# CONTROLS ON THE SULFUR CYCLE IN ESTUARINE SEDIMENTS ON

# THE CENTRAL TEXAS COAST

A Thesis

by

HEATHER THOMSON

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2006

Major Subject: Oceanography

# CONTROLS ON THE SULFUR CYCLE IN ESTUARINE SEDIMENTS ON THE

# CENTRAL TEXAS COAST

A Thesis

by

HEATHER THOMSON

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Approved by:

| | |
|---|---|
| Chair of Committee, | John Morse |
| Committee Members, | Luis Cifuentes |
| | Jennifer McGuire |
| Head of Department, | John Morse |

August 2006

Major Subject: Oceanography

# ABSTRACT

Controls on the Sulfur Cycle in Estuarine Sediments on the Central Texas Coast.

(August 2006)

Heather Thomson, B.S., Lehigh University

Chair of Advisory Committee: Dr. John Morse

The sedimentary sulfur cycle is one of the main components of estuarine biogeochemical systems. It is initiated by the oxidation of organic matter via sulfate reducing bacteria which produce hydrogen sulfide ($H_2S$). The S(II) then reacts via both abiotic and biotic pathways to form sulfur with other oxidation states. The three most widely-studied "operationally"–defined components of the sedimentary sulfur system are total reduced (inorganic) sulfur (TRS), acid volatile sulfide (AVS), and dissolved (=filter-passing) sulfide.

This study focused on several parameters that are widely held to be important in determining TRS in sediments and the relative proportions of TRS, AVS and dissolved S(II) forms. The formation of iron sulfide minerals requires metabolizable organic matter and $SO_4^{2-}$ to produce S(II) and "reactive"-Fe as a source for the iron in iron sulfide minerals. One of these components is generally the limiting factor in TRS formation (e.g., Berner 1970). Nine different sites from three locations on the Central Texas coast were studied for a variety of parameters including organic matter, sulfate concentrations, sulfate reduction rate, solid "reactive" and dissolved iron, and grain size, as well as TRS, AVS, and $\Sigma H_2S$. At each site five sediment cores were taken to a depth

of 20 cm whenever possible. The cores were sectioned in 2 cm intervals. The porewater was extracted and both solid and dissolved components were analyzed using a variety of methods, including carbon and sulfur coulometry, acid extraction, chromium extraction, and drying the sediment. The results of he analyses showed that the central Texas coast is a widely diverse system. Some sites were very sandy while others were fine-grained. This variety was especially true for the Nueces Bay and Baffin Bay sites. The East Matagorda Bay sites showed more homogeneity in almost all analysis. While the heterogeneity of locations along the Central Texas coast makes it difficult to make a definitive statement about the controls on TRS in this area, most sites are controlled by the low amounts of iron in the system, which limits the amount of iron sulfide that can form. Low reactive iron concentrations and high degrees of pyritization (DOPs) support this argument. Exceptions exist for low-salinity (sulfate-limited) or very fine-grained (organic matter limited) sites.

# ACKNOWLEDGEMENTS

**TABLE OF CONTENTS**

# LIST OF FIGURES

## LIST OF TABLES

# 1. INTRODUCTION AND BACKGROUND

The sedimentary sulfur cycle is one of the main components of estuarine biogeochemical systems. In the sedimentary sulfur cycle, organic matter is oxidized by sulfate reducing bacteria which produce hydrogen sulfide ($H_2S$). Further reactions can subsequently transform the $H_2S$ into several different solid or dissolved chemical species that can occur in oxidation states ranging from S(VI) to S(-II). Two of the most widely studied forms of sedimentary sulfur are total reduced (inorganic) sulfur (TRS) and acid volatile sulfides (AVS). TRS does not include elemental sulfur and organic sulfur which are usually at minor concentrations compared to TRS. AVS is part of TRS and has been often considered to be simply solid FeS (mackinawite). However, AVS may also contain the minerals greigite ($Fe_3S_4$), an HCl-reactive portion of pyrite ($FeS_2$), as well as dissolved (= filter passing) $H_2S$ species and complexes, iron sulfide complexes, clusters, and nanoparticles, polysulfides, and sulfur oxyanions (Rickard and Morse, 2005). Although many exceptions have been found, TRS usually is primarily the mineral pyrite ($FeS_2$), which is usually the dominant form of S buried in anoxic sediments.

Many different factors can control the concentrations and ratios of TRS and AVS in sediments and the fraction of AVS which is in the dissolved versus sold phase. This study focused on several parameters that are widely held to be important in determining the total reduced sulfur in sediments and the relative proportions of TRS,

---

This thesis follows the style of *Aquatic Geochemistry.*

AVS and dissolved forms. The formation of iron sulfide minerals requires metabolizable organic matter and $SO_4^{2-}$ to produce S(II) and "reactive"-Fe as a source for the iron in iron sulfide minerals. One of these components is generally the limiting factor in TRS formation (e.g., Berner,1970). Although no quantifying procedure exists to determine the amount of organic matter that is metabolizable, Martens and Klump (1984) estimate that 24 ± 5 % of the initially deposited organic carbon is remineralized during diagenesis. They state that approximately 98% of this remineralization occurs in the top 25 cm of sediment.

The term "reactive"-Fe is an operationally defined term, and is based on the extraction procedure used. The overall stoichiometry of the reaction is:

$$2\ FeOOH + H_2S \rightarrow 2\ Fe^{2+} + S^0 + 4\ OH^-$$
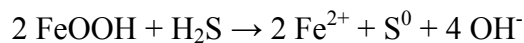
However, the iron can exist in many different forms of iron (oxyhyr)oxides, such as ferrihydrite, lepidocrocite, goethite, and hematite, as well as coming from sheet silicates. These can be further divided into highly reactive, poorly reactive, and unreactive pools. The highly reactive fraction is anything that can be dissolved in dithionite, while the poorly reactive fraction can be dissolved in 12 N HCl. (Poulton and Canfield, 2005) Further discussion of the extraction methods will occur in the Methods section.

The major variable that controls the amount of sulfate available is the salinity of the water. In most sediments in which the salinity of the overlying water is >~5, the amount of labile organic matter is the limiting factor in the process. There is currently no general agreement on an analytical method to quantify the fraction of total organic

carbon (TOC) that is labile. Consequently, only TOC was determined which will at least make it possible to break sediments into the general classes of TOC rich (>2 dry wt% e.g. sapropels), intermediate (0.5 <dry wt% <2) and poor (dry wt% <0.5). Sediments where the amount of reactive iron that can form iron sulfide minerals limits amount of TRS formation include those dominated by sand and $CaCO_3$ (e.g., Morse and Berner, 1995), consequently the weight fraction of these components was also determined (note that I report wt% <63 μm, the silt and clay fraction, as is traditional; the balance is the sand fraction).

