TIDAL CREEK OXYGEN DEMAND DRIVEN BY SUBMARINE GROUNDWATER DISCHARGE ON SAPELO ISLAND, GA

by

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(Under the direction of Samantha B. Joye)

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

Introduction

A variety of naturally occurring ecosystems serve as long term sinks for atmospheric carbon dioxide. “Blue Carbon” refers to atmospheric carbon dioxide that is stored as organic carbon within marine environments (Nelleman et al. 2009, Laffoley 2009). Blue carbon systems such as salt marshes, seagrasses, and mangroves serve as carbon sinks due to their high primary productivity and rate of organic carbon burial. Although these ecosystems only account for 0.5% of all marine systems, they are responsible for sequestering over 50% of the marine organic carbon globally (Duarte et al. 2005, Mcleod et al. 2011, Krause-Jensen and Duarte 2016). Salt marshes and mangroves have an average carbon burial rate of over 200 g C $m^{-2}y^{-1}$, which is over forty times higher than organic carbon burial in temperate forests (Mcleod et al. 2011). Because they can store carbon in their soils and wood for hundreds of years, blue carbon systems are critical for climate change mitigation and should be prioritized in conservation efforts (Nelleman et al. 2009 and Laffoley 2009).

Salt marshes are coastal wetlands defined by seawater salinity and regular tidal inundation. Marshes provide ecosystem services including shoreline protection, nutrient removal, and carbon sequestration. Marsh carbon sinks include vascular plants that form marshes around sea level, brush and trees in the coastal upland for additional carbon sinks in marine environments. Salt marshes are intersected by tidal creeks and develop in areas where there is protection from high energy coastal waves, such as in bays or estuaries, and where soil accretion rates exceed sea level rise rates (Vernberg 1993, Chapman 1974). Salt marshes are found globally in both warm and cold environments. Salt marshes also provide habitat and nurseries for commercially important species , supporting biodiversity and coastal economies (Beck et al. 2001).

In Georgia, salt marshes cover approximately 368,000 acres, (Burns et al. 2020 and Burns et al. 2021)and they provide coastal protection and a number of key ecosystem services as noted previously. Marshes along the coast and on barrier islands are found parallel to the shoreline, with major salt marshes located along Sapelo Island, Cumberland Island, and in the Altamaha River Estuary. Georgia's coastal marshes are dominated by varieties of *Sporobolus,* a resilient grass species. The salt marsh grasses and the microalgae in light gaps and along the tidal creeks contribute significantly to marsh production, and this leads to large rates of carbon sequestration; the marshes along Sapelo Island sequester 75-85 g C $m^{-2}y^{-1}$ (Craft 2023) (Pomeroy 2003, Dai & Wiegert 1996). These high productivity marshes support a large biomass of both resident and transient fishery species (McLusky 1971). Georgia salt marshes are essential habitats that are crucial in the conservation of biodiversity and mitigating climate change.

Groundwater is defined as water that is found underground within the soil or within rock pores or fractures. Often groundwater is found within aquifers, a stratum of porous rock that is saturated with water. As groundwater moves through coastal aquifers, it undergoes biogeochemical transformations, accumulating dissolved organic matter, metals, and reduced species. Subterranean estuaries are places where fresh groundwater and seawater converge, mix, and interact with surrounding sediment within an aquifer ((Moore and Joye 2021, 2004, Moore et al. 2024, Slomp and Van Cappellen). The saline groundwater in subterranean estuaries is particularly nutrient-laden as the ionic strength of the fluid mobilizes recycled nutrients from the solid phase and *in-situ* organic matter remineralization further increases nutrient concentrations in groundwater (Santos et al. 2009, Wilson 2005).

Submarine groundwater discharge (SGD) supplies nutrients and drives biogeochemical cycling in coastal ecosystems. Submarine groundwater discharge encompasses all water flow from the seafloor to the coastal oceans, including shallow porewater exchange (Moore 2010). While the fluid flux of SGD is on par with riverine flux, SGD often contains higher nutrient concentrations, making it a more important nutrient source to coastal waters (Church 1996, Moore 2010, Moore et al. 2008, Santos et al. 2021). Submarine groundwater discharge frequently contains high concentrations of dissolved nitrogen, and since nitrogen is often the limiting nutrient in the coastal oceans, SGD-derived nutrients can stimulate primary production (Santos et al. 2021).

There are two potential pathways through which SGD impacts the oxygen demand (OD) in coastal waters. First, oxidation of groundwater-derived organic matter (OM) drives oxygen consumption, and second, oxidization of groundwater-derived reduced species consumes oxygen. Furthermore, discharge of anoxic groundwater reduces the oxygen content of tidal creeks by dilution of oxygenated creek water; this impact is particularly significant when low tides occur at night. The aerobic decomposition of SGD-derived OM consumes oxygen and produces CO_2, and it is well documented that high respiration/OM oxidation events can lead to low oxygen events in coastal systems (Rabouille et al. 2008, Rabalais et al. 2014, Su et al. 2017). Similarly, oxidation of SGD-derived reduced constituents can drive high rates of oxygen consumption (Moore et al. 2024). The term SGD-oxygen demand (SGD-OD) refers to the oxygen demand resulting from SGD inputs to coastal systems (Moore et al. 2024).

Within coastal aquifers, as organic matter degrades, the groundwater becomes oxygen-depleted and enriched in reduced metabolites. Discharge of anoxic groundwater into coastal ecosystems sometimes induces hypoxia (Peterson et al. 2016, Guo et al. 2020). Introduction of reduced species, such as H_2S, Fe(II), CH_4 and NH_4^+, into coastal waters has potentially important impacts. These reducing agents undergo abiotic and/or biotic oxidation reactions, consuming oxygen. While the full impact of this mechanism is unclear, model calculations suggest that the SGD-OD could drive a substantial fraction of the oxygen demand in tidal creeks (Moore et al. 2024). While SGD-OD could be a key driver of coastal oxygen cycles, its full impacts are unclear, underscoring the need for further research.

Submarine groundwater discharge and SGD-OD are controlled by a combination of regional geology, hydrogeologic conditions, and dynamic coastal factors such as waves, tides, and winds. Pressure changes are important drivers as groundwater travels along the hydraulic gradient and theoretically discharges wherever the hydraulic head exceeds sea level. The hydraulic gradient depends on pressure changes from factors including tides, precipitation (extreme flooding), groundwater extraction, and evapotranspiration. The coast generally has lower pressure than the higher elevation inland aquifer, and this facilitates groundwater discharge. On the East Coast, aquifers are often unconstrained, shallow, and permeable, making nearshore seepage common (Gallardo and Marui 2006). Pressure fluctuations driven by wind, waves, and bottom currents can also drive SGD (Shum and Sundby 1996, Vincent et al. 2025). While tides can significantly impact SGD, the extent of their influence depends on the regional geology (Burnett et al. 2006). At high tide, seawater infiltrates sediments, creating a circulation cell that drives the return flow of groundwater at low tide (Robinson et al. 2009). Coastal wind fields can also drive SGD (George et al. 2020, Vincent et al. 2025). When SGD is substantial, it may influence nearshore OD considerably. This effect is particularly pronounced in areas with permeable sediments, and especially in fracture-dominated aquifers and karst aquifers (Gallardo and Marui 2006).

