sigma_T}{\partial t} \quad (1)$$

where K is hydraulic conductivity, Ψ is negative pressure head, h is hydraulic head, S_w is water saturation, ϕ is porosity, σ_T is total stress (calculated based changes in the height of the water column above the simulation domain (Gardner and Wilson, 2006; Wilson and Gardner, 2006)), and S_s is the specific storage:

$$S_s = \rho g (\alpha_s + \phi \beta) \quad (2)$$

where ρ is the density of water, g is gravity, α_s is sediment compressibility and β is fluid compressibility. Freshwater-saltwater transport was described by a variable-saturation form of the solute transport equation

$$\frac{\partial}{\partial t} (\phi S_w c) = \nabla \cdot \phi S_w \mathbf{D} \nabla c - \phi S_w \mathbf{v} \cdot \nabla c \quad (3)$$

Where c is the salinity, $\mathbf{v}$ is the average linear velocity of the groundwater, and $\mathbf{D}$ is the dispersion tensor

$$D_L = \alpha_L |\mathbf{v}| + D_m \quad (4a)$$

$$D_T = \alpha_T |\mathbf{v}| + D_m \quad (4b)$$

where D_L and D_T are the longitudinal and transverse coefficients of dispersion, α_L and α_T are the longitudinal and transverse dispersivities, and D_m is the coefficient of molecular diffusion. Parameters used in the simulations are representative of clean, well-sorted fine (180 μ) sand; the marsh mud was assumed to be four orders of magnitude less conductive than the sand (Table S1). The dispersivities were chosen to be consistent with Gelhar et al. (1992) and Smith (2004) and the flow field generated by the model showed a negligible response to increasing dispersivity values by an order of magnitude.

The model domain was built to represent the topography of the shore-perpendicular axis of Cabretta Island's beach. The domain was discretized into 11402 elements and 11807 nodes. Mesh density was increased in areas where rapid fluctuations in pressure and salinity were expected. Element sizes ranged from 0.3 m by 0.3 m in the shallow subsurface to 1 m by 1 m in areas of the model domain where higher mesh density could be sacrificed for computational efficiency. The larger elements deeper in the subsurface did not affect the model results.

Initial conditions for the groundwater simulations were developed using a preliminary run in which tidal fluctuations were neglected. At the outset of the preliminary run, the pore pressure was set to hydrostatic pressure at each node. All nodes within the model domain were assigned a salinity of 34. Sea level was held constant. The model was then run without any tidal pumping and with downward infiltration of fresh rainwater through the land surface boundary. The model was run until quasi-equilibrium was reached (110 years with 10 minute time steps). The resulting simulated salinity distribution was consistent with observed data from the Cabretta Island well transect. These model results were then used as the initial conditions in the model domain for subsequent simulations involving the hydraulic response to tidal fluctuations. Final model results were not affected by initial conditions because the system was allowed to reach quasi-steady state.

2.7. Drivers of surface water CH₄ concentration

Data were gathered for several variables that potentially control the concentration of CH₄ in surface waters adjacent to Cabretta Island. The tidal range and mean water

level of the ocean can influence the rate of groundwater discharge (and therefore CH₄ flux) to the ocean. The values of these parameters at the time of surface water CH₄ sampling were calculated using tidal data for the National Oceanic and Atmospheric Administration's station at Fort Pulaski, GA (<http://1.usa.gov/1gTf7YM>). Mean water level was estimated as a 30-day running average of the water level data, and the tidal range was calculated as the difference in water level between consecutive low and high tides that bracketed CH₄ sample collection. Wind speed and wave height are two factors that control gas exchange between the atmosphere and the surface ocean. These data, from the times of surface water CH₄ sampling, were acquired from the National Data Buoy Center's buoy located at Gray's Reef (<http://1.usa.gov/1KpHVEX>).

3. Results

3.1. Groundwater geochemistry

The salinity distribution in groundwater across Cabretta Island shows clearly the freshwater lens beneath the island upland (TT-4, Fig. 3a) where the salinity in the shallowest well was typically around one (Table 1). Groundwater from these low salinity wells also tended to have high concentrations of CH₄ (Fig. 3b) and DOC (Fig. 3c), and low concentrations of SO₄²⁻ (Fig. 3d). The highest H₂S concentrations were observed in groundwater from the dunes and salt marsh nearest to the island upland (Fig. 3e). The highest sulfate depletion was observed in the TT-3 cluster of marsh wells nearest the upland (Table 1), while the sulfate depletion was highest relative to the remaining sulfate pool in wells from the island upland and dunes.