Previous studies have been performed in some of the areas in this study, but not as many parameters were examined, nor were the detailed pore water profiles obtained as measured by microelectrodes in this study. Morse et al. (1992) studied iron sulfide mineral diagenesis in Baffin Bay, Texas. They found that there was a high correlation between the TRS content and the amount of the sediment that was fine-grained. They also found elevated C/S ratios and high degrees of iron pyritization (DOP was calculated using the equation DOP = pyrite-Fe / Re-Fe, with pyrite-Fe = ½ (TRS – AVS)). This indicated that in their sediments reactive iron was the limiting factor in the formation of TRS. However, when Morse (1999) studied the Laguna Madre, Texas, no relationship between TRS and the grain size of the sediments was found. This was attributed to the high organic carbon content in the sediments, due partially to seagrass beds, and the high pH of the sediments, which inhibited the transition of AVS to pyrite.

## 2. METHODS

### *2.1. Study Sites and Sampling Plan*

Three different locations were chosen along the central Texas coast in collaboration with Dr. Wayne Gardner at the University of Texas Marine Science Institute (UTMSI), who is studying sedimentary nitrogen cycling at these sites. At each location three different sites with varying salinities were chosen, for a total of nine sampling sites. The three locations were East Matagorda Bay, the Nueces River and estuary, and Baffin Bay (see Figure 1). Each site was visited in late summer and fall. The eighteen site samplings are used as a measure of "mega" heterogeneity along the central Texas coast. General characteristics of the nine sites are given in Table 1.

Cores were collected from a small boat using an ~3m long pole with plastic core liners attached to the end of it. At each site five different cores were taken so that the previously described parameters in the sediments could be analyzed, as well as microelectrode analyses of dissolved sulfur and iron (core 1) by David Finneran, a fellow graduate student in Dr. Morse's lab. The second core was sectioned and then the sections were frozen. The sections were analyzed for grain size, porosity, organic-C, carbonate-C, and reactive-Fe. The third core was sectioned and squeezed on a Reeburgh (1967)-type squeezer to extract the porewater, from which chloride and sulfate were analyzed when insufficient amounts were obtained by centrifuging, and the remaining sediment sections frozen for subsequent AVS and TRS analyses. The fourth core was sectioned and centrifuged. The porewater was analyzed for chloride and sulfate. All sectioning was done under an inert $N_2$ atmosphere. The fifth core was

injected with $Na_2^{35}SO_4$ and incubated for approximately 12 hours so that the sulfate