Little is known about how groundwater-derived constituents impact the oxygen demand in coastal waters. This study aimed to determine whether groundwater is an important driver of oxygen consumption in nearshore coastal systems. Originally, it aimed to determine whether the groundwater-derived biological oxygen demand is greater than the groundwater-derived abiotic oxygen demand, but this was not accomplished. This study consisted of a mixing ratio experiment where groundwater (GW) and creek water (CW) from Sapelo Island were combined within Hungate tubes in ratios of 100% GW, 75% GW:25% CW, 50% GW:50% CW, 25% GW:75% CW, and 100% CW. An additions experiment was also performed, where creek water was amended with common reductants in coastal Georgia GW, methane, sulfide, iron (II), dissolved organic carbon, and ammonium. Samples for both experiments were incubated over a time series and then a membrane inlet mass spectrometer (MIMS) was used to determine the oxygen concentration in each sample. I hypothesized that 25% to 50% GW:CW would have the largest oxygen consumption rate. Adding excess low-oxygen groundwater can create a low-oxygen environment, leaving less oxygen that can be consumed and resulting in lower oxygen consumption. Oxidation rates slow down as oxygen concentrations decrease. For the addition experiment, I hypothesized that DOC NH_4^+, and H_2S would have the largest oxygen consumption as they have significant oxidation potential. These are high-energy, labile compounds that are often abundant in salt marsh ecosystems. Estimates of DO consumption on Sapelo Island by Moore et al. 2024 indicated that DOC, NH_4^+ , and H_2S were the primary contributors to oxygen drawdown. Although Fe(II) and CH_4 are important reductants, they can be affected by both biotic and abiotic oxidation. Fe(II) can be regulated by mineral precipitation and pH. CH_4 has a low solubility in the aqueous phase, which can facilitate its escape to the atmosphere. A literature review was also conducted to estimate potential oxygen consumption due to reductant loading from submarine groundwater discharge at nine sites. These sites were chosen because they had published submarine groundwater fluxes and at least two reductant concentrations. Potential oxygen consumption was determined by multiplying the reductant concentrations by the mols of oxygen needed to oxidize it completely. The submarine groundwater discharge flux was then used to determine the potential mols of oxygen consumed within a day. Together the experiments and literature aimed to assess how submarine groundwater discharge can influence the oxygen dynamics within coastal ecosystems due to the introduction of reductants.

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CHAPTER 2

TIDAL CREEK OXYGEN DEMAND DRIVEN BY SUBMARINE GROUNDWATER DISCHARGE ON SAPELO ISLAND, GA

Methods

Study Site

Sapelo Island, GA is a barrier island off the coast of Georgia (Figure 1). Sapelo Island is tidally affected by diurnal tides ~2.1m. Two study sites, Moses Hammock and Cabretta Island, were selected on Sapelo Island. Moses Hammock is a small hammock next to the Duplin River on the northwest side of the island; the area is used seasonally for hunting. Cabretta is a small island with a tidal creek and marsh on the southeast side of the island. These sites were selected for access to groundwater monitoring wells, tidal creeks, and available data from previous studies characterizing groundwater biogeochemistry. Groundwater discharge rates into tidal creeks have been reported for these two study sites (Porubsky et al. 2009, Wilson et al. 2011, Shutte et al. 2015, Shutte et al. 2016, Peterson et al. 2019).

Figure 1. Map of Sapelo Island with insets showing Moses Hammock and Cabretta Island. Map generated using CalTopo.

Field Sampling

Samples for laboratory experiments were collected in September, October, and November 2024. September sampling was impacted by Tropical Storm Ernesto, which impacted the area ~1.5 weeks before collection. The October sampling campaign was impacted by Hurricane Helene, which impacted the area around 1 week before collection. Large storm events can impact the groundwater discharge by changing the pressure gradient and altering discharge of nutrients into the tidal creek (Wilson et al. 2011). Groundwater samples were collected using a peristaltic pump and plastic tubing. Groundwater was collected from the well closest to the creek at each location and stored in headspace free 1L Nalgene polyethylene terephthalate glycol (PETG) bottles. Cabretta groundwater was collected from well TT1-5, which is a 5 meter deep well adjacent to the creek. The screened interval was flushed for 15 minutes before sample collection. Samples were also collected for quantification of nutrients and redox metabolites. Ammonium samples were collected in 10 mL centrifuge tubes containing 200 µL of phenol to halt microbial activity. Sulfide sample tubes contained 100 µL of 20% wt./vol zinc acetate to trap hydrogen sulfide as zinc sulfide. Creek water was collected and stored in headspace-free 1L PETGs. All water samples were stored at +/- 5 ºC of collection temperature.

Laboratory experiments

Every effort was made to maintain sample integrity – specifically, by preventing oxygen contamination of the samples. This was critical to ensure that the experiments would simulate *in-situ* conditions. Two experiments were executed, a mixing ratio experiment and an additions experiment.

Mixing Ratio Experiment

The mixing ratio experiment involved combining groundwater (GW) and creek water (CW) in different ratios in ~17 mL Hungate tubes: 100% GW, 75% GW, 50% GW, 25% GW, and 100% CW. Triplicate samples were prepared for each ratio at each time point, 0 hr, 24 hr, and 36 hr. Both groundwater and creek water were transferred from sample PETGS to experimental tubes using a modified Widdel flask assembly (Sibert 2021). A stopper with two ports was inserted into the PETG bottles. One port was attached to a N_2 gas cylinder, and the other to a silicone tube with a stopcock, which was connected to a glass 1 mL pipette inside the bottle. N_2 gas flowed constantly into the bottle to create sufficient overpressure to force a water sample into the experiment tube while minimizing atmospheric contamination.

Six nitrogen-purged 50 mL syringes were used to prepare experimental samples. Three syringes were needed per ratio because all replicates and time points were prepared together. Three syringes were used for groundwater and the other three were for creek water. Syringes were attached via a nitrogen-purged stopcock, and water was exchanged between the syringes approximately six times to ensure thorough mixing. The final mixture was dispensed as quickly as possible into the Hungate tubes using silicone tubing, sealed with a black rubber stopper, and then the sample tubes were capped.

For example, to prepare a 50:50 GW:CW sample, a slight excess of 18 mL of combined water was required per Hungate tube to ensure it was filled completely. The total for the treatment was 54 mL of mixed solution (18 mL x 3 replicates) for each 50 mL syringe per time point. 27 mL of each groundwater and creek water were measured into their respective syringes and mixed. For 100% groundwater and creek water, a 5 mL syringe was used to measure the additional 4 mL needed to achieve 54 mL total volume. The same procedure was followed for the rest of the treatments.

The mixing ratio samples were incubated at +/- 5 ºC of *in-situ* temperature. For September and October samples, the time 0 samples were killed with 100 µL of zinc chloride immediately after all samples were filled and run on a Membrane Inlet Mass Spectrometer (MIMS) to determine oxygen concentrations at a later point in time. The 24 hr and 36 hr samples were killed at their respective times. The time between killing samples and analyzing the samples was 1-2 weeks. For November, mixing ratio samples were prepared and the samples were analyzed immediately after incubations were terminated. These samples did not have the potential for oxygen to be consumed abiotically before sample analysis, which created a storage artifact for the September and October samples.