When data from all wells that sampled the salt marsh and beach groundwater were pooled, the median CH₄ concentration was 6 μM with an interquartile range (IQR) of 2.3–15 μM (n=159). This is three orders of magnitude higher than the 1.3–3.1 nM expected for groundwater equilibrated with the atmosphere (Wiesenburg and Guinasso, 1979) given the range in temperature (12.6°C and 36.4°C) and salinity (0.3–67) observed in all groundwater wells sampled over the two-year study period and assuming an atmospheric CH₄ concentration of 1.8 ppm (Myhre et al., 2013). Groundwater CH₄ concentrations beneath the island upland exceeded the background concentration observed elsewhere by two orders of magnitude. The well with the highest median CH₄ concentration, 726 μM (IQR 566–1730 μM), was located near the center of Cabretta Island at 3.4 meters depth (Fig. 3b), and had a maximum concentration of 2780 μM. Methane concentrations were higher than the background groundwater concentration beneath the upland and dunes, covering at least a 1.7 meter depth range and extending across at least 22 m of the island cross section.

3.2. Upland CH₄ dynamics

Methane cycling was investigated in greater detail in the top two meters of sediment within the zone of high CH₄ concentrations observed at the center of Cabretta Island during the winter (February–March) and summer (July–August) of 2012. In both seasons, CH₄ concentrations increased with depth from a median value of 0.02 μM (IQR = 0.02–0.06) at 0.25 meters to 151 μM (IQR = 143–158, n=9) in the summer and 189 μM (IQR = 182–195, n=6) in the winter. These concentrations were similar to the median groundwater CH₄ concentration (326 μM, IQR = 278–787 μM, n=13) in the closest

neighboring monitoring well (TT-4, 1.6 meters). Methane was consumed from 0.25-1.25 meters and produced at 1.75 meters (Fig. 4b). There was no statistically significant difference between summer and winter potential methane production rates at 1.75 meters (2-sample t-test, $p > 0.025$), so all replicates were averaged to calculate a net potential CH_4 production rate of $22 \pm 11 \text{ mmol m}^{-2} \text{ day}^{-1}$ ($n=5$). Maximum rates of potential CH_4 consumption were observed at 0.75 meters: $98 \pm 18 \text{ mmol m}^{-2} \text{ day}^{-1}$ ($n=3$) under oxic conditions in the summer, $40 \pm 20 \text{ mmol m}^{-2} \text{ day}^{-1}$ ($n=3$) under anoxic conditions in the summer, and $15 \pm 8.7 \text{ mmol m}^{-2} \text{ day}^{-1}$ ($n=3$) under anoxic conditions in the winter. At 1.25 and 1.75 meters depth (the only depths where the sediment was saturated enough to collect porewater samples), the salinity was low (less than 3), DO and H_2S concentrations were below the detection limit, and DOC concentrations were in the millimolar range (Fig. 4c).

3.3 Beach CH_4 dynamics

Methane concentrations in sediments from the upper beach also increased from 0.25 to 1.75 meters depth (Fig. 4d). However, the mean CH_4 concentrations observed in this deepest layer ($10 \pm 5.2 \text{ } \mu\text{M}$ in the winter and $40 \pm 21 \text{ } \mu\text{M}$ in the summer) were much lower than the concentrations observed at the same depth in the island center, and no CH_4 production was observed (Fig. 4e). Net potential CH_4 consumption was observed from 0.25-1.25 meters depth in beach sands, and the consumption rate did not vary significantly with depth or season. The median rate across all measurements was $10 \text{ mmol CH}_4 \text{ m}^{-2} \text{ day}^{-1}$ (IQR = 7.8–18 $\text{mmol m}^{-2} \text{ day}^{-1}$, $n = 17$). Porewater salinity was much higher beneath the beach than the island center, and decreased from 20-30 at 0.75-

1.25 meters depth to 10-20 at 1.75 meters (Fig. 4f). Dissolved oxygen concentrations were low ($<40 \mu\text{M}$) at all depths, and decreased sharply to $0 \mu\text{M}$ at 1.75 meters. Sulfide concentrations were below the detection limit from 0.75-1.25 meters depth and increased dramatically to greater than $600 \mu\text{M}$ at 1.75 meters while DOC concentrations remained in the millimolar range across all depths.