reduction rate could be analyzed.
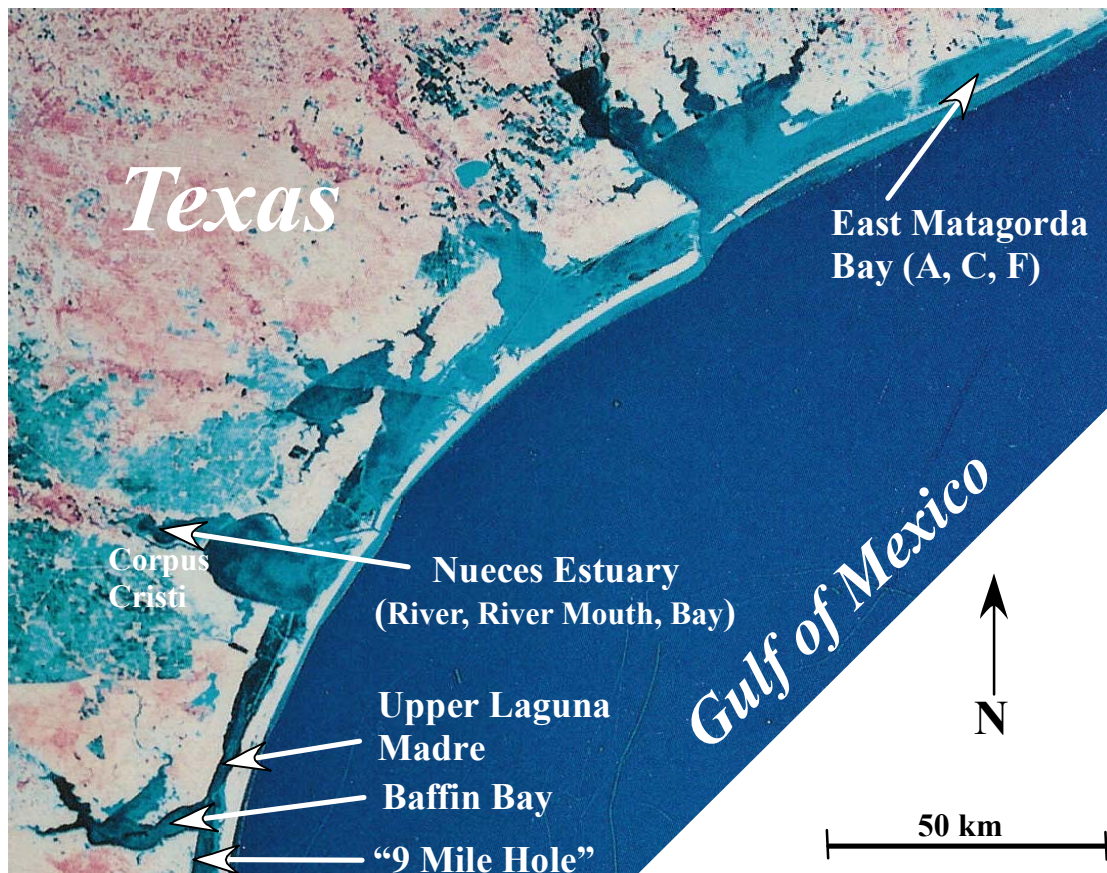


Figure 1  Map of Sampling Sites

Table 1  General Site Characteristics

| Location | Site | Season | Depth (m) | Salinity (‰) | Temp $^o$C | Avg. % < 63 $\square$m | Porosity |
|---|---|---|---|---|---|---|---|
| Baffin Bay | Baffin Bay | Summer | 2.80 | 28.49 | 29.61 | 92 | 0.853 |
| | | Fall | Not sampled due to high winds | | | | |
| | Nine Mile Hole | Summer | 1.00 | 41.80 | 30.52 | 83 | 0.887 |
| | | Fall | 1.12 | 35.48 | 21.57 | 67 | 0.724 |
| | Upper Laguna | Summer | 1.13 | 36.81 | 29.83 | 15 | 0.494 |
| | | Fall | 0.91 | 37.21 | 22.76 | 28 | 0.589 |
| Nueces | River | Summer | 1.65 | 0.94 | 28.15 | 61 | 0.634 |
| | | Fall | 0.7 | 1.51 | 21.84 | 23 | 0.455 |
| | River Mouth | Summer | 1.18 | 7.6 | 27.72 | 90 | 0.787 |
| | | Fall | 1.14 | 16.82 | 20.8 | 93 | 0.820 |
| | Bay | Summer | 1.43 | 21.74 | 27.04 | 34 | 0.614 |
| | | Fall | 1.32 | 29.01 | 21.84 | 35 | 0.638 |
| East Matagorda Bay | A | Summer | 1.34 | 21.74 | 29.41 | 92 | 0.766 |
| | | Fall | 1.24 | 24.71 | 27.09 | 97 | 0.741 |
| | C | Summer | 0.79 | 21.82 | 29.25 | 68 | 0.654 |
| | | Fall | 1.52 | 22.04 | 27.2 | 68 | 0.633 |
| | F | Summer | 0.87 | 24.7 | 29.83 | 81 | 0.761 |
| | | Fall | 1.07 | 15.49 | 27.42 | 87 | 0.700 |

## *2.2. Analytical Methods*

Electrode profiles were made using solid-state, gold-mercury amalgam (100 μm diameter) microelectrodes to simultaneously measure $Fe^{2+}$ and $H_2S$ (Brendel and Luther, 1995).  Calibration curves were generated from seawater for $Mn^{2+}$ and the pilot ion method was used to create calibration curves for the other previously mentioned analytes (Brendel and Luther, 1995).  Minimum detection limits using a DLK-100 electrochemical analyzer from Analytical Instrument Systems (AIS) are 0.5 μM for $HS^-$ and 40 μM for $Fe^{2+}$, as given in Brendel and Luther (1995).  Depth intervals used

in this study ranged from 2 to 5 mm.  Three vertical microelectrode profiles with three different working electrodes were obtained using a multiplexer from AIS.  There was a two second interval between microelectrode scans at each depth.  Individual results were averaged to give a mean profile for each core.  When the core was long enough, each core was analyzed to a depth of 100 mm below the surface.  The exceptions were EMB-A summer (60 mm), EMB-C summer (90 mm), 9MH summer (95 mm), ULM summer (50 mm), and ULM fall (90 mm).  This data is presented and discussed in Appendix A.

Grain size (wt% < 63 μm) was measured by wet sieving.  Porosity was determined by drying the sediment in an ~ 80°C oven and calculating the ratio of % solid to % water.  Total organic carbon (TOC) was calculated as weight % carbon in acidified dry sediment samples in a UIC furnace that was coupled to a UIC carbon coulometer.  Appropriate corrections were made based on total carbon determined from unacidified samples.

AVS was analyzed by the cold 6N $HCl + SnCl_2$ method of Cornwell and Morse (1987).  TRS was analyzed by the hot $CrCl_2$ method of Canfield et al. (1986).  Iron was extracted by the cold 1 M HCl (24 hour incubation) and citrate-dithionate (2 hour incubation) methods of Raiswell, et. al. (1994).  Porewater dissolved sulfate and chloride were determined on a DIONEX Ion chromatograph using an IAPSO seawater standard.  Chloride was also determined via titration with $AgNO_3$ also using an IAPSO seawater standard.

The sulfate reduction rate was determined by injecting cores with radiolabeled sulfate in the form of $Na_2^{35}SO_4$ at 2 cm intervals and incubating for ~12 hours. The cores were then frozen. Extracted S(II) was then analyzed on a liquid scintillation counter after hot chromium extraction of the frozen sediment (Jørgensen, 1978); (Canfield et. al., 1986). This data is presented in Appendix A.

# 3. RESULTS

## 3.1 Analytical Results

The overlying water salinity and major sediment characteristics are presented in Table 2. As previously described, salinity was a primary variable used in site selections within the three coastal regions investigated. Salinity is of great importance because it controls the initial concentration of dissolved sulfate in the sediments. The only site where the salinity was low enough for sulfate to be potentially limiting was in the Nueces River. The salinity increased at the river mouth and out in the bay. The salinity at the East Matagorda Bay sites was close to consistent at ~22, with the exception of F fall, which had an S of 15. The salinity at Upper Laguna Madre was typical of open Gulf of Mexico waters, at around 36. Salinity at Nine Mile Hole was also ~36 in the fall. However, it was higher in the summer (41). The salinity at Baffin Bay was low (28), which was unexpected given that previous studies have found Baffin Bay to be hypersaline, with salinities ranging from 45 to 85. (Behrens, 1969; Morse et. al., 1992).

The proportion of sediments composed of silt and clay was determined by determining the weight fraction of sediment <63 μm. This was done because both the reactive-Fe fraction and the amount of org-C are usually associated with the silt and clay fraction. (e.g Morse et. al., 1992), (Morse, 1999). Based on the grain size the sites can be classified as mostly sandy (%<63μm <25), intermediate (25 < %<63μm <75), or mostly fine-grained (%<63μm >75). Upper Laguna Madre and the Nueces River can both be categorized as sandy, although the sample collected in the fall from

the Nueces had a drastic change in grain size with depth, possibly indicating a storm layer.  Intermediate sites include Nueces Bay and East Matagorda Bay C, although both sites showed some variability with depth.  The other five sites are dominantly fine-grained, but again one site (Nine Mile Hole summer) varied greatly with depth. Most sites had a high porosity (>0.7) consistent with near-surface sediments. Exceptions were Upper Laguna Madre, Nueces River, Nueces Bay, and East Matagorda Bay C, which is consistent with more sandy sediments.