A membrane inlet mass spectrometer (MIMS) is a versatile instrument used to quantify the concentration of dissolved gases in water. For these experiments, the instrument quantified the change in O_2 concentration by tracking changes in the O_2/Ar ratio over time. Argon is a biologically inert gas, so the O_2/Ar ratio is a robust way to quantify biological oxygen production or consumption. The mass spectrometer in the MIMS is a quadrupole instrument that employs a vacuum and a semi-permeable membrane to introduce gasses into the instrument. A quadrupole mass spectrometer does not have a flight tube; it uses a quadrupole mass filter comprised of four parallel rods to which voltages are applied. This design separates ions based on the mass-to-charge (m/z) ratio.

Reductant additions experiment

The reductant addition experiment involved adding 500 µM of various reductants to creek water in ~17 mL Hungate tubes. Triplicates were prepared for each time point: 0 hr, 36 hr, and 72 hr. The following reductants were used - NH_4^+ (solution prepared from reagent grade ammonium chloride), Fe(II) (prepared using reagent grade Fe(II) chloride), CH_4, H_2S (prepared from reagent grade sodium sulfide), and an equimolar mixture of reagent grade sodium lactate and sodium acetate to mimic dissolved organic carbon in groundwater. The methane solution was made by purging de-oxygenated milliQ with methane gas. Methane and sulfide solutions were freshly prepared each time the experiment was performed.

Creek water was measured into syringes using the same procedure described above for the mixing ratio experiment. Reductant solutions were added to the creek water syringe using a 3 mL syringe, except methane additions, which required a 10 mL syringe. The mixture of creek water and reductant was transferred between the creek water syringe and an empty, nitrogen purged syringe.

The samples were incubated for 0, 36, and 72 hours. Longer incubation times were used to ensure that oxygen drawdown would have time to occur; this is especially important for biological oxidation processes. For September and October experiments, the time 0 samples were killed with 100 µL of zinc chloride and run on a Membrane Inlet Mass Spectrometer (MIMS) at a later point in time. For November, the addition samples were prepared and run on the MIMS right away, eliminating the potential for oxygen consumption during storage.

This experiment involved three caveats. First, the addition solutions for NH_4^+, Fe(II), and DOC were not de-oxygenated before being added to the creek water, meaning that oxygen was added to samples along with the reductant into the vials. The amount of oxygen can be constrained to some extent by comparing the 100% creek water oxygen concentrations at time 0 to the treatments with oxygenated reductant time 0. Second, *in-situ* concentrations of most reductants in nature are not as high as the concentrations used in these additions; high concentrations were used to ensure that oxygen consumption was detectable. Third, concentrations of reductants were not tracked in the experiments which made it impossible to quantify the stoichiometry of oxygen consumption versus reductant oxidation.

Field samples of groundwater and creek water for determining ammonium concentrations were run within 1 week of sample collection. NH_4^+ concentrations were determined using a colorimetric method (Solorzano 1969) and run on a Shimadzu UV-1601 Spectrophotometer. Samples used to determine sulfide concentrations were run within a month of sample collection using a colorimetric method (Cline 1969) with samples run on a Shimadzu UV-1601 Spectrophotometer. Fe(II) concentrations were determined using a colorimetric method (Sorensen 1982). These analyses had a detection limit of 0.1 µmol/L. Groundwater methane and DOC samples were collected but those samples were never run.

Literature review

A literature review was conducted to assess the potential oxygen demand resulting from the introduction of reductants through submarine groundwater discharge. Nine locations, Neuse River Estuary, NC, Okatee River, SC, NW Florida, Delaware Inland Bays, Sydney Harbor, AUS, Bay of Puck, Poland, South Bay of Bengal, and Argentona, Catalonia, were selected because both reductant concentration and SGD flux data were available. These estuaries vary in size and environment from small, enclosed bays such as the Delaware Inland Bays, to larger coastal systems such as the Bay of Bengal. Each location's minimum reductant concentration was used and converted to µM. The SGD flux was converted to m^3/d for all locations.

The dissolved oxygen reduction potential for reductants was calculated by multiplying the moles L^{-1} of the reductant by the moles L^{-1} of oxygen required to oxidize it (eq 1). Two moles L^{-1} of oxygen are required to oxidize 1 mole of NH_4^+, H_2S, and CH_4 L^{-1}. I assumed that 1% of the DOC will be oxidized within several days because Moore et al. (2024) assumed that 15% of the DOC reacted on a 2-4 day time scale; I assumed that 10% of the NH_4^+ will be oxidized per day; this reflects the amount of NH_4^+ used in the reductant additions experiment, and the potential of CH_4 oxidation was deceased by 60% due to the chance of CH_4 escaping to the atmosphere in shallow systems (Moore et al. 2024). A quarter of a mole of oxygen is required to oxidize one mole of Fe(II) to goethite. The DO reduction potentials were summed for each location where data was available even if only a subset of reductants was available for a given site. This means that the reductant load for the sites considered is not the same.

$$Dissolved\ Oxygen\ Reduction\ Potential = \sum(Reductant\ concentration * mols\ O_2\ required\ to\ oxidize) \quad (1)$$

$$Submarine\ groundwater\ discharge\ reductant\ loading = (\sum of\ OD\ potential * SGD\ flux) \quad (2)$$

Reductant loading from submarine groundwater discharge was calculated by multiplying the ∑ DO reduction potential by the SGD flux to yield a submarine groundwater oxygen demand (SGD-OD) rate for the estuary in mol/d (eq 2). The SGD-OD flux was then divided by 24 hours to calculate the SGD-OD rate in mol/hr. This number reflects reductant loading and its potential oxygen demand. There is no way to know how much of the reductant load is oxidized by aqueous dissolved oxygen.

This method was also used to scale up the SGD-OD for Sapelo Island using Moses Hammock and Cabretta reductant concentrations and SGD flux for the Cabretta Island shoreline and the Duplin River (Table 1). Maximum and minimum SGD-OD rates were calculated; minimum and maximum rates calculated using the smallest and largest published reductant concentrations from Shutte et al. 2020.

Table 1. Maximum and Minimum concentrations of reductants in Moses Hammock and Cabretta creek and groundwater. From Shutte et al. 2020.

Reductant	**Minimum Moses Hammock GW (µmol /L)**	**Maximum Moses Hammock GW(µmol /L)**	**Minimum Cabretta GW (µmol /L)**	**Maximum Cabretta GW(µmol /L)**
Fe(II)	0.6	0.6	1	12.8

DOC	305.0	2784.6	419.8	1157.0
H2S	0	0.15	0	196.6
NH4+	18.7	44	63	196.03
CH4	0.1	0.75	4.8	30

Results

Experimental Problems

Geochemistry samples for each time-point were not collected during these experiments; this was a mistake and made it difficult to constrain how much of the OD was due to the specific substrate added. In order words, it is impossible to know how the measured oxygen consumption is related to changes in reductant concentration. The difference between abiotic and biotic oxygen consumption cannot be parsed from the data available. A major improvement would be collecting geochemistry samples at every time point. Another improvement would be de-oxygenating all of the addition solutions.: After calculating oxygen concentration at the different time points, I observed that some samples had higher oxygen concentrations at the last time point, compared to the middle time point. In the presence of no oxygen consumption, oxygen concentrations should be stable over time. Increased oxygen concentration requires photosynthesis, which could not have happened during these dark incubations. The most likely explanation for the observed oxygen increase is that the tubes for the final time point were not sealed properly. Measuring H_2S and Fe(II) amended samples immediately was critical for understanding the kinetics of abiotic oxidation of these reductants. It would be beneficial to measure oxygen concentrations in sulfide and iron (II) amended samples with instrumentation, such as optical oxygen sensors or oxygen microelectrodes, which can effectively track the decrease in oxygen concentration continuously over time. Given the problems with the September and October data due to the time lag between treatment implementation and sample analyses, only November samples are considered here because those samples were analyzed immediately.