Data from the equilibration chamber transect down the beach (installed in October 2012 and washed away after a single measurement) showed that elevated CH_4 relative to the atmospheric equilibrium persisted in the pore space down to the low tide line (Fig 5a). The degree of CH_4 supersaturation in the pore space depended on the sediment layer, however. The median CH_4 concentration in the top meter of beach sand from the entire study period was $0.11 \mu\text{M}$ (IQR = $0.03\text{--}0.25 \mu\text{M}$, $n = 105$). In contrast, the median CH_4 concentration in the mud layer underlying the beach over the same time period was $22 \mu\text{M}$ (IQR = $8\text{--}51 \mu\text{M}$, $n = 47$).

3.4. Flux of CH_4 to the atmosphere

Atmospheric CH_4 was consumed at a rate of $-247 \mu\text{mol m}^{-2} \text{day}^{-1}$ (IQR = -222 to $-278 \mu\text{mol m}^{-2} \text{day}^{-1}$, $n = 6$) in surface soils overlying the freshwater lens at the center of Cabretta Island (Fig. 5b). In contrast, the median efflux of CH_4 from the upper beach was $0 \mu\text{mol m}^{-2} \text{day}^{-1}$ (IQR = -116 to $228 \mu\text{mol m}^{-2} \text{day}^{-1}$, $n = 84$). This high range in CH_4 efflux values was also observed in the middle of the beach (median = $42 \mu\text{mol m}^{-2} \text{day}^{-1}$, IQR = $0\text{--}128 \mu\text{mol m}^{-2} \text{day}^{-1}$, $n = 6$) and near the low tide line on the beach (median = $-58 \mu\text{mol m}^{-2} \text{day}^{-1}$, IQR = -242 to $64 \mu\text{mol m}^{-2} \text{day}^{-1}$, $n = 12$).

3.6. *Surface water CH₄ concentrations*

While CH₄ concentrations in the surf zone of the Atlantic Ocean and Cabretta Creek, the surface water bodies adjacent to Cabretta Island, tended to be below the detection limit (~0.5 μM), they exceeded 3 μM on four occasions during the study period. These high CH₄ concentrations indicate supersaturation of surface waters with respect to the atmosphere. The most likely source of this excess CH₄ was groundwater discharge, indicating occasional pulses of groundwater-derived CH₄. However, there was no correlation between CH₄ concentration and mean water level or tidal range, which control groundwater discharge, or between CH₄ concentration and wind speed or wave height, which control exchange of CH₄ between surface waters and the atmosphere (Fig. S1).

3.7 *Net groundwater flow paths*

Net groundwater flow paths were determined by averaging simulation results over a tidal period. This analysis indicated net infiltration below the center of the upland, with relatively rapid horizontal flow (on the order of tens of centimeters per day) through the unconfined aquifer from the upland to the ocean (Fig. 5c). The confined aquifer also served as a conduit for flow from the upland to the ocean, with slower flow rates of several centimeters per day. Net downward flow through the mud layer that separated the confined and unconfined aquifers was slow (less than one centimeter per day).

4. Discussion

4.1.. Barrier island methanogenesis

The dissolved CH₄ concentrations observed in fresh groundwater on Cabretta Island (median = 597 µM) is among the highest ever reported in coastal groundwater systems. They rival concentrations found in a Texas aquifer (350–1733 µM) (Grossman et al., 1989), and exceed concentrations observed in coastal groundwater in Denmark (400–600 µM) (Jakobsen and Postma, 1999) and Florida (40–271 µM) (Bugna et al., 1996). These CH₄ concentrations were lower than those reported for other coastal environments such as fresh (up to 2400 µM) and salt marshes (up to 1100 µM) (Segarra et al., 2013), a tidal creek bed (500 µM) (Parkes et al., 2012), and organic-rich, subtidal sediment (1000–8000 µM) (Heyer and Berger, 2000; Jørgensen and Parkes, 2010; Martens et al., 1998; Thang et al., 2013).

The high groundwater CH₄ concentrations observed beneath the Cabretta Island upland were supported by high rates of potential methanogenesis ($22 \pm 11 \text{ mmol m}^{-2} \text{ day}^{-1}$). This rate was of the same order of magnitude as the rates reported in organic-rich sediments of Cape Lookout Bight, North Carolina, USA (Martens et al., 1998) and exceeded those measured in a variety of other coastal sediments (Deborde et al., 2010; Jakobsen and Postma, 1999; Jørgensen and Parkes, 2010; Parkes et al., 2012). The high potential methanogenesis rates observed on Cabretta Island were restricted to a small zone where the freshwater lens overlapped with organic-rich, buried marsh sediment (Fig. 6a, red polygon). The pore water within this zone was characterized by low salinity, low sulfate and dissolved oxygen concentrations, and high concentrations of dissolved organic carbon (Table 1), which provided ideal conditions for methanogenesis (Cicerone and Oremland, 1988).