Table 2 Sediment Characteristics

| Site | Season | Depth Range Measured (cm) | # measurements | Wt % org-C | | Wt % CaCO3 | |
|---|---|---|---|---|---|---|---|
| | | | | Max | Avg | Max | Avg |
| Baffin Bay | Summer | 0-10 | 2 | 1.47 | 1.43 | 6.12 | 3.96 |
| | Summer | 0-20 | 3 | 3.2 | 3.02 | 6.4 | 4.49 |
| 9 Mile Hole | Fall | 0-20 | 3 | 3.25 | 1.62 | 4.1 | 3.7 |
| Upper | Summer | 0-10 | 2 | 1.25 | 0.92 | 6.04 | 5.89 |
| Laguna | Fall | 0-10 | 2 | 2.8 | 1.82 | 30.2 | 20.14 |
| Nueces | Summer | 0-8 | 2 | 1.99 | 1.13 | 2.4 | 2.17 |
| River | Fall | 0-12 | 3 | 0.57 | 0.42 | 3.94 | 3.61 |
| Nueces | Summer | 0-12 | 2 | 1.22 | 1.16 | 7.06 | 6.24 |
| River Mouth | Fall | 0-14 | 3 | 1.52 | 1.22 | 5.95 | 5.77 |
| | Summer | 0-8 | 1 | 0.45 | 0.45 | 4.86 | 4.86 |
| Nueces Bay | Fall | 0-8 | 1 | 1.61 | 1.61 | 13.77 | 13.77 |
| East | Summer | 0-8 | 2 | 1.09 | 1.06 | 5.68 | 5.65 |
| Matagorda | Fall | 0-20 | 3 | 1.17 | 0.96 | 6.26 | 4.24 |
| East | Summer | 0-10 | 2 | 0.67 | 0.67 | 7.16 | 6.4 |
| Matagorda | Fall | 0-14 | 3 | 0.88 | 0.74 | 7.41 | 6.51 |
| East | Summer | 0-20 | 3 | 0.79 | 0.71 | 4.74 | 4.45 |
| Matagorda | Fall | 0-20 | 3 | 0.75 | 0.71 | 4.75 | 4.28 |

The concentrations of calcium carbonate were minor (wt % <10) at all sites except for Upper Laguna Madre in the fall.  Most sites contained >0.5 wt % org-C, which is typical of estuarine sediments (Morse et. al., 1992), (Cooper and Morse, 1996).  Only the Nueces River and the summer Bay sites had a lower concentration. While overall there is only a slight correlation ($r^2$=0.12) between Wt % Org-C and Wt % < 63μm (Figure 2), when looking at each individual location the correlation improves, with the Nueces being the highest ($r^2$=0.68).  This weak correlation has previously been observed in sandy sediments in the area by Morse (1999).
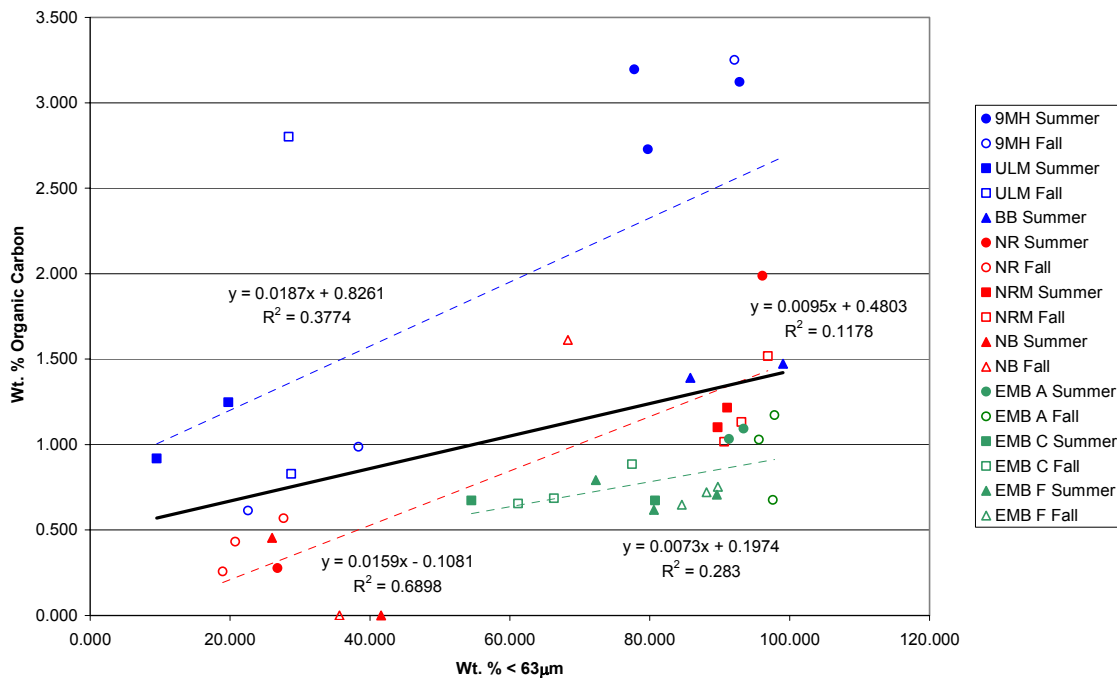


Figure 2 Organic Carbon Content vs. Weight %

After examining these site characteristics it is apparent that the Central Texas coast is a very complex area, with some complexity found even within certain sites. The variability within some cores makes comparison between sites difficult, as the heterogeneity of the sites themselves is not accounted for. It will be difficult to determine correlations when even major variables do not correlate. Instead, this study is looking at the mega-heterogeneity of the Central Texas coast.

A summary of the major characteristics of the AVS and TRS profiles is given in Table 3. Representative profiles are shown in Figure 3. At all but the Baffin Bay and 9 Mile Hole sites AVS was low (<15 μmol/gdw) and generally constant with depth. Other than that it is difficult to determine any sort of site groupings as all of the profiles vary so much. Only the East Matagorda Bay sites were similar seasonally, indicating that there is likely not a significant seasonal variation at those locations. In general the total amount of both AVS and TRS was larger in the fall than in the summer.

Iron data is shown in Table 4. As expected, the amount of iron extractable by the HCl method is much higher than the amount extracted by the CD method. This is because the HCl method leaches iron that is available during geologic timescales, while CD only extracts that that is available during early diagenesis. There is significant iron at all sites, with some sites ranging up to 160 μmol/gdw. There is much ambiguity in the literature, as some authors describe this extractable-Fe as the total Reactive-Fe, while others include pyrite-Fe into the total reactive-Fe pool. For the purposes of this paper the extractable-Fe will be described as Extractable Reactive-Fe, or E-Re-Fe.