Mixing ratio experiment

Cabretta and Moses Hammock creek water contained more oxygen than did groundwater from the respective sites, and groundwater had higher nutrient and reductant concentrations than creek water. For Cabretta, November samples had detectable oxygen concentrations with a groundwater oxygen concentration of 29.02 µmol/L and creek water oxygen concentration with 127.99 µmol/L. For Moses Hammock, the creek water oxygen concentration was 148 µmol/L and the groundwater oxygen concentration was 89 µmol/L.

Cabretta's intermediate mixing ratios followed the expectant gradient – samples with more creek water had higher oxygen concentrations (Figure 2). All samples showed significant oxygen consumption at 24 hours and concentrations continued to decrease at the 36 hr time point. The 50% GW samples, followed by 75% GW samples, had the highest oxygen consumption rate with a maximum of 3.2 µmol/L/h and 2.54 µmol/L/h, respectively. These results demonstrate that oxygen consumption rates are influenced by mixing ratios and incubation time, with peak consumption occurring at 25%-50% GW ratios within the first 24 hours of incubation.

Figure 2. Oxygen concentrations plotted for Cabretta Island mixing ratio samples.

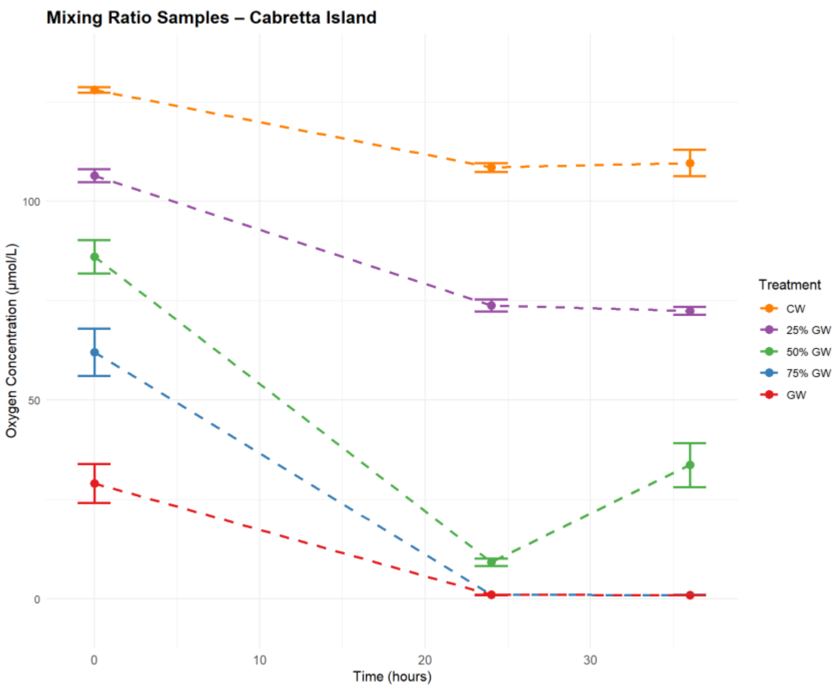
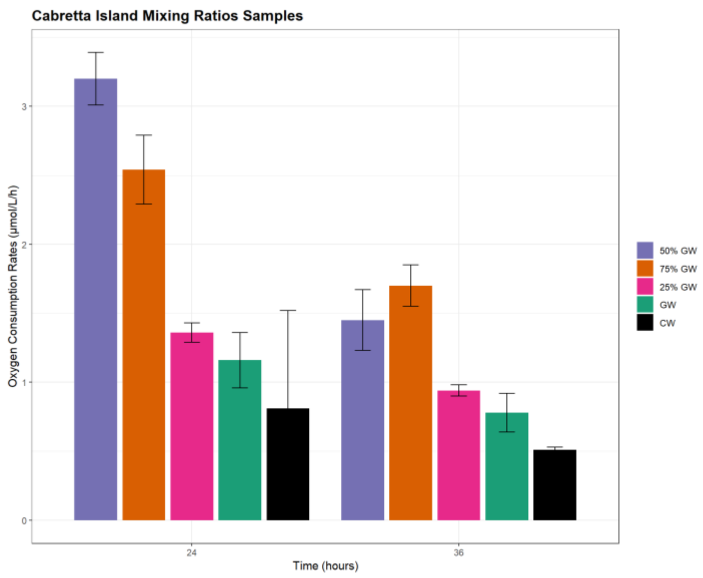


Figure 3. Oxygen consumption rate plotted for Cabretta mixing ratio samples across September, October, and November.



Moses Hammock samples were slightly different from Cabretta samples, as the oxygen concentrations did not consistently align with the proportion of creek water in the sample. In November, the samples that had the highest oxygen concentrations after 36 hours were the 25%

groundwater samples (Figure 4). Oxygen consumption rates samples followed a similar trend to Cabretta with oxygen consumption being maximal at 24 hours and decreasing at 36 hours (Figure 5). November 75% mixing ratio samples had the highest oxygen consumption rate, with November's sample maxing at 2.23 µmol/L/h. It should be noted that GW consumption was negative at 36 hours – this is an artifact. Either there was a momentary issue with the MIMS or there was oxygen contamination of the sample tubes due to tubes not being completely sealed. Overall, Moses Hammock samples were less predictable across mixing ratios than Cabretta.

Figure 4. Oxygen concentrations are plotted for Moses Hammock mixing ratio samples.

