Spring 5-5-2023

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Recommended Citation

Ballard, Jacey, "Suboxic and anaerobic respiration across a sandy-shore-to-estuarine gradient" (2023). *Honors Theses*. 458.
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Suboxic and anaerobic respiration across a sandy-shore-to-estuarine gradient

By

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Marine Science

Submitted in Partial Fulfillment of the
Requirements for the Degree of Bachelor of Science
In the HTC Honors College at
Coastal Carolina University

Spring 2023

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Abstract

Sulfate is an inorganic ion that is one of the major ions of seawater. Sulfate is also an essential reactant in microbially mediated anaerobic respiration that produces sulfide, an energy source during chemosynthesis. Sulfide is widely found in sediment, and water rich in decaying organic material, as well as hydrothermal vents. While sulfate reduction occurs extensively in muds, such as those of marshes, it is not expected to occur in sand which is much better aerated. Recent research in our group documented extensive sub aerobic respiration in coastal sands which suggests that sulfate reduction may have also been happening. This reduction of sulfate in coastal sands can be significant because it may potentially remove harmful amounts of organic matter pollution from land and prevent it from entering the coastal ocean. A sulfide analysis method that was established in the sand biogeochemistry lab determined that sulfate reduction occurs both near the shoreline and the back of the swash by measuring sulfide concentrations in the sediment column at two stations in Singleton Swash. Sediment permeability was higher at the beach station which also had higher oxygen concentrations and lower sulfide concentrations than the swash station, suggesting a role for permeability in determining respiration type.

Introduction

Unconsolidated grains of matter, called sediments, are a significant component of many environments. They aid in storage and burial of organic matter, such as CO_2, and thus regulate CO_2 concentrations in the atmosphere. Sediments also facilitate benthic recycling which is the process of regeneration of nutrients in the sediment column via anaerobic respiration, which may then enter the euphotic zone and fuel photosynthesis (Froelich et al., 1979). This is achieved through the Redox cascade, a series of biogeochemical reactions below the sediment-water interface that is identified by a gradient of reactive compounds (Anschutz and Charbonnier, 2021). The Redox cascade begins with processes of aerobic respiration and continues to processes of anaerobic respiration as oxygen depletes with depth, which happens rather quickly in less permeable sediments. Once aerobic respiration is limited by oxygen, nitrate reduction, manganese reduction, iron reduction, and sulfate reduction occur respectively (Figure 1).

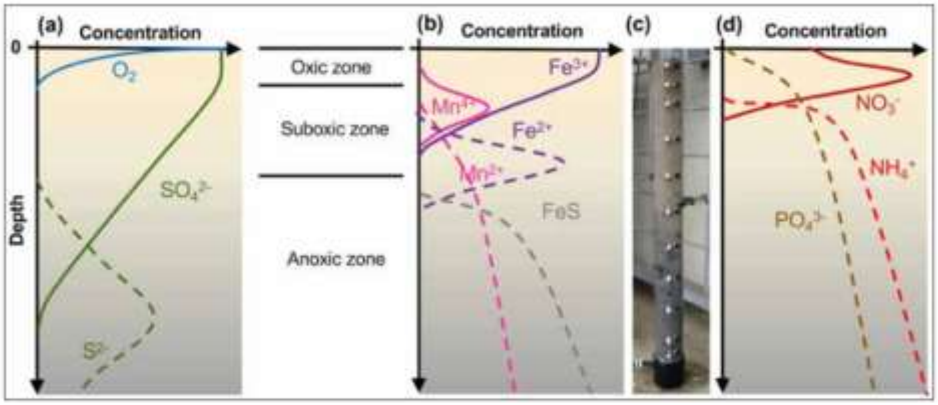


Figure 1. Occurrence of redox reactions within a sediment interface beginning with processes of aerobic respiration and continuing to processes of anaerobic respiration as oxygen depletes with depth (Hannides et al., 2014).

Muds are dominated by diffusion, so when oxygen diffuses into the sediment it is rather immediately taken up by aerobic respirers (microorganisms). Suboxic reactants aren't as abundant (nitrate, iron, manganese), therefore suboxic respiration isn't as abundant. Due to this, sulfate reduction dominates in muddy sediments. However, in permeable sediments like sand, physical mixing by waves, currents, and tides mixes pore water within the sand with the overlaying water causing the exchange of chemicals, such as oxygen, between pore water and overlying water. This aeration of the sand sediment column limits redox reactions via anerobic respiration, meaning that not all the processes occur, are occurring less, or are occurring over a greater depth. Grain size and porosity, along with permeability, also affect redox reaction occurrence and vary between muddy and sandy environments.