By assuming that methanogenesis was active over a 0.5 meter depth range, it is possible to calculate the total organic carbon pool that was available to methanogenic microorganisms. Multiplying the 0.5 m^3 volume of this zone (beneath each 1 m^2 of barrier island upland) by the porosity of 0.45 and the median DOC concentration of $1532 \text{ } \mu\text{M}$ ($= 1532 \text{ mmol m}^{-3}$) in upland groundwater (Table 1) yields a DOC pool of 1300 mmol m^{-2} . On average, there was 0.0064 grams of particulate organic carbon (POC) in each gram of sediment in the mud layer comprising the methanogenic zone. Multiplying the volume of the methanogenic zone (0.5 m^3) by this POC concentration and the mean sediment density (1.32 g cm^{-3}), and converting the resulting mass of carbon into molar units yields a POC pool of $352,000 \text{ mmol m}^{-2}$. Summing the DOC and POC pools results in a total organic carbon pool of $353,000 \text{ mmol m}^{-2}$. Assuming that all of this organic carbon was in a form that methanogens are capable of using, this is sufficient carbon substrate to support the observed rate of methanogenesis for more than 40 years.

4.3. Competition with sulfate reduction

Not all of this organic carbon was available to methanogens, however, as there would be competition from microorganisms capable of using other terminal electron acceptors such as dissolved oxygen, nitrate, oxidized metals, or sulfate. No dissolved oxygen or nitrate was detected at this depth (data not shown). While sulfate reduction rates were not measured, sulfate reduction activity was indicated by high sulfate depletion (Table 1). Therefore, sulfate reduction was likely to be active in the same locations where high CH_4 concentrations were observed, and this process was likely the main competitor with methanogenesis for organic carbon substrates. It is possible that

methanogenesis and sulfate reduction occurred contemporaneously, fueled by noncompetitive substrates (Oremland and Polcin, 1982). Even if this was not the case, the total organic carbon pool was sufficient to support both processes. Assuming the median sulfate concentration in upland groundwater (0.1 mM, Table 1), the total sulfate pool was 22 mmol m⁻². Further assuming a sulfate reduction stoichiometry of 2 carbon atoms oxidized for every one sulfur atom reduced (Konhauser, 2007), complete consumption of the sulfate pool would have a negligible impact on the amount of organic carbon available to methanogens.

4.4. Organic carbon supply

While the total organic carbon pool within the zone of methanogenesis was large, methanogenesis must be supported by an equivalent flux of organic carbon into the sediment at this location over the long term. The most probable source of organic carbon to the methanogenesis zone is soil organic carbon storage by island vegetation. The Cabretta Island upland was inhabited by pine trees and Post and Kwon (2000) report an average soil organic carbon storage rate of 2.6 mmol C m⁻² day⁻¹ in warm temperate moist pine forest, an order of magnitude lower than the measured methanogenesis rate of 22 mmol C m⁻² day⁻¹. Salt marshes, on the other hand, store carbon at an average rate of 50 mmol C m⁻² day⁻¹ (McLeod et al., 2011), a high enough rate to support barrier island methanogenesis. Groundwater generally flows from the upland at the center of the island towards the low water line on the beach (Fig. 5c) and the creek bank on either side of the island (Wilson et al., 2015b). Therefore, transport of dissolved organic carbon from the salt marsh to the island center was unlikely. This mechanism of carbon transport is

possible during storm events, however, as groundwater flow has been shown to reverse direction in response to storm surges (Wilson et al., 2011).

The more likely mechanism for delivery of salt marsh-derived organic carbon to the methanogenesis zone is migration of the barrier island itself. On retrograding barrier islands such as Cabretta, salt marshes are buried by overwashing sand as the island is pushed shoreward (Fig. 6a). The mud layer in which high methanogenesis rates were observed was likely formed via this process. As the island migrates shoreward, the island upland and associated freshwater lens are pushed back over relatively freshly buried salt marsh sediments. Thus, the particulate carbon consumed by methanogens at the island center was likely stored earlier in the island's history through high rates of primary production and sedimentation by an active marsh. Retrograding barrier islands act as conveyer belts that, through the constant burial of salt marsh sediment, maintain a supply of sedimentary organic carbon within the freshwater lens that is capable of supporting high rates of methanogenesis (Fig. 6a).