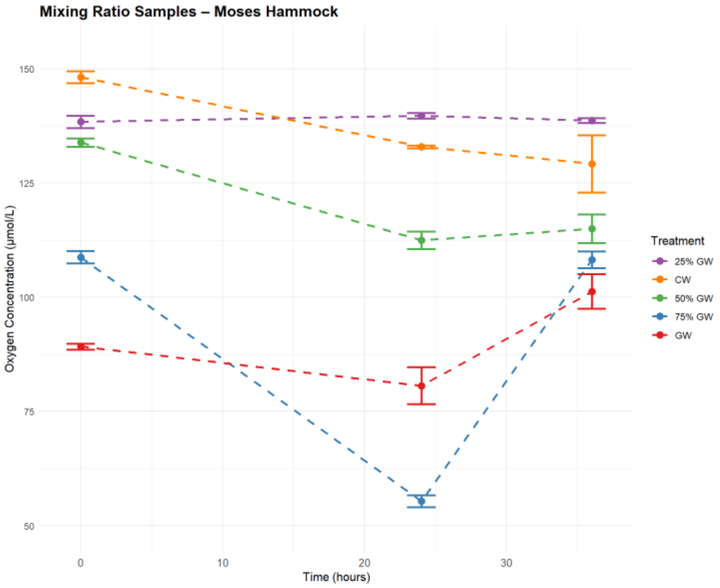
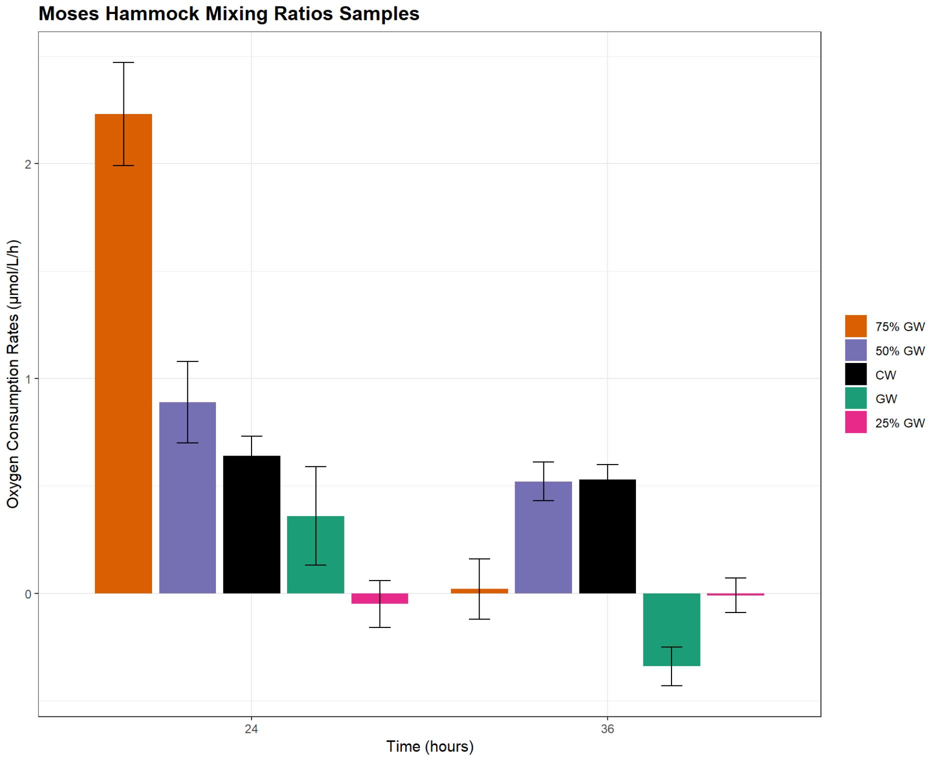


Figure 5. Oxygen consumption rates plotted for Moses Hammock mixing ratio samples.



Reductant Additions

Cabretta reductant addition samples followed the expected trend. For Cabretta, DOC, H_2S, and CH_4 amended samples supported the highest oxygen demand. Fe(II) also supported high rates of oxygen consumption (Figure 6). NH_4^+ amended samples had the highest oxygen concentration after 72 hours. For all months, DOC amended samples had the highest oxygen consumption rate, with the maximum being in November of 5.04 µmol/L/h (Figure 7). Some reductant addition samples started with higher oxygen concentrations than creek water because these additions were not de-oxygenated, so they added some oxygen to the treatment tubes.

Figure 6. Oxygen concentrations plotted for Cabretta Island reductant additions samples.

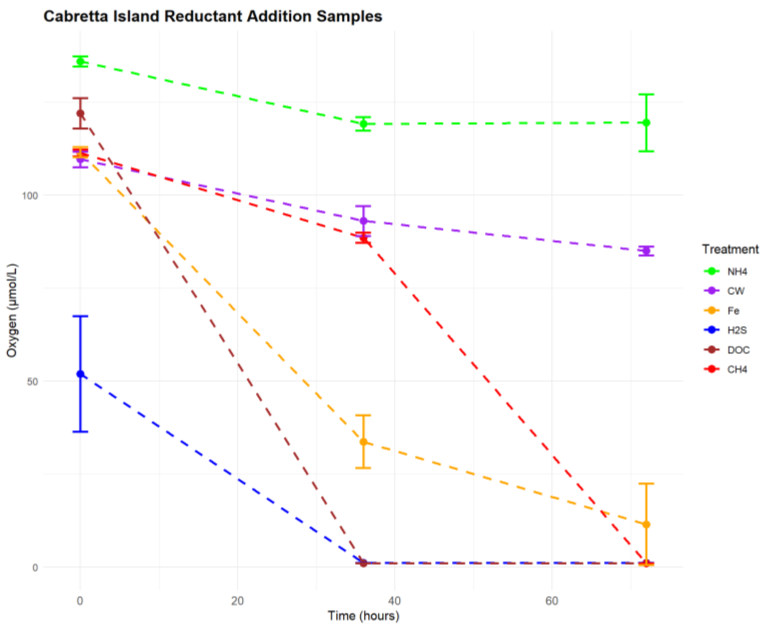
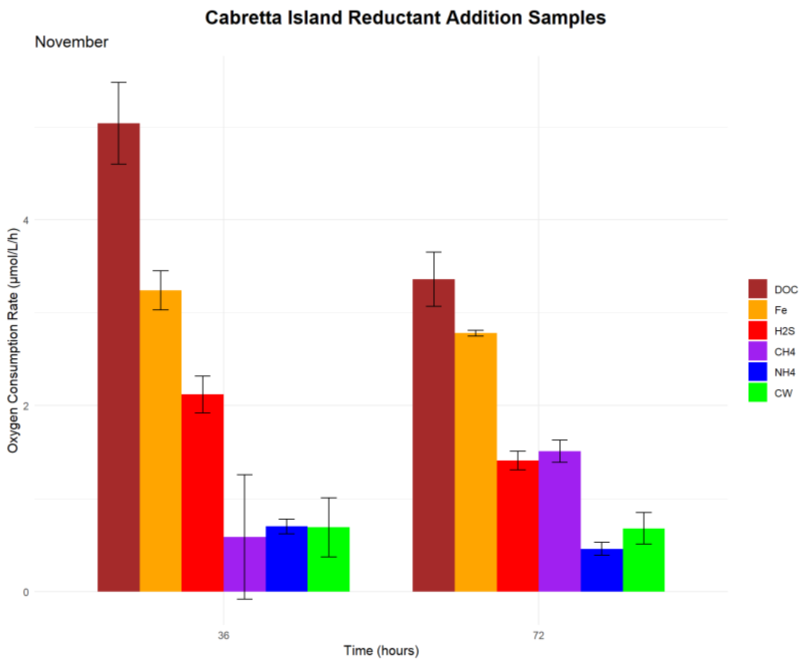


Figure 7. Oxygen consumption rate plotted for Cabretta Island reductant additions samples.



Moses Hammock showed similar patterns to Cabretta in that DOC and H_2S additions supported consumption of almost all of the available oxygen by the 72-hour time point (Figure 8).

Fe(II) additions also supported significant oxygen consumption. A major difference between sites was observed with methane: methane addition did not support significant oxygen demand at Moses Hammock. In fact, CH_4 amended samples had higher oxygen concentrations than CW. NH_4^+ amended samples consistently maintained the highest oxygen concentrations across all time points. It should be noted that there was oxygen added to the these samples because the ammonium solution was not de-oxygenated. Fe(II) supported the highest rates, with a maximum of 2.15 µmol/L/h (Figure 9). In contrast to Cabretta samples, the addition of CH_4 resulted in minimal oxygen depletion, with CH_4 treatments supporting some of the lowest oxygen consumption rates during those months. DOC, H_2S, and Fe(II) were consistently strong drivers of oxygen consumption, but methane was more variable and lagged.

Figure 8. Oxygen concentration plotted for Moses Hammock reductant additions samples.