Since oxygen poisons sulfate reducers, the sediment must be truly anoxic for sulfate reduction to occur and consequently the introduction of oxygen to sediment via physical mixing makes sulfate reduction impossible. Because of this, we would not find sulfide in permeable sediments. However, ferrous iron, Fe^{2+}, the product of iron reduction by anaerobic respiration which occurs prior to the reduction of sulfate, has been found in permeable sediments away from intense physical mixing with limited flow (Diaz, 2021). Based on this, it is reasonable to expect to find a buildup of sulfide, the product of sulfate reduction, after the ferrous iron and thus indicating that sulfate reduction is occurring at a greater depth. The limited flow of water may make sulfate reduction possible in sediments because the exchange of pore water and overlaying water (i.e., oxygen) is slower. Furthermore, the smell of sulfide is a valid indicator of the occurrence of sulfate reduction and was also detected at the areas of limited flow (Diaz, 2021). The goal of this study was to expand upon the understanding of sulfate reduction and total dissolved sulfide influenced by sediment permeability, physical mixing, and water flow in sandy sediments, and how analysis of other biogeochemical processes aids in this. Porewater data collected from sediments in Singleton Swash in Myrtle Beach, South Carolina were used to evaluate the limitations of sulfate geochemistry and how this may change in the coastal gradient.

Hypotheses

Overarching Hypothesis: Sulfate reduction does not occur in sandy permeable sediments.

Hypothesis 1: Sulfide will not be found in the sandy sediment column due to its permeability and the exchange of water supplying oxygen to the sandy permeable column.

Hypothesis 2: If sulfide is found, it will be found at the lower depth of the less permeable sediment column.

Methods

Study Site

Porewater data was collected at Singleton Swash, Myrtle Beach in South Carolina, an estuarine tidal creek that flows through a sandy beach into Long Bay (Figure 1). Data was gathered from 2 stations, one near the shoreline and the other at the back of the swash on February 18, 2023 and March 7, 2023, indicated on the figure. A third station was also sampled on February 18, 2023, also indicated on the figure.

Figure 2. Study site (as captured by Google Earth on 2/04/2020) and stations where data was collected on February 18, 2023, and March 7, 2023, in Singleton Swash, South Carolina.

Field Observations

Prior to sampling, latitude, longitude, dissolved O_2, salinity, and temperature of the overlying water were measured using a YSI ProDSS meter with a temperature-conductivity-oxygen sensor and a built-in GPS.

Sampling

Duplicate surface water and pore-water samples were collected using a pure titanium MHE PushPoint sampler (MHE Products, East Tawas, MI, USA) and a 50-mL polypropylene polyethylene syringe in 15-cm increments beneath the sediment surface down to 90 cm at both stations on February 18, 2023 and March 7, 2023. Pore-water samples were also collected at a third station on February 18, 2023 for station comparison, as there fine-grained sediments are expected to be sulfidic.

The samples were transferred by tubing from the PushPoint sampler into a 5 mL syringe and immediately filtered through a 0.2 µm cellulose acetate in-line filter into a 1 mL syringe. The filtered samples were then dispensed into microcentrifuge tubes containing 1 mL of 0.05 mol L^{-1} zinc acetate reagent (Cline, 1969) and stored in a cooler. Dissolved oxygen content within the sediment column was also measured for every sample using the YSI ProDSS meter mounted in an inverted syringe barrel through which the sample was gently injected. Sediment samples from the top 5-10 cm were collected directly into plastic bags for permeability and porosity analysis.

Laboratory Analysis

Permeability was determined using the constant-head method (Klute & Dirksen, 1986; Rocha et al., 2005). Porosity was measured thermogravimetrically (Breitzke, 2006). Samples were analyzed for sulfide, (S^{2-}) by spectrophotometry using the methylene blue method (Cline, 1969).