This includes residual unreacted Fe (Res-Fe) and AVS-Fe, and the total Reactive-Fe pool (Re-Fe) will include pyrite and E-Re-Fe. If it is assumed that the HCl-E-Re-Fe is the "available" iron, then there is a significant amount available for pyritization (DOP <0.8) at all sites. However, if the CD-E-Re-Fe is used, then there is iron available only at Upper Laguna Madre in the fall, Nueces River Mouth in the fall, Nueces Bay in the fall, and the East Matagorda Bay sites in both seasons. This further emphasizes the differences in the two leaching methods. Another indicator of iron availability that is commonly used is the Degree of Sulfidization (DOS) which is calculated as (pyrite-Fe + AVS-Fe) / Re-Fe (Boesen and Postma, 1988). However, in most of the samples the DOS was greater than 1, indicating that possibly some AVS-Fe was included in the extracted pool. Sulfate concentrations including the percentage of sulfate reduced are presented in Table 5.

Table 3: Descriptions of AVS and TRS Profiles

| Site | Season | Depth Range Measur | TRS Avg. (μmol/gdw) | TRS Range (μmol/gdw) | TRS Depth of max value (cm) | TRS Comments | AVS Avg. (μmol/gdw) | AVS Range (μmol/gdw) | AVS Depth of max value (cm) | AVS Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| Baffin Bay | Summer | 0-14 | 102 | 85-129 | 13 | Generally constant with depth | 14 | 0.7-26 | 3 | Drops to 0 at 9 cm |
|  | Summer | 0-20 | 136 | 65-576 | 5 | Peak at 5 cm | 42 | 27-58 | 9 | Peak at 9 cm |
| 9 Mile Hole | Fall | 0-20 | 39 | 17-73 | 19 | No discernable pattern | 15.5 | 0.9-53 | 3 | Decreases with depth |
| Upper Laguna Madre | Summer | 0-8 | 13.5 | 6-20 | 1 | Inverse peak at 5 cm | 3 | 1.5-5 | 7 | Small inverse peak at 5 cm |
|  | Fall | 0-16 | 20 | 4-36 | 15 | Increases with depth with drop at 13 cm | 3 | 1-5 | 13 | Slight increase with depth |
|  | Summer | 0-10 | 16 | 5-33 | 1 | Decreases with depth | 2 | 0.1-3 | 5 | Constant with depth |
| Nueces River | Fall | 0-20 | 114 | 49-270 | 7 | Peaks at 7 cm and 16 cm | 2 | 0.4-3 | 13 | Constant with depth |
|  | Summer | 0-20 | 153 | 74-324 | 1 | Peak near surface, then constant with depth | 5 | 3-9 | 3 | Constant with depth |
| Nueces River Mouth | Fall | 0-20 | 38 | 20-50 | 5 | Generally constant with depth | 4 | 0.6-14 | 3 | Constant with depth |
|  | Summer | 0-10 | 60 | 41-77 | 1 | Inverse peak at 3 cm | 2 | 0.5-4 | 5 | Constant with depth |
| Nueces Bay | Fall | 0-10 | 42 | 17-115 | 9 | Decreases with depth, peak at 9 cm | 5 | 2-10 | 5 | Constant with depth |
| East Matagorda Bay A | Summer | 0-8 | 44 | 38-49 | 5 | Increases with depth | 1 | 0.3-1.6 | 3 | Constant with depth |
|  | Fall | 0-20 | 85 | 36-127 | 19 | Increases with depth | 6 | 2-8 | 11 | Constant with depth |
| East Matagorda Bay C | Summer | 0-12 | 52 | 25-80 | 11 | Increases with depth | 3 | 1.8-4 | 5 | Constant with depth |
|  | Fall | 0-18 | 57 | 20-90 | 17 | Increases with depth | 1 | 0.5-3 | 3 | Constant with depth |
| East Matagorda Bay F | Summer | 0-20 | 42 | 22-61 | 1 | No discernable pattern | 3 | 0.4-5 | 7 | Constant with depth |
|  | Fall | 0-20 | 58 | 40-90 | 11 | No discernable pattern | 1 | 0.3-3 | 11 | Constant with depth |