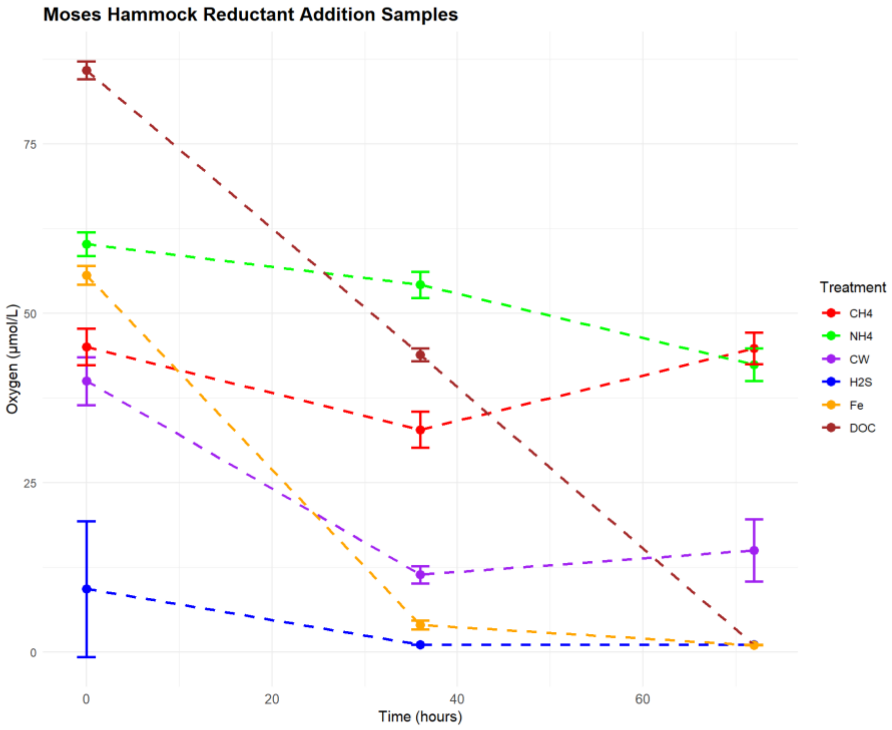


Figure 9. Oxygen consumption rates plotted for Moses Hammock reductant additions samples.

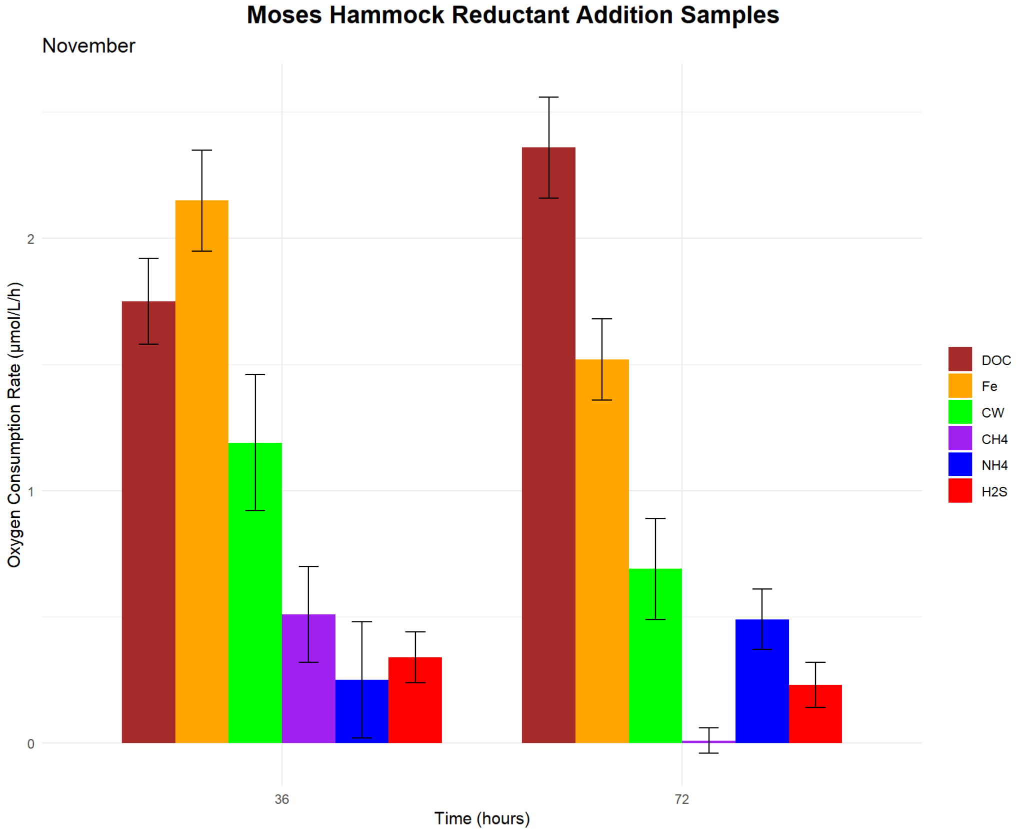


Table 2. Minimum potential oxygen demand due to reductant concentrations at nine separate locations.

Place	∑ Potential-OD (mol/ m^3)	SGD Flux (µmol/ m^3)	SGD-OD Rate (mol/d)	SGD-OD Rate (mol/yr)
Cape Cod, MA[1]	271,494	37,000	1.00E+04	3.67E+06
Neuse River Estuary, NC[2]	443	1,036,800	4.60E+02	1.68E+05
Okatee River, SC[3]	126,840	86,400	1.10E+04	4.00E+06
NW Florida[4]	54,680	3,400	1.86E+02	6.79E+04
Delaware Inland Bays[5]	10,400	397,440	4.13E+03	1.51E+06
Sydney harbor, Aus[6]	2,437	780,000	1.90E+03	6.94E+05
Bay of Puck[7]	9,346	1,382,400	2.43E+05	8.88E+07
South Bay of Bengal[8]	32,735	5,338,809	4.53E+04	1.65E+07

Argentona, Catalonia (Spain)[9]	1,797	910,000	2.66E+01	9.71E+03

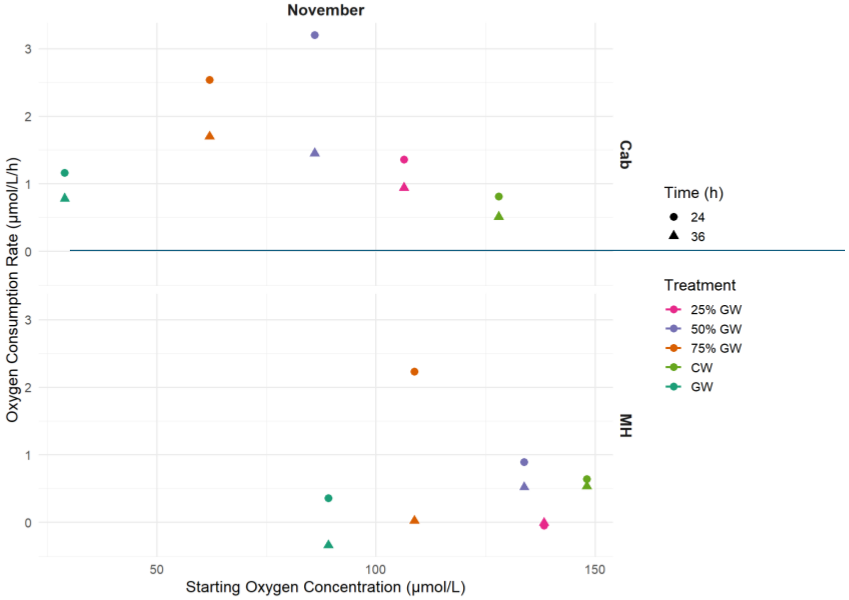
Data was sourced from the following references: (1) Charette et a. 2001. Frimpter and Gay, 1979. Pabich et al. 2022. (2) Spruill and Bratton 2008. (3) Moore et al. 2021. Porubsky et al. 2022. (4) Santos et al. 2023. Bugna et al. 2023. (5) Sawyer et al. 2021. Bratton et al. 2020. (6) Correa et al. 2020. Sadat-Noori et al. 2018. (7) Klostowska et al. 2019. Szymczycha et al. 2020. Von Ahn et al. 2024. ((8) Zhou et al. 2019. Prakash et al. 2020. Kumar et al. 2024. (9). Diego-Feliu et al. 2022. Goyetche et al. 2022. Ruiz-González et al. 2022. Calderer et al. 2010.