Data Analysis

Total sulfide concentration (in mmol m^2), as well as oxygen concentration on the second sampling day, was calculated for stations 1 and 2 using concentration profiles and porosity, φ. This was done using the following calculation:

$$\sum_{Depth\ interval\ i=1}^{Depth\ interval\ i=f} Solute = [Solute]_i \times \varphi \times z_i \times \frac{L}{10^3\ cm^3} \times \frac{10^4\ cm^2}{m^2}$$

A bar graph depicting the total sulfide concentration of stations 1 and 2 was produced for comparison of inventory concentrations. Tables including station characteristics and sulfide and oxygen concentration statistics for all stations on both days were also created. Oxygen concentration with depth profiles were also generated for stations 1 and 2 from March 7, 2023. Permeability and oxygen integrated concentration were also separately plotted against sulfide integrated concentration. All graphing and statistical analysis were performed using Microsoft Excel (2022).

Results

The oxygen concentrations (mg L^{-1}) measured in overlaying water were very similar at both stations, with a highest difference of 1.54 mg L^{-1} on the March sampling date (Table 1). Oxygen concentration also decreased at both stations from the first sampling date to the second. The characteristics of sulfide (µmol/L) in the sediment column at stations 1 and 2 on February 18 and March 7 showed that station 1 always had a lower maximum, minimum, average and total (mmol/m^2) sulfide concentration than station 2 (Table 2). The depths (cm) of the maximums on February 18, 40 cm at station 1 and 15 cm at station 2, suggest that sulfide is occurring at a shallower depth in the sediment column at station 2. Sulfide concentrations also decreased at both stations from February 18 to March 7. The characteristics of oxygen (µmol/L) in the sediment column at stations 1 and 2 (only measured on March 7) showed that station 1 had a higher average and total (mmol/m^2) oxygen concentration than station 2 (Table 3). The depths of the minimums, 75 cm at station 1 and 60 cm at station 2, suggest that oxygen is depleting quicker in the sediment column at station 2. Profiles of sulfide concentrations with depth from February 18 show a higher peak of sulfide and at a shallower depths at station 2 than station 1 (Figure 3). On March 7, much lower concentrations of sulfide were measured in the sediment column at both stations with larger error bars as well. Profiles of oxygen with depth from March 7 show oxygen present at all depths within the sampled range, however, oxygen concentration depleted quicker with depth at station 2 (Table 3; Figure 4).

When comparing the total sulfide concentrations at stations 1 and 2 on February 18 and March 7, station 2 always had a higher total concentration of sulfide than station 1 (Table 2; Figure 5). Permeability (m^2) was plotted against the total sulfide concentrations and against the total oxygen concentrations. This showed that as permeability increased, oxygen concentration increased and sulfide concentration decreased (Figure 6). Profiles of Salinity (PSU) with depth at stations 1 and 2 from March 7 showed that salinity increased quicker with depth at station 2 than station 1, indicating increasing water density with depth at station 2 (Figure 7).

Table 1: The characteristics of each station. The distance was measured along the primary channel with station 1 at 0 m. Oxygen, salinity and temperature values are for overlying water. Listed values are averages with ± one standard deviation. N.c. : Not collected.

Property	**Station 1**		**Station 2**		**Station 3**
Latitude	33.75536		33.75734		33.7585
Longitude	-78.7931		-78.79453		-78.79299
Sampling Date	2/18/23	3/7/23	2/18/23	3/7/23	2/18/23
O_2 (mg L^{-1})	9.17 ± 0.01	7.05 ± 0.37	9.30 ± 0.01	8.59 ± 0.06	10.58 ± 0.01
Salinity (PSU)	21.14 ± 0.09	31.13 ± 0.15	21.6 ± 0.00	30.83 ± 0.58	20.44 ± 0.00
Temperature (°C)	14.30 ± 0.00	22.63 ± 0.53	13.3 ± 0.00	20.05 ± 0.21	13.73 ± 0.06
Sulfide smell	None	None	Mild	None	Strong
Porosity	N.c.	0.41 ± 0.01	N.c.	0.44 ± 0.01	N.c.
Permeability (m^2)	N.c.	$4.8\times10^{-11} \pm 4.1\times10^{-13}$	N.c.	$5.2\times10^{-12} \pm 6.2\times10^{-14}$	N.c.