St. Catherine's Island, just north of Cabretta, retreated at a rate of several meters per year between 1945 and 1990 (Goodfriend and Rollins, 1998). For a small island like Cabretta that is only ~250 meters wide, this means that marsh buried on the landward side of the island will be exhumed on the seaward side in less than a century. Indeed, buried marshes on the seaward side of St. Catherine's were less than a century old (Goodfriend and Rollins, 1998). Given the small spatial scale of the methanogenesis zone (tens of meters), the residence time of buried marsh sediment within this zone would likely be less than a decade, much shorter than the approximately 40 years required for total consumption of the organic carbon pool via methanogenesis.

496

497 *4.5. Methanotrophy rates*

498 The CH₄ oxidation rates on Cabretta Island (18 mmol m⁻² day⁻¹ during summer at
499 1.25 meters depth beneath the upland, and 10 mmol m⁻² day⁻¹ in beach sands) fall within
500 the range reported by Deborde et al. (2010) (0.3–199 mmol m⁻² day⁻¹) and are comparable
501 to rates reported in other intertidal and subtidal coastal sediments (Carini et al., 2003;
502 Jørgensen and Parkes, 2010; Segarra et al., 2013; Treude and Ziebis, 2010). Groundwater
503 flow patterns show that it is unlikely that CH₄ was transported into the shallow barrier
504 island aquifer from a deeper or more distant groundwater source, suggesting that the only
505 source of CH₄ to Cabretta Island was methanogenesis within the freshwater lens.
506 Therefore, the rate of methanotrophy in shallow sediments across the island was likely to
507 be limited by the rate of CH₄ transport from the freshwater lens. The potential for
508 methanotrophy under both oxic and anoxic conditions was observed from the sediment
509 surface to 1.25 meters deep beneath the island upland and the beach (orange boxes in Fig.
510 6b). Dissolved oxygen concentrations were 0 μM in water-saturated sediment from the
511 island center (Fig. 4d) and less than 40 μM from the beach (Fig. 4h), so CH₄ most likely
512 oxidized anaerobically. It is possible that oxygen penetrated into the shallower,
513 unsaturated sediment, but this was not measured. Whether or not oxygen was available in
514 these strata, the potential for methanotrophy was demonstrated, providing the mechanism
515 for the constantly decreasing CH₄ concentrations from the deep production zone to the
516 sediment surface.

517 The methanotrophy observed in surficial sediment was likely responsible for the
518 soil overlying the freshwater lens acting as a sink for atmospheric CH₄, with a median

consumption rate of $-247 \mu\text{mol m}^{-2} \text{ day}^{-1}$. This rate of atmospheric CH_4 consumption is at the high end of the range observed across a variety of forest, grassland, and tundra environments (King, 1997). Assuming that this rate was constant across the 11.5-meter freshwater lens (half the distance between the TT-4 well cluster that sampled fresh groundwater at the island center and the TT-5 well cluster that sampled brackish water in the dunes), the integrated rate of atmospheric CH_4 consumption per meter of barrier island shoreline was $-2.8 \text{ mmol CH}_4 \text{ m}^{-1} \text{ day}^{-1}$ (IQR = -2.6 to $-3.2 \text{ mmol CH}_4 \text{ m}^{-1} \text{ day}^{-1}$). Atmospheric CH_4 consumption was not consistently observed in sediments and soils elsewhere on Cabretta Island, however. This is likely because the methanogenic community in the freshwater lens sustained the population of methanotrophs that occupied shallower strata, facilitating their consumption of atmospheric CH_4 (Le Mer and Roger, 2001).

4.6. Groundwater-derived CH_4 flux to the ocean

The concentration of CH_4 in the coastal ocean is a function of inputs from groundwater and riverine discharge, loss to the atmosphere, and oxidation in the water column (Bugna et al., 1996; Santos et al., 2009b). Rates of groundwater discharge are highest in the late winter when mean water level is at a minimum and on spring tides when the tidal range is highest (Wilson et al., 2015a). The rate of atmospheric loss is controlled by the extent of wave and wind driven mixing (Grunwald et al., 2009) and should be higher with larger waves and higher winds. Occasional supersaturated CH_4 concentrations in the surf zone of the ocean show that dissolved CH_4 was exported from the barrier island aquifer at least some of the time. The lack of supersaturation at other

times could indicate that either there was little CH₄ export at those times, or that the exported CH₄ was rapidly lost from surface waters to the atmosphere. However, elevated CH₄ concentrations in the surface ocean adjacent to Cabretta had no relationship with mean water level, tidal range, wind speed, or wave height (Fig. S1). This implies that a different process controlled CH₄ concentrations in these waters. Methanotrophy in beach sands may have prevented CH₄ export much of the time despite high rates of CH₄ production at the island upland.