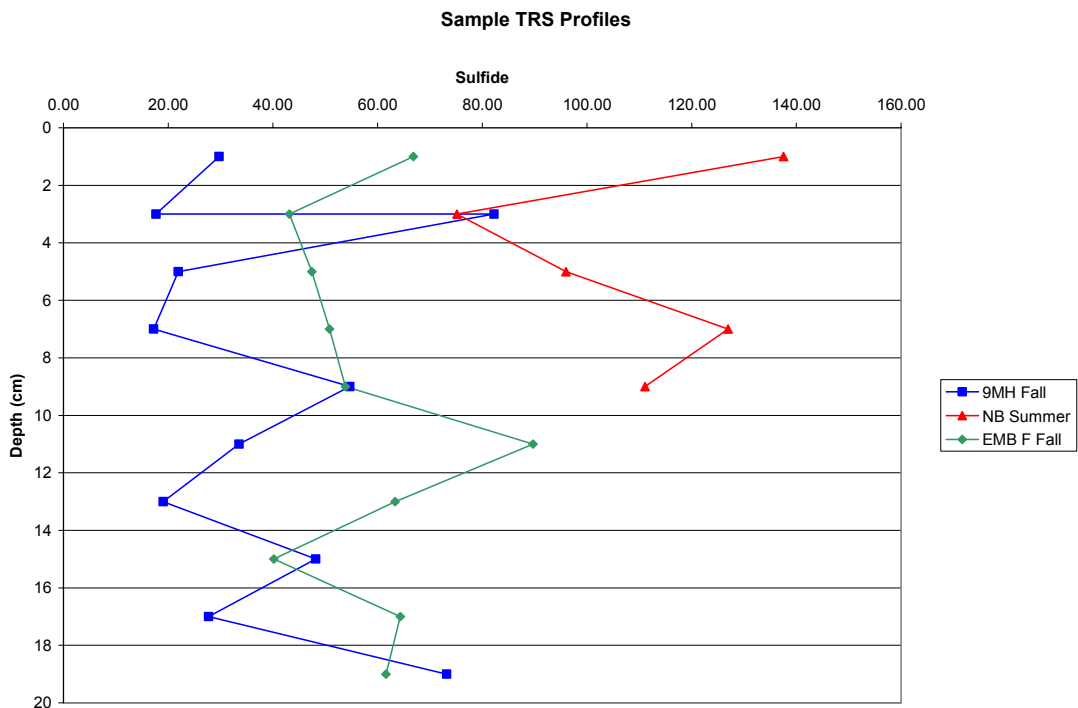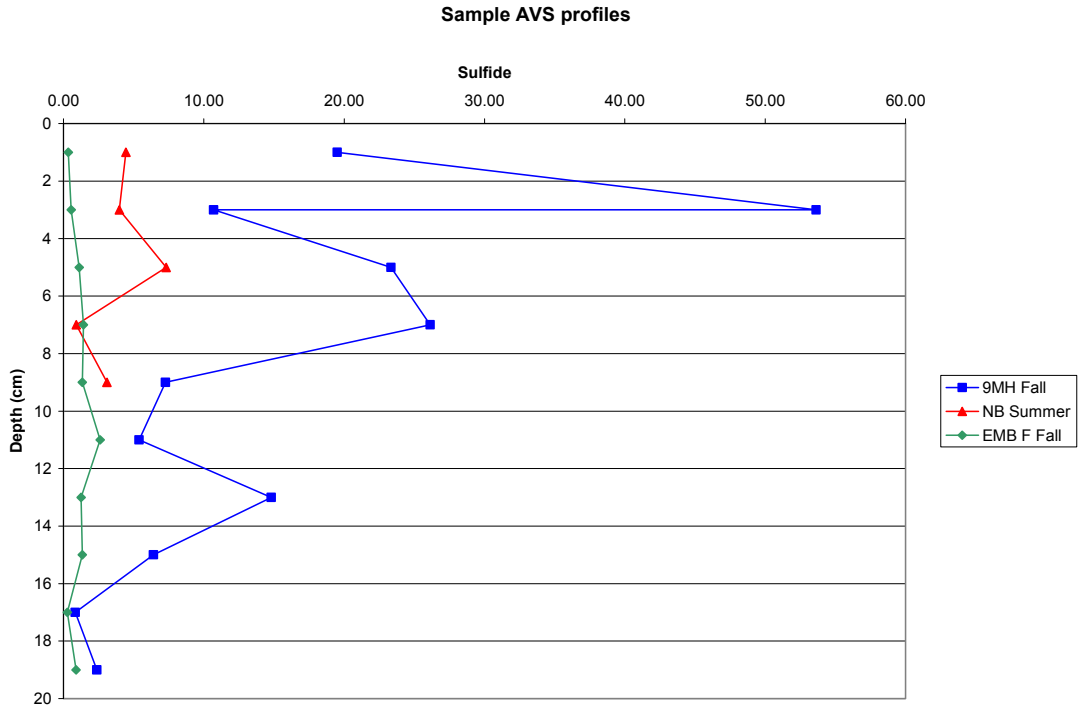**Sample AVS profiles**



**Sample TRS Profiles**



Figure 3   Representative AVS and TRS Profiles

Table 4  Iron Analysis Data

| Site | Season | Depth Range Measured (cm) | # measurements | Extractable Iron-CD | | Extractable Iron-HCl | | DOP-CD | | DOP-HCl | | DOS-CD | | DOS-HCl | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Max | Avg | Max | Avg | Max | Avg | Max | Avg | Max | Avg | Max | Avg |
| Baffin Bay | Summer | 0-10 | 2 | 11.38 | 5.83 | 69.46 | 58.19 | 0.99 | 0.88 | 0.43 | 0.42 | 1.2 | 1.12 | 0.68 | 0.56 |
| 9 Mile Hole | Summer | 0-20 | 3 | 3.21 | 2.67 | 58.01 | 44.53 | 0.92 | 0.89 | 0.61 | 0.36 | 4.15 | 2.66 | 1.11 | 0.92 |
| | Fall | 0-20 | 3 | 0.65 | 0.44 | 85.6 | 71.22 | 0.99 | 0.98 | 0.39 | 0.22 | 4.78 | 2.37 | 0.41 | 0.34 |
| Upper Laguna | Summer | 0-8 | 2 | 1.61 | 0.97 | 58.52 | 43.41 | 0.96 | 0.87 | 0.23 | 0.16 | 1.43 | 1.37 | 0.34 | 0.24 |
| | Fall | 0-10 | 2 | 6.63 | 4.91 | 49.77 | 49.39 | 0.64 | 0.62 | 0.19 | 0.14 | 0.78 | 0.77 | 0.23 | 0.17 |
| Nueces River | Summer | 0-10 | 2 | 2.91 | 2.47 | 82.17 | 59.35 | 0.89 | 0.75 | 0.31 | 0.18 | 0.95 | 0.92 | 0.33 | 0.2 |
| | Fall | 0-12 | 3 | 23.09 | 15.56 | 93.77 | 58.94 | 0.83 | 0.7 | 0.51 | 0.41 | 0.84 | 0.74 | 0.55 | 0.44 |
| Nueces River Mouth | Summer | 0-12 | 2 | 3.29 | 3.09 | 58.4 | 56.13 | 0.98 | 0.95 | 0.75 | 0.56 | 1.02 | 1.01 | 0.78 | 0.59 |
| | Fall | 0-14 | 3 | 25.87 | 13.56 | 67.77 | 65.99 | 0.75 | 0.59 | 0.25 | 0.19 | 0.97 | 0.71 | 0.26 | 0.22 |
| Nueces Bay | Summer | 0-8 | 2 | 4.77 | 4.2 | 71.72 | 61.31 | 0.91 | 0.89 | 0.42 | 0.37 | 0.97 | 0.93 | 0.45 | 0.39 |
| | Fall | 0-8 | 2 | 17.28 | 12.27 | 108.75 | 82.77 | 0.47 | 0.43 | 0.16 | 0.11 | 0.79 | 0.64 | 0.21 | 0.15 |
| East Matagorda Bay A | Summer | 0-8 | 2 | 15.96 | 13.25 | 152.59 | 125.03 | 0.64 | 0.61 | 0.16 | 0.15 | 0.65 | 0.64 | 0.16 | 0.15 |
| | Fall | 0-20 | 3 | 17.06 | 11.26 | 177.18 | 143.15 | 0.84 | 0.75 | 0.26 | 0.2 | 1 | 0.93 | 0.28 | 0.24 |
| East Matagorda Bay C | Summer | 0-10 | 2 | 15.44 | 14.63 | 238.3 | 178.91 | 0.67 | 0.56 | 0.12 | 0.1 | 0.67 | 0.63 | 0.12 | 0.11 |
| | Fall | 0-14 | 3 | 15.03 | 12.24 | 141.66 | 133.79 | 0.7 | 0.58 | 0.21 | 0.13 | 0.72 | 0.65 | 0.22 | 0.14 |
| East Matagorda Bay F | Summer | 0-20 | 3 | 15.87 | 12.01 | 161.43 | 145.43 | 0.65 | 0.56 | 0.15 | 0.1 | 0.7 | 0.63 | 0.17 | 0.11 |
| | Fall | 0-20 | 3 | 13.59 | 12.85 | 104.33 | 91.91 | 0.76 | 0.73 | 0.3 | 0.28 | 0.81 | 0.76 | 0.34 | 0.29 |