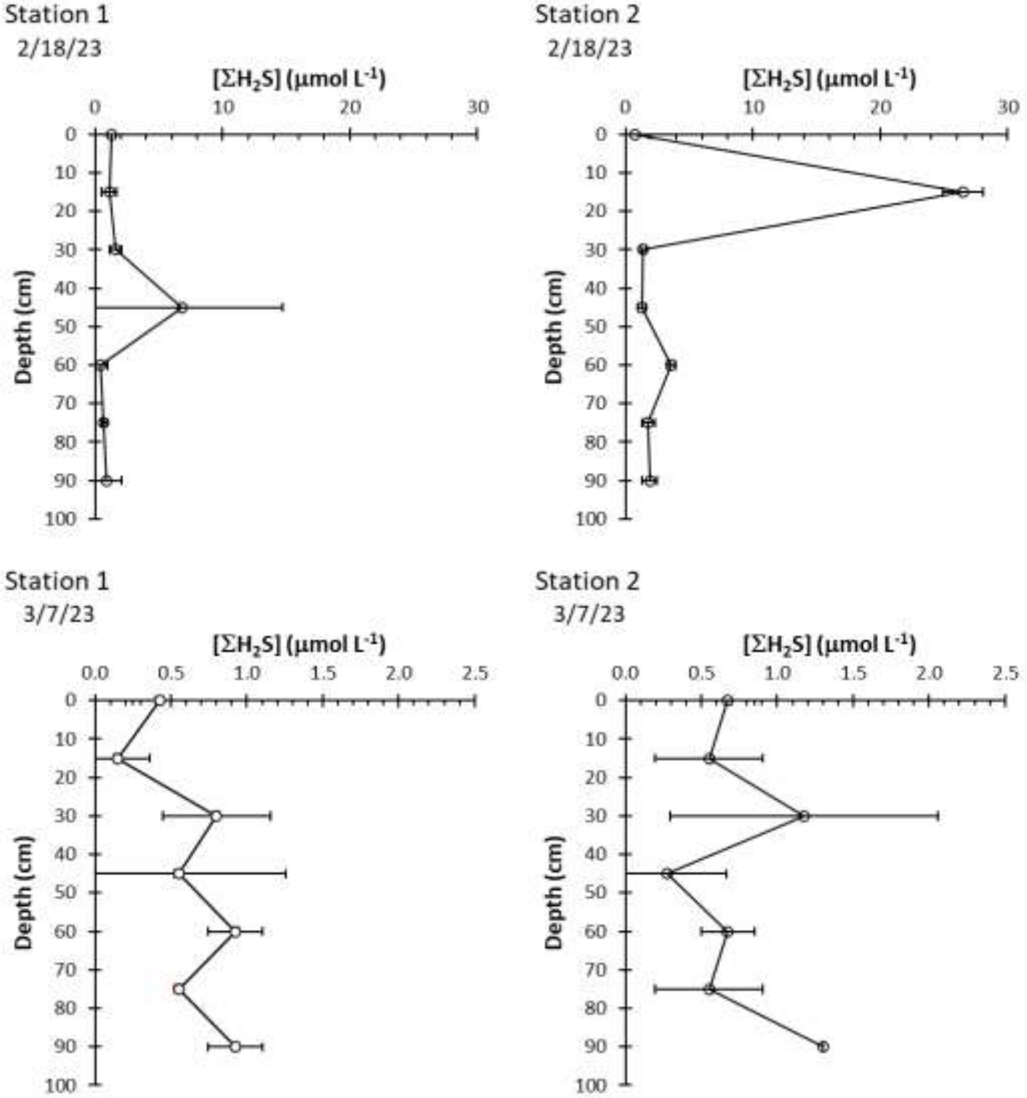
Table 2: The characteristics of [ΣH_2S] (µmol/L) at each station on February 18 and March 7.

Property	**Station 1**		**Station 2**		**Station 3**[a]
Sampling Date	2/18/23	3/7/23	2/18/23	3/7/23	2/18/23
Maximum [ΣH_2S] (µmol/L)	6.8	0.9	26.5	1.3	171.7
Depth of maximum (cm)	45	60 & 90	15	90	15
Minimum [ΣH_2S] (µmol/L)	0.4	0.1	0.7	0.3	0.3
Depth of minimum (cm)	60	15	0	45	0
Average [ΣH_2S] (µmol/L)	1.83 ± 2.23	0.62 ± 0.28	5.13 ± 9.39	0.74 ± 0.36	86.0 ± 121.19
Total H_2S (mmol/m^2)	0.72	0.22	2.38	0.28	6.32

[a] Samples at station 3 were only retrieved at 0 and 15 cm.