The residence time of groundwater within the aquifer as it transits the distance between the loci of CH₄ production and CH₄ discharge determines the exposure of groundwater CH₄ to methanotrophy. There were two aquifers beneath the beach on Cabretta Island through which CH₄ could have been transported to the ocean: an unconfined sandy aquifer and a confined sandy aquifer (Fig. 6b) that were separated by a muddy confining layer (likely buried marsh sediment). Based on the groundwater flow model, a representative flow rate of 0.64 m day⁻¹ was chosen for the unconfined sandy aquifer, which was directed horizontally toward the point of discharge near the low tide line. This location was around 125 meters from the zone of methane production at the island center. The resulting residence time for groundwater within this aquifer was around 195 days. The light orange box in Fig. 6c shows the range in groundwater residence time and methanotrophy rates measured for this aquifer. The gray polygon represents the range in these values over which CH₄ discharge to the ocean would have been possible given the average CH₄ concentration of 0.11 μM observed in this aquifer. Methanotrophy was an efficient CH₄ sink in the unconfined sandy aquifer that prevented groundwater-derived CH₄ discharge to the ocean.

The more probable pathway for CH₄ export was downward advection through the mud layer at the island center where the CH₄ was produced. No methanotrophy was measured within this confining unit anywhere on the island (white box in Fig. 6b) such that most of this CH₄ would end up in the confined sandy aquifer. Within this aquifer, lateral advection toward the low tide discharge point occurred at a representative rate of 0.025 m day⁻¹, resulting in very long groundwater residence times (>10 years) under average conditions. Methanotrophy rates were not measured in this aquifer, but it is possible to imagine a low but non-zero rate of methanotrophy that prevented groundwater-derived CH₄ discharge under steady state conditions (Fig. 6d), even assuming that the high CH₄ concentrations (726 µM) observed in the 3.7 m deep well at TT-4 (the island center) were representative of the confined sandy aquifer. However barrier island aquifers can be flushed out over time scales of days to weeks by storm surges (Wilson et al., 2011). Under these conditions, the same low methanotrophy rates would allow CH₄ export from the barrier island (Fig. 6d).

4.7. Implications for the use of CH₄ as a tracer of groundwater discharge

Methane has been used as a tracer for submarine groundwater discharge in a number of studies (Cable et al., 1996; Kim and Hwang, 2002). However, CH₄ is only an effective tracer if its transport via groundwater flow is faster than rates of methanotrophy within the aquifer. The tight correlation between CH₄ concentration in surface water and the rate of groundwater discharge in these studies demonstrates that this is a safe assumption in cases where groundwater discharge is rapid and concentrated at point sources, such as near springs (Cable et al., 1996). However, groundwater discharge is

588 slower and more evenly distributed in aquifers composed of silt, mud, and sand that are
589 typical of many coastlines. Under these conditions, methanotrophy will have a significant
590 impact on the groundwater-derived flux of CH₄ to surface waters. It may still be possible
591 to use CH₄ as an indicator or qualitative tracer of groundwater discharge (Dulaiova et al.,
592 2010), but even this should be done with caution, as a lack of CH₄ in surface waters does
593 not necessarily preclude the presence of discharging groundwater.

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Figure Captions

Figure 1. The location of Sapelo Island (red dot) on the coast of Georgia, USA (a). A map of the study site, Cabretta Island, showing its position relative to Sapelo Island and the location of the groundwater monitoring well transect (red line) (b). A cross section of Cabretta Island showing its main geological features and the position of each groundwater monitoring well (circles) (c). Note that the name of each cluster of monitoring well (TT-1 to TT-7) is listed across the top of the panel. The heavy black line represents the sediment surface (10:1 vertical exaggeration) and the sinusoid on the left side of the panel shows the average tidal range. The red box on the surface of the lower beach shows the position where the photograph in panel (d) was taken. A photograph of the mud outcrop near the low tide line on the beach taken near the northern tip of Cabretta Island in October 2012 (d).

Figure 2. A schematic diagram of an equilibration chamber connected to the field gas monitor (a). The components of this system are: A – the field gas monitor; B – gas impermeable FEP-lined polyethylene tubing; C – a thick, butyl rubber stopper; D – the PVC pipe that provides the structure for the chamber; E – the silicone rubber membrane

that allows gas equilibration between the chamber and its surroundings (note that this membrane covers the entire chamber and only a piece of it is shown here so that the internal structure of the chamber can be seen); F – holes drilled in the PVC pipe that allow the gas inside the chamber to contact the membrane; G – a PVC cap glued to the bottom of the chamber. Time required for the CH₄ concentration within an equilibration chamber to equilibrate with the atmosphere following CH₄ addition (b). Diagram showing the arrangement of individual equilibration chambers within a PVC housing to form a profiler capable of measuring CH₄ concentrations across multiple depths (c).