Table 5  Percent of Sulfate Reduced

| Date | Sample ID | Salinity | Sulfate (mmol/ kg) | Ideal Sulfate | % Reduced | Error |
|---|---|---|---|---|---|---|
| 9/04 | BB 0-2 | 28.52 | 21.03 | 23.01 | 8.62 | 0.60 |
| 9/04 | BB 2-4 | 24.15 | 14.48 | 19.48 | 25.70 | 0.73 |
| 9/04 | BB 4-6 | 15.56 | 5.82 | 12.55 | 53.62 | 1.22 |
| 9/04 | BB 6-8 | 31.62 | 18.17 | 25.51 | 28.77 | 0.56 |
| 9/04 | BB 8-10 | 19.59 | 7.84 | 15.80 | 50.41 | 0.96 |
| 9/04 | BB 10-12 | 42.08 | 21.54 | 33.95 | 36.55 | 0.43 |
| 9/04 | BB 12-14 | 55.82 | 33.10 | 45.04 | 26.51 | 0.31 |
| | | | | | | |
| 9/04 | 9MH 0-2 | 39.12 | 31.64 | 31.56 | -0.25 | 0.44 |
| 9/04 | 9MH 2-4 | 38.50 | 29.04 | 31.07 | 6.52 | 0.44 |
| 9/04 | 9MH 4-6 | 39.39 | 25.20 | 31.78 | 20.71 | 0.44 |
| 9/04 | 9MH 8-10 | 38.39 | 21.29 | 30.97 | 31.26 | 0.46 |
| 9/04 | 9MH 10-12 | 35.80 | 12.17 | 28.88 | 57.86 | 0.54 |
| 9/04 | 9MH 12-14 | 35.38 | 5.15 | 28.55 | 81.98 | 0.60 |
| 9/04 | 9MH 14-16 | 46.40 | 5.34 | 37.44 | 85.74 | 0.47 |
| 9/04 | 9MH 16-18 | 33.51 | 0.60 | 27.04 | 97.77 | 0.68 |
| | | | | | | |
| 11/04 | 9MH 0-2 | 33.16 | 28.34 | 26.75 | -5.94 | 0.52 |
| 11/04 | 9MH 2-4 | 34.18 | 28.73 | 27.58 | -4.18 | 0.50 |
| 11/04 | 9MH 4-6 | 34.97 | 26.43 | 28.21 | 6.33 | 0.49 |
| 11/04 | 9MH 6-8 | 37.53 | 25.95 | 30.28 | 14.29 | 0.46 |
| 11/04 | 9MH 8-10 | 38.28 | 23.01 | 30.89 | 25.48 | 0.46 |
| 11/04 | 9MH 10-12 | 37.10 | 19.47 | 29.94 | 34.96 | 0.48 |
| 11/04 | 9MH 12-14 | 36.43 | 19.74 | 29.39 | 32.83 | 0.49 |
| 11/04 | 9MH 14-16 | 37.84 | 20.87 | 30.53 | 31.65 | 0.47 |
| 11/04 | 9MH 16-18 | 37.22 | 18.73 | 30.03 | 37.62 | 0.49 |
| | | | | | | |
| 9/04 | ULM 4-6 | 36.09 | 24.02 | 29.12 | 17.51 | 0.48 |
| | | | | | | |
| 11/04 | ULM 0-2 | 37.28 | 30.71 | 30.08 | -2.08 | 0.46 |
| 11/04 | ULM 2-4 | 35.41 | 30.13 | 28.57 | -5.44 | 0.48 |
| 11/04 | ULM 4-6 | 35.69 | 31.33 | 28.80 | -8.79 | 0.48 |
| 11/04 | ULM 6-8 | 30.82 | 27.39 | 24.87 | -10.12 | 0.56 |
| 11/04 | ULM 8-10 | 30.84 | 26.33 | 24.88 | -5.82 | 0.55 |
| | | | | | | |
| 9/04 | EMB A 0-2 | 35.19 | 31.98 | 28.40 | -12.62 | 0.49 |
| 9/04 | EMB A 2-4 | 19.88 | 14.08 | 16.04 | 12.21 | 0.86 |
| 9/04 | EMB A 4-6 | 21.83 | 15.82 | 17.62 | 10.18 | 0.79 |
| 9/04 | EMB A 6-8 | 41.64 | 28.78 | 33.60 | 14.34 | 0.41 |
| | | | | | | |