Table 3: The characteristics of $[O_2]$ (µmol/L; mmol/m^2) on March 7 at stations 1 and 2.

Property	**Station 1**	**Station 2**
Maximum $[O_2]$ (µmol/L)	220.16	268.44
Depth of maximum (cm)	0	0
Minimum $[O_2]$ (µmol/L)	18.20	7.03
Depth of minimum (cm)	75	60
Average $[O_2]$ (µmol/L)	62.03 ± 72.98	49.12 ± 96.85
Total O_2 (mmol/m^2)	18.33	13.52



Station 1
2/18/23

Station 2
2/18/23

Station 1
3/7/23

Station 2
3/7/23

Figure 3. Profiles of [ΣH_2S] (μmol/L) with depth (cm) measured on February 18 and March 7 at stations 1 and 2.

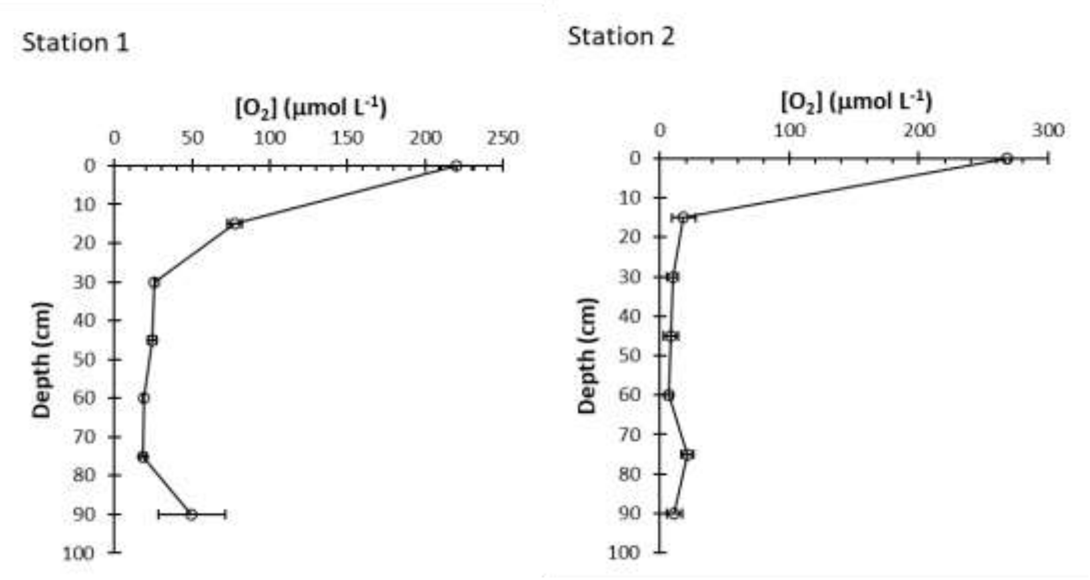


Figure 4. Profiles of [O_2] (µmol/L) with depth (cm) measured on March 7 at stations 1 and 2.