Figure 3. A cross section of Cabretta Island with the black line showing the island surface (10:1 vertical exaggeration). Each circle represents a groundwater monitoring well that was sampled every other month from August 2008 – August 2010 (n=13). The color of each shape displays the median salinity (a) or concentration of CH₄ (b), DOC (c), SO₄²⁻ (d), or H₂S (e) dissolved in the groundwater (circles) or surface water (rectangle or triangle) at that location. Note that dissolved oxygen concentration data is not displayed here because it was considered to be below the detection limit in all wells during the study period.

Figure 4. Panels a–c show data from the center of Cabretta Island. Panels d–f show data from the upper beach. Median CH₄ concentration in the pore space (a, d) with error bars showing the interquartile range. The mean rate of methane production (positive) and consumption (negative) under anoxic conditions in winter and summer 2012 and oxic conditions during summer 2012 (b, e), with error bars showing the standard deviation.

The mean salinity and concentrations of DOC, H₂S, and DO in small piezometers installed at the central depth of each equilibration chamber (c, f). Error bars show the standard deviation. Where no error bars were present, only one sample was collected.

Figure 5. Methane concentrations on the beach at Cabretta Island (a, 5:1 vertical exaggeration). The dashed black line represents the surface of Cabretta Island from 2008-2010 (as shown in Figure 1). The heavy black line represents the island surface in 2012. Stacked rectangles represent gas equilibration chambers installed from the island center to the low tide line on the beach. The colors of these boxes display the log-transformed CH₄ concentration. Methane efflux from the sediment surface to the atmosphere (b). Negative values represent consumption of atmospheric methane in surficial sediment. Model-based groundwater velocity estimates (c, 5:1 vertical exaggeration). The arrows show the direction of groundwater flow across the island and the arrow color shows the log-transformed speed of that flow.

Figure 6. A cross section of Cabretta Island (10:1 vertical exaggeration) showing a conceptual model of physical sediment transport processes (blue arrows) and biological carbon transformation processes (red arrows) (a). The different colored aquifer zones match those in Figure 1, and the red polygon shows the zone of methanogenesis. A cross section of the seaward half of Cabretta Island (10:1 vertical exaggeration) showing methane transport and cycling within the two aquifers and the confining unit on the island (b). The orange boxes and text show the position and rate of measured methanotrophy and the white box shows where no methanotrophy or methanogenesis was present. The

811 blue arrows show the dominant direction of groundwater flow in each aquifer, and the
812 blue text shows its average flow rate and residence time. The black text shows the CH₄
813 concentration. The rate of methanotrophy versus the residence time of groundwater for
814 the unconfined sandy aquifer (c) and the confined sandy aquifer (d). In each panel, the
815 solid black line represents the median CH₄ concentration and the dashed lines show the
816 IQR. These data came from October 2012 equilibration chamber measurements for the
817 unconfined aquifer, and the deepest well at the island center (TT-4, 3.7 meters) during the
818 2008-2010 survey for the confined aquifer. The tray polygons below these lines represent
819 the range of methanotrophy rates and groundwater residence times under which
820 groundwater-derived CH₄ discharge to the ocean is possible. Outside of that polygon,
821 groundwater is exposed to methanotrophy within the aquifer for enough time to
822 completely consume all of the CH₄ measured there. If the rate of methanotrophy and the
823 residence time for an aquifer plot below the line representing the CH₄ concentration
824 within that aquifer, then not all of the CH₄ in the groundwater will be consumed and the
825 potential for a positive flux of CH₄ to adjacent surface waters exist. The light orange
826 boxes in each panel represent the range of residence times calculated from the
827 groundwater flow model and the interquartile range of the measured methanotrophy rate
828 for each aquifer. Methanotrophy rates for the confined aquifer were not measured; these
829 values are displayed to show the hypothesized rates that could prevent CH₄ discharge to
830 the ocean under steady state conditions but allow it during storm-generated aquifer
831 flushing events.

Table 1

Table 1. Groundwater geochemical data for each well labeled in Figure 1c. In most columns, the median value is listed followed by the interquartile range in parenthesis. The temperature column contains the range between the minimum temperature recorded in the winter and the maximum temperature recorded in the summer. Dissolved oxygen concentrations are not presented here because they were assumed to be zero due to the scent of sulfide detected in all samples. Thirteen measurements of all parameters were made at most wells except for TT-6, 0.7 meters where only three measurements were made before the well was washed away. BDL = below detectable limit.