The literature review indicates that submarine groundwater discharge has the potential to contribute substantially to oxygen demand across a range of estuarine systems, as suggested by Moore et al. (2024). For most areas assessed in the review, the oxygen consumption rate is above 1,000 mols/d for the estuary system (Table 2). Northwest Florida had the lowest SGD-OD flux of ~115 mol/day due to lower rates of submarine groundwater discharge rates. Delaware Inland Bays had the highest SGD flux and the highest SGD-OD flux of 1.15 x 10^5 mol/day. The primary productivity of the Bay of Puck is 5.9 x 10^9 mol O_2/y (Kruk-Dowgiałło and Szaniawska 2008) and SGD-OD is on the order of 10^7 mol O_2/y. These calculations suggest that in many coastal systems, submarine groundwater discharge influences oxygen dynamics.

Discussion

Oxygen consumption rate patterns varied between Moses Hammock and Cabretta samples, driven by differences in *in-situ* reductant concentrations and site-specific biogeochemical dynamics. Cabretta samples exhibited higher oxygen consumption rates, and 50% and 75% GW treatments dominated. A similar pattern was observed with Moses Hammock samples in November, where the 75% GW samples had the highest oxygen consumption rates (Figure 10).

Figure 10. Initial oxygen concentration vs oxygen consumption rate. Circles are 24 hr and triangles are 36 hr.



The experimental results partially supported predictions about which mixing ratio and reductant concentration would lead to the highest oxygen demand. While it was predicted that 25% - 50% GW samples would support the greatest oxygen consumption rates, 50%-75% GW samples for Cabretta and Moses Hammock generated the highest oxygen consumption rate. The initial oxygen concentration in the November Moses Hammock 75% GW samples were ~108 µM, while the 25% and 50% GW Cabretta samples were ~47 µM and ~86 µM. The prediction that DOC, CH_4, and H_2S would result in the largest oxygen consumption was partially supported: DOC and H_2S amended samples supported high consumption for both sites, but elevated oxygen consumption from CH_4 was only observed in Cabretta samples across all months.

Ammonium oxidation supported the lowest oxygen drawdown among all reductants used in the reductant additions experiment. Assuming all observed oxygen consumption in the ammonium treatments was due to ammonium oxidation, average oxidation rates over 72 hours were calculated. On average, Moses Hammock had an ammonium oxidation rate of 4.17 µmol/L/d and Cabretta 4.39 µmol/L/d. These rates are higher than nitrification rates measured in a Chesapeake Bay subterranean estuary (0.366-1.09 µmol/L/d ; Wilson et al. 2024) and North San Francisco Bay (0.150 µmol/d; Damashek 2016), but lower than rates reported within Cabretta Beach pore water (23.5 ± 3.60 µmol/L/d; Shutte et al. 2017). Aerobic ammonium oxidation requires 1.39 µmol O_2/µmol N to occur (Liu and Wang 2012), and oxygen concentrations in the experimental samples for the most part exceeded this requirement. Although the added ammonium had an OD potential of 1000 µM O_2 because the concentration of NH_4 was 500 µM, observed oxygen drawdown was significantly lower. Ammonium concentrations measured at the end of the reductant additions experiment showed that approximately 50 µM of ammonium was consumed over 72 hours, which would theoretically result in 100 µM of oxygen consumption. However, oxygen consumption for the ammonium additions was less than 50 µM, suggesting that much of the ammonium was assimilated into biomass rather than oxidized. These findings indicate that most of the added ammonium remained unused within the samples, and that assimilation – not aerobic oxidation – was the dominant pathway for ammonium uptake.

The oxidation of methane exhibited a noticeable lag compared to the other reductants, suggesting a smaller methanotrophic population and/or slower microbial activity rates. Unlike the rapid oxidation of sulfide or iron, oxygen consumption supported by methane additions did not peak until after 36 hours. This delayed response may reflect slower activation or growth of methanotrophic communities, previous studies have reported a lag of around 21 days in offshore waters. All Cabretta samples amended with CH_4 exhibited low oxygen concentrations after 72 hours. In contrast, for November, the oxygen consumption due to the addition of methane was minimal. These results raise the question of whether longer incubation times would be necessary to capture the full extent of methane oxidation, especially in Moses Hammock. The methanotrophic community could be more robust in Cabretta, where higher *in-situ* methane concentrations could prime the microbial community. Overall, the observed lag in oxygen consumption and variability between sites suggest that the oxidation of methane is variable and influenced by differences in microbial communities and environmental conditions.

Submarine groundwater discharge introduces nutrients and reductants into coastal systems, and these inputs can substantially influence oxygen dynamics within surface waters. Based on maximum and minimum groundwater reductant concentrations (Shutte et al. 2020) in Moses Hammock and Cabretta Island, the estimated SGD-OD rates were calculated. The minimum and maximum SGD-OD rates for Moses Hammock are 1.14×10^5 mol/yr and 7.41×10^5 mol/yr. The minimum and maximum SGD-OD rates for Cabretta are 1.92×10^4 mol/yr and 3.70×10^5 mol/yr. The minimum hourly rates of ~26 mol/hr for Moses Hammock and 4.39 mol/hr for Cabretta are more likely to be representative of the actual SGD-OD. This is using a SGD rate of 4.2×10^3 m^3/d for the Cabretta Island creek (Evans and Wilson 2017) and 6.19×10^4 m^3/d for the Duplin River (Peterson et al. 2019). For context, the estimated respiration rate for the Sapelo Island Estuary is 43 mols/m^2 marsh/y (Wang et al. 2018). Extrapolating the estimated respiration rate leads to a respiration rate for the Duplin River of 4.26×10^7 mol/y and for the Cabretta creek of 1.81×10^5 mol/y. The Cabretta SGD-OD estimates are similar to the creek respiration, but the respiration of the Duplin River is two orders of magnitude higher for Moses Hammock. These estimates do not account for the complex dynamics of a coastal system including seasonal variability, variations in SGD during storm events, or decreased oxygen consumption rates with lowering oxygen concentrations. I assumed that 1% of the DOC is labile, while this could be smaller in the environment. While unconstrained oxygen consumption is important, there is enough oxygen in the tidal creeks to support oyster communities and large fauna like dolphins, which suggests that the SGD-OD estimates are higher than the actual creek respiration rates. Extrapolating to a year does not reflect changes in tidal and storm dynamics, possible variability in SGD, and surface water-atmosphere interactions. These experimental results also do not distinguish between biotic and abiotic oxygen demand. Given that SGD is tidally driven and can occur multiple times daily, it likely contributes to recurring low-oxygen events in nearshore and tidal creek environments. Anthropogenic influences are a major concern, as runoff from agriculture and groundwater contamination can both cause oxygen depletion. These findings highlight the potential for SGD – especially when influenced by anthropogenic nutrient and contaminants - to exacerbate oxygen depletion in coastal systems and exert negative impacts on estuarine health.