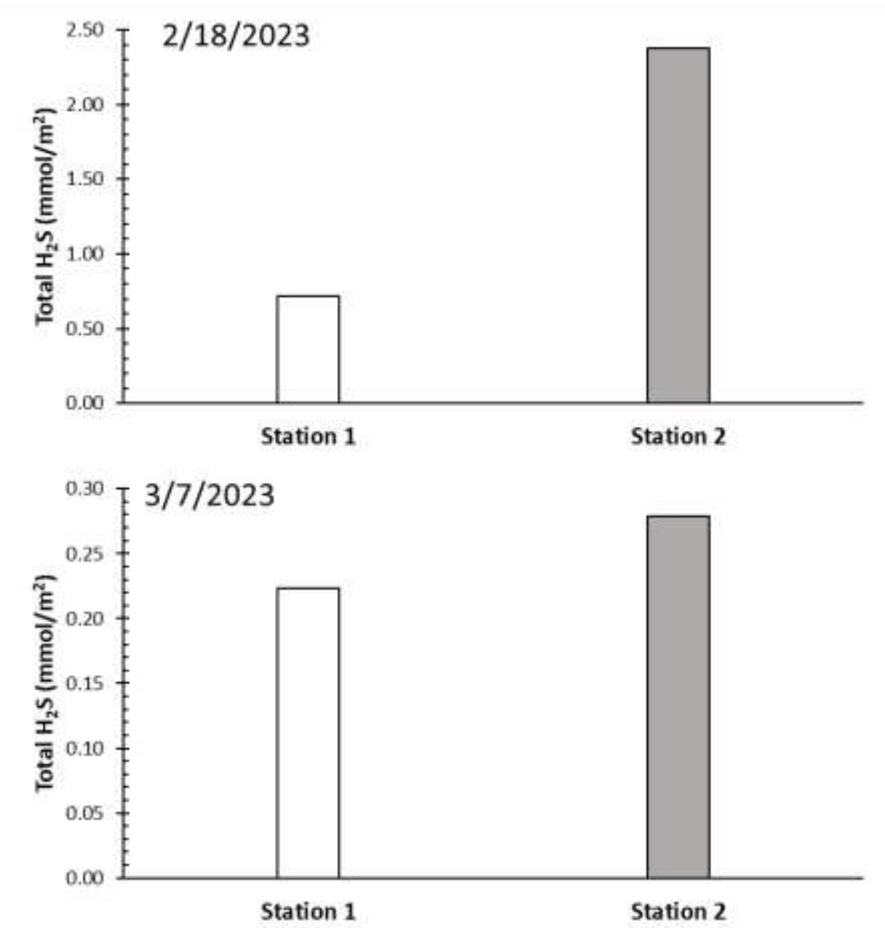


Figure 5. Comparison of Total [H_2S] (mmol/m^2) at stations 1 and 2 on February 18 and March 7.

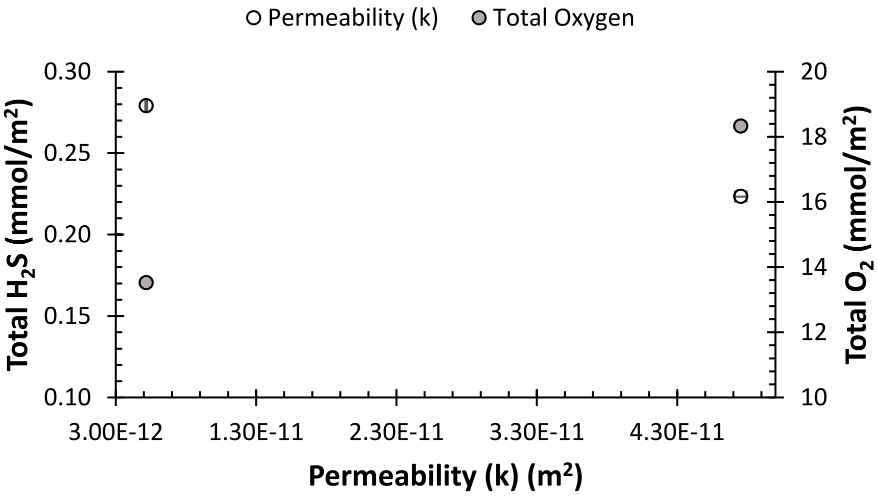


Figure 6. Total [H_2S] (mmol/m^2) against Total [O_2] (mmol/m^2) and permeability (m^2).