Loc.	Depth (m)	Salinity	Temp. (°C)	[CH ₄] (μM)	[DOC] (μM)	[SO ₄ ²⁻] (mM)	[SO ₄ ²⁻] _{DEP} (mM)	[H ₂ S] (μM)
Creek	N/A	31.2 (30.1-34.7)	11.4-32.3	0.8 (BDL-1.0)	481 (332-550)	25 (23-28)	0.2 (0.0-0.5)	BDL
TT-1	0.8	31.0 (28.9-33.7)	13.9-33.7	0.6 (0.5-1.9)	508 (325-615)	27 (25-29)	-0.2 (-1.0-0.2)	BDL
TT-1	2.2	33.8 (32.8-34.4)	17.4-25.9	4.1 (3.1-5.4)	416 (395-488)	28 (27-28)	-0.5 (-1.0-0.3)	BDL (BDL-2.3)
TT-1	4.7	37.3 (34.9-38.2)	19.8-24.7	13 (7.8-17)	845 (721-960)	28 (25-29)	1.8 (1.5-2.1)	2.8 (BDL-22)
TT-2	0.6	31.6 (30.7-34.5)	15.4-32.9	1.8 (1.1-4.1)	461 (404-611)	26 (25-28)	1.5 (0.3-2.0)	BDL (BDL-0.6)
TT-2	2.3	39.0 (35.8-39.9)	18.4-26.0	6.2 (3.8-8.8)	537 (477-554)	30 (30-31)	0.4 (-0.1-0.7)	BDL (BDL-3.1)
TT-2	4.6	38.2 (36.4-39.9)	19.4-25.1	19 (16-34)	971 (864-1010)	28 (27-28)	2.5 (2.2-2.7)	1.1 (BDL-5.3)
TT-3	0.7	43.0 (37.0-49.2)	15.0-33.0	2.4 (1.0-5.4)	936 (842-1020)	34 (29-38)	5.3 (3.1-7.2)	BDL
TT-3	1.8	30.9 (28.8-37.1)	17.3-27.2	29 (24-42)	1540 (1420-1590)	19 (16-20)	6.2 (5.7-6.7)	932 (198-1170)
TT-3	5.6	40.0 (38.1-41.7)	19.3-26.4	16 (13-27)	1060 (978-1130)	28 (27-29)	3.6 (3.3-3.9)	3.1 (BDL-14)
TT-4	1.6	1.0 (0.8-1.1)	15.1-38.8	326 (278-787)	1100 (1040-1330)	0.2 (0.1-0.3)	0.4 (0.2-0.4)	BDL (BDL-4.1)
TT-4	3.4	3.8 (3.1-6.4)	19.3-28.4	726 (566-1730)	2240 (1960-2860)	0.1 (0.1-0.2)	2.7 (2.1-4.1)	305 (115-626)
TT-5	2.4	4.2 (3.9-4.8)	16.4-27.9	285 (163-425)	1420 (1230-1530)	0.2 (0.1-0.4)	2.5 (2.2-2.9)	585 (137-2780)
TT-5	4.1	4.7 (4.4-4.9)	18.9-33.0	226 (150-335)	3340 (2490-3730)	1 (0.9-1)	2.3 (2.0-2.5)	1820 (372-2660)
TT-6	0.7	15.0 (10.5-19.0)	18.4-36.4	3.5 (1.3-8.1)	1180 (916-1450)	11 (7.5-12)	-0.6 (-1.2-0.9)	BDL
TT-6	1.7	21.0 (18.9-27.0)	12.6-28.6	4.5 (2.8-10)	299 (238-401)	16 (14-22)	-0.1 (-0.5-0.1)	BDL (BDL-4.1)
TT-6	3.7	22.1 (16.2-26.3)	15.2-31.4	5.6 (3.9-11)	369 (258-595)	18 (14-23)	-0.3 (-0.5--0.1)	5 (BDL-19)
TT-7	2.8	22.3 (21.0-24.0)	18.9-27.1	1.6 (0.8-4.2)	521 (368-662)	19 (17-25)	-0.1 (-0.2-0.1)	BDL (BDL-1.6)
Ocean	N/A	32.0 (30.7-34.0)	11.5-31.8	BDL (BDL-1.9)	279 (235-293)	27 (25-28)	0.2 (-0.1-0.2)	BDL

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6