SGD-OD broader view

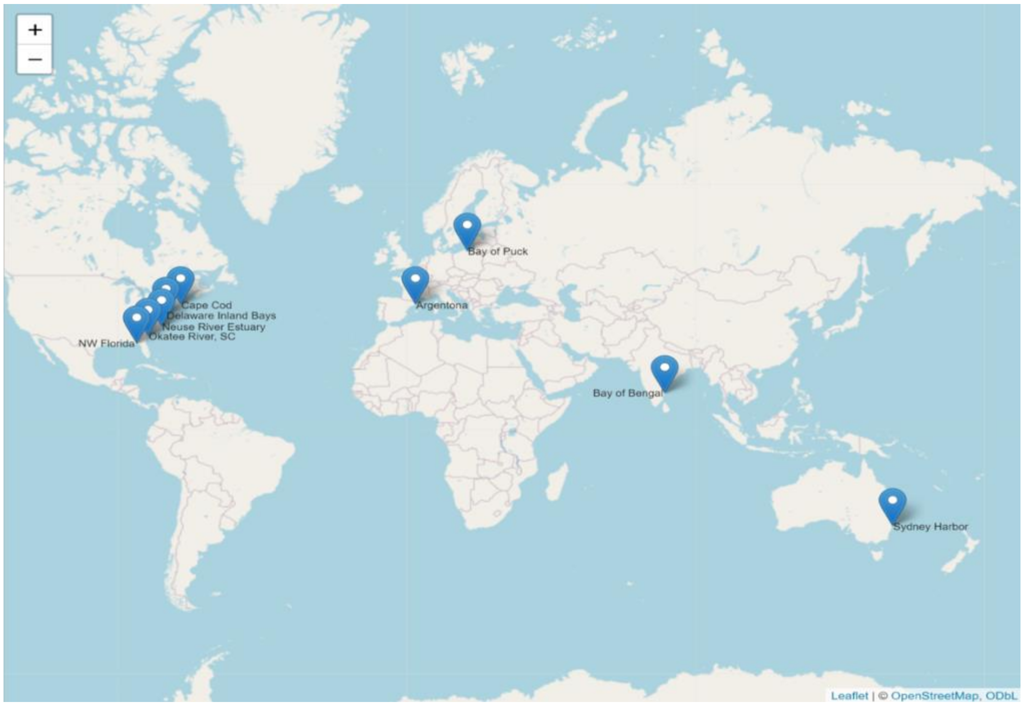
To address the limitations of the experimental dataset and advance the understanding of the role of submarine groundwater discharge on coastal oxygen demand, a literature review was conducted. This review modeled the approach of Moore et al. (2024), who estimated submarine groundwater discharge oxygen demand (SGD-OD) due to inputs of reductants H_2S, NH_4^+, CH_4, and DOC. To build on this framework, I expanded the reductant list to also include Fe(II), when available, and aimed to estimate SGD-OD due to the flux of reductants in different estuary locations globally.

Sites were selected based on two criteria: availability of published reductant concentrations and reported SGD fluxes. Nine locations were chosen to compare the potential for SGD-OD resulting from reductant loading (Figure 11). The goal was to generate estimates of reductant loading and potential SGD-OD across diverse hydrological and biogeochemical settings. In calculating these values, several assumptions were made: (1) any reductant introduced via SGD is oxidized upon entering the coastal waters; (2) reductants are evenly dispersed within the groundwater; (3) SGD flux occurs at a constant rate; and (4) seasonality does not impact reductant concentrations or SGD flux. These assumptions, while necessary for consistency, introduce limitations. In reality, both nutrient concentrations and SGD flux rates vary as a function of rain events, seasonality, and other factors. It should also be noted that not every system had data available for each reductant concentration, some systems only had two out of the five, and therefore some SGD-OD potential estimates are likely to be underestimates.

The results reveal considerable variability in potential SGD-OD across systems (Table 2). Even systems relatively close in proximity to each other, such as Cape Cod, MA and Delaware Inland Bays, exhibited markedly differing SGD-OD – differing by over three orders of magnitude, 9.57×10^3 mol/yr and 2.29×10^6 mol/yr, respectively. The primary production of Cape Cod Bay is at least 9.9×10^7 mol O_2/yr (Hyde et al. 2008), which is several orders of magnitude greater than predicted SGD-OD. The potential SGD-OD for all of these locations is significant. Fluctuations in SGD are in part due to differences in aquifer type, porosity, tides, and hydraulic head between the sites. Additionally, even areas with relatively low SGD fluxes can have significant oxygen drawdown potential if reductant concentrations are high enough. The estimates are likely high because of the complex nature of SGD. These results do not account for fluctuations in SGD and oxidation of the reductants because of tidal influence. At least half the time, SGD is discharging at low tide, the reductants are being oxidized by atmospheric oxygen, and during high tide, there is less SGD. The amount of time SGD is providing reductants to the system to drive oxidative processes depends on the tidal range, which can fluctuate throughout the year. All together, these results support the idea that concentrations of reductants within groundwater, groundwater flow, and ecosystem reactions to large storm events should be monitored in sensitive locations because SGD-OD can drive ecosystem changes.

This review supports the hypothesis that SGD can significantly contribute to oxygen depletion in coastal waters. The extent of this contribution varies across systems, but any increase in oxygen consumption may have meaningful ecological consequences. These findings highlight the need for increased monitoring of groundwater chemistry and fluxes, especially in coastal zones that are sensitive to eutrophication and hypoxia. Understanding the interactions between SGD and oxygen dynamics is essential for a comprehensive oxygen budget and managing coastal ecosystem health under environmental change and anthropogenic pressures.

Figure 11. Map with markers of locations used for estimating potential SGD-OD through reductant loading.



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Overall Conclusions and Future Directions

The results from this study and the literature review suggest that submarine groundwater oxygen demand is substantial in many estuary systems. Some coastal systems have SGD-OD that is on par with or exceeds that of riverine inputs (Santos 2021). Unlike riverine discharge, the concentrations of both nutrient and reductants from SGD have not been routinely characterized. These inputs have the potential to draw down significant oxygen in estuarine systems, and more attention should be paid to their role in coastal biogeochemical cycles. Constraining the oxygen budget for coastal ecosystems is critical, in part to understand the current dynamics, but also to prepare for future climate scenarios these sensitive systems will experience. To support enduring coastal health, it is essential to quantify as many contributing factors as possible.

Future work on this topic should be done with the limitations of this experiment in mind. Placing oxygen sensors in wells, creeks, and nearshore ocean would be interesting to capture how and when the oxygen concentration changes. These sensors would also be interesting to compare with tidal sequences, storm events, and seasonality. Another future direction would be comparing DO levels in light vs dark conditions and using the stable isotope, ^{18}O, to trace photosynthesis vs respiration.

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