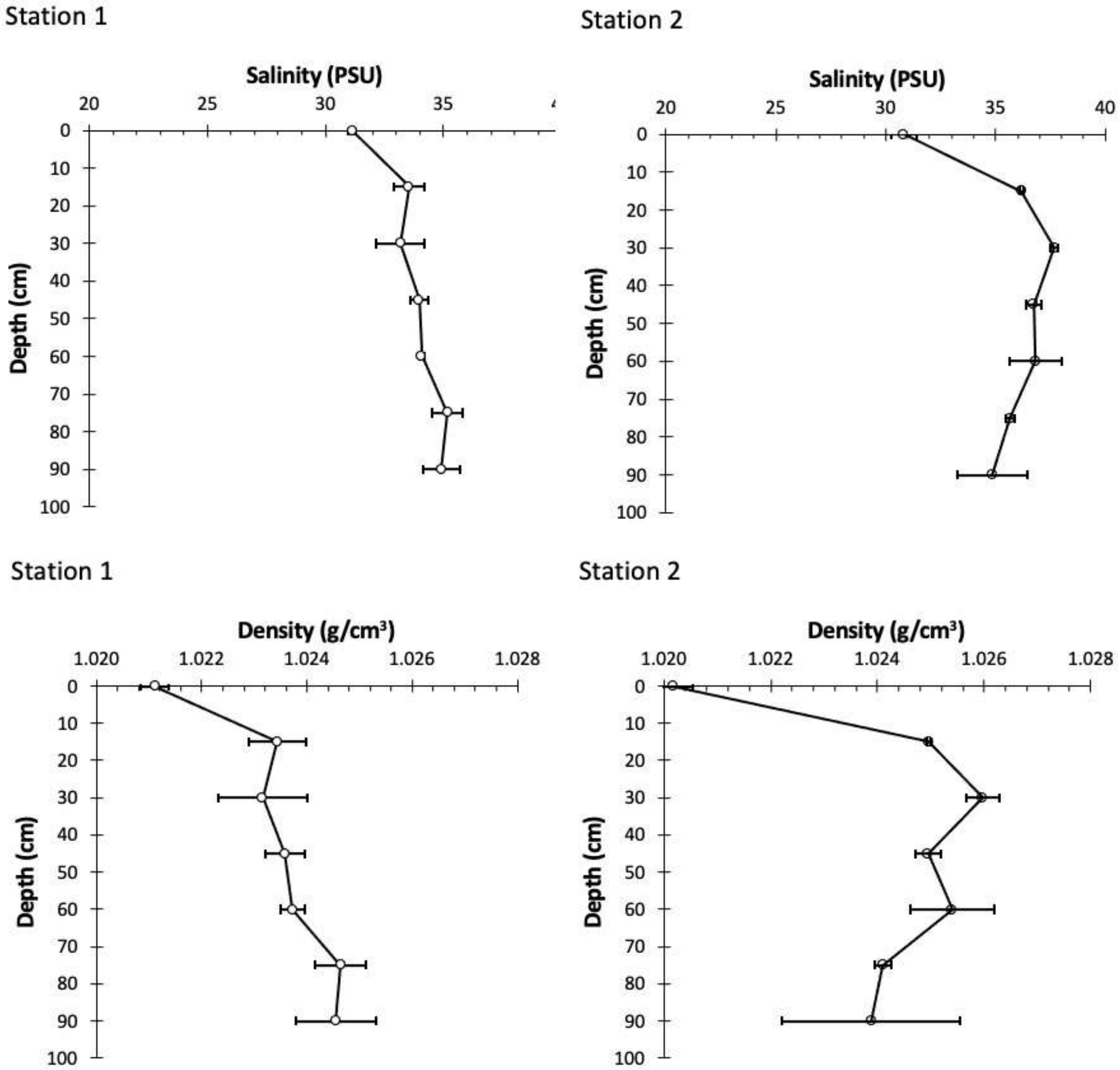


Figure 7. Profiles of Salinity (PSU) and density with depth (cm) measured on March 7 at stations 1 and 2.

Discussion

Sulfide was found at both station 1 and station 2 at various depths and in highly varying concentrations. A shallower depth of minimum oxygen concentration, as well as a shallower depth of maximum sulfide concentrations at station 2 suggests that oxygen is depleting quicker within the sediment column and resulting in a quicker transition to and increased rate of the redox cascade processes. Sulfate reduction is being utilized at shallower depths at station 2 compared to station 1 due to quickly depleting oxygen. Lower permeability and higher pore water salinity i.e. increased water density) at station 2 could explain the lower total oxygen concentration as pore water exchange (i.e. aeration) is more limited in comparison to station 1 where permeability is higher and pore water salinity is lower. However, some oxygen was present at all depths, and thus occurring simultaneously with sulfide. But, oxygen poisons sulfate reducers and thus the sediment must be truly anoxic for sulfate reduction to occur. This can be explained by sulfide being produced in “microzones”, spots of high organic matter resulting in high rates of respiration that exhausts oxygen and proceeds by sulfate reduction. These vary in location in the heterogeneous sediment column. It is likely that porewater from adjacent oxic and sulfidic zones was mixed during sampling (Sørensen et al., 2007).

Interestingly, sulfide concentrations were not undetectable at surface samples of any station. Addressing this peculiarity and its causes would be a significant and beneficial continuance of this study.

Acknowledgments

I would like to thank my advisor, Dr. Angelos Hannides, for allowing me this opportunity and for his mentorship throughout my Honors Thesis experience. The guidance, patience, and facilities he provided were invaluable to the success of this project. I would also like to thank the HTC Honors College for their encouragement and support in multiple facets.

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