| Date | Sample ID | Salinity | Sulfate (mmol/ kg) | Ideal Sulfate | % Reduced | Error |
|------|-----------|----------|--------------------|---------------|-----------|-------|
| | | | | Table 5 Continued | | |
| 10/04 | EMB A 2-4 | 20.35 | 14.71 | 16.42 | 10.46 | 0.84 |
| 10/04 | EMB A 4-6 | 32.51 | 24.49 | 26.23 | 6.63 | 0.53 |
| 10/04 | EMB A 6-8 | 31.29 | 20.75 | 25.25 | 17.81 | 0.55 |
| 10/04 | EMB A 8-10 | 21.14 | 15.60 | 17.06 | 8.56 | 0.81 |
| 10/04 | EMB A 10-12 | 54.00 | 45.48 | 43.57 | -4.37 | 0.32 |
| 10/04 | EMB A 12-14 | 37.24 | 21.38 | 30.05 | 28.84 | 0.47 |
| 10/04 | EMB A 14-16 | 27.74 | 19.42 | 22.38 | 13.23 | 0.62 |
| | | | | | | |
| 9/04 | EMB C 0-2 | 37.59 | 36.53 | 30.33 | -20.45 | 0.46 |
| 9/04 | EMB C 2-4 | 44.71 | 46.72 | 36.07 | -29.51 | 0.40 |
| 9/04 | EMB C 4-6 | 45.58 | 41.75 | 36.78 | -13.52 | 0.38 |
| 9/04 | EMB C 6-8 | 18.75 | 7.98 | 15.13 | 47.23 | 0.99 |
| 9/04 | EMB C 8-10 | 18.53 | 13.50 | 14.95 | 9.71 | 0.93 |
| 9/04 | EMB C 10-12 | 19.17 | 13.70 | 15.47 | 11.39 | 0.90 |
| | | | | | | |
| 10/04 | EMB C 0-2 | 20.33 | 16.27 | 16.40 | 0.81 | 0.84 |
| 10/04 | EMB C 2-4 | 18.28 | 14.95 | 14.75 | -1.36 | 0.93 |
| 10/04 | EMB C 4-6 | 26.62 | 21.18 | 21.48 | 1.39 | 0.64 |
| 10/04 | EMB C 8-10 | 51.81 | 51.45 | 41.80 | -23.08 | 0.34 |
| | | | | | | |
| 9/04 | EMB F 0-2 | 30.93 | 21.44 | 24.96 | 14.08 | 0.56 |
| 9/04 | EMB F 2-4 | 32.36 | 26.11 | 26.11 | 0.00 | 0.53 |
| 9/04 | EMB F 4-6 | 29.55 | 22.76 | 23.84 | 4.53 | 0.58 |
| 9/04 | EMB F 6-8 | 32.57 | 25.63 | 26.28 | 2.46 | 0.52 |
| 9/04 | EMB F 8-10 | 26.40 | 20.70 | 21.30 | 2.81 | 0.65 |
| 9/04 | EMB F 10-12 | 25.15 | 21.25 | 20.29 | -4.73 | 0.68 |
| 9/04 | EMB F 12-14 | 27.46 | 21.31 | 22.16 | 3.81 | 0.62 |
| 9/04 | EMB F 14-16 | 29.07 | 19.04 | 23.46 | 18.82 | 0.60 |
| 9/04 | EMB F 16-18 | 29.34 | 20.99 | 23.67 | 11.34 | 0.59 |
| 9/04 | EMB F 18-20 | 27.20 | 16.53 | 21.95 | 24.67 | 0.64 |
| | | | | | | |
| 10/04 | EMB F 0-2 | 28.18 | 30.98 | 22.74 | -36.25 | 0.64 |
| 10/04 | EMB F 2-4 | 15.54 | 12.54 | 12.54 | -0.04 | 1.10 |
| 10/04 | EMB F 4-6 | 16.22 | 12.89 | 13.09 | 1.55 | 1.05 |
| 10/04 | EMB F 6-8 | 17.42 | 14.76 | 14.06 | -4.97 | 0.98 |
| 10/04 | EMB F 8-10 | 17.55 | 14.37 | 14.16 | -1.47 | 0.97 |
| 10/04 | EMB F 10-12 | 16.43 | 13.52 | 13.25 | -2.02 | 1.04 |
| 10/04 | EMB F 12-14 | 17.23 | 13.95 | 13.90 | -0.32 | 0.99 |
| 10/04 | EMB F 14-16 | 17.60 | 14.92 | 14.20 | -5.05 | 0.97 |

## 4. DISCUSSION

### *4.1 Examination of Locations*

4.1.1   Baffin Bay

The three sites (Baffin Bay – BB, Nine Mile Hole – 9MH, and Upper Laguna Madre – ULM) around the Baffin Bay area were the only sites with more than a few μmol of AVS present.  This might indicate that BB and 9MH both have rapid deposition, and that FeS does not have time to convert to pyrite before being buried. These sites are not sulfate limited, as they have the highest salinities studied (S~35). ULM does not have high AVS or TRS, which is most likely due to its sandy nature. These low concentrations further inhibit pyrite growth due to transport kinetics in diffusion controlled reactions, as seen by Morse (1999).  While 9MH does not have high TRS, the AVS fraction is greater than 40% of the TRS.  This is a further indication of a rapidly deposited sediment with slow reaction kinetics.  This was also found by Morse (1999) in Laguna Madre sediments.  In both seasons the AVS generally decreases with depth and the % of sulfate reduced increases, indicating the possibility that sulfate does become limiting with depth.  As previously stated, BB sediments were unusual in that the salinity was lower than the average ocean whereas normally this is a hypersaline environment.  TRS was fairly high and AVS was present. Morse et. al (1992) determined that this site was iron limiting.  In this study CD-DOP was very high (>0.8), agreeing with their findings.

4.1.2    Nueces Estuary

The three sites (Nueces River – NR, Nueces River Mouth – NRM, Nueces Bay – NB) in the Nueces Estuary showed the greatest variability among the locations studied.  This is to be expected as they are the closest to a river, and thus the most likely to experience changes in inputs to the system.   As with the EMB sites, all sites had low AVS values in both seasons.  However, NR and NRM both showed dramatic differences in TRS values seasonally.  While salinity varied a great deal between the sites, this did not seem to have a large affect on the differences in TRS.  In fact, the opposite of what might be expected is true, as the two sites with high TRS both had low salinities (S<8).  Iron also does not appear to be the limiting factor for TRS.  The only site with a high DOP is NRM summer, which is also the site with the highest TRS values.  This might indicate that whatever the limiting factor is at the other sites it is not present here, and TRS was produced until the iron ran out.

4.1.3    East Matagorda Bay

As previously stated, the three sites in East Matagorda Bay (EMB A, EMB C, and EMB F) are all fairly similar to each other.  Organic-C is not limiting at any site.  Given that iron was present in the microelectrode profiles and the DOP was <0.8 at all sites regardless of which extraction procedure was used, it is unlikely that iron is the limiting reagent at any site.  AVS and TRS are very similar at all sites, with only a slight seasonal change, indicating that the salinity difference of EMB F is not significant.  AVS is always a small component of TRS, which is consistent with the observations of Goldhaber and Kaplan (1974).  They hypothesized that the availability

of both organic compounds and reactive sulfur would enable $H_2S$ to form pyrite directly and that near the upper layer of sediment the FeS would be able to rapidly transform to pyrite. While EMB A showed a dramatic increase in both AVS and TRS from summer to fall, the lack of change in any other measured parameter indicates the possibility that this is not a seasonal effect, but merely demonstrates the heterogeneity of the site.

### 4.2 General Discussion

4.2.1 Controls on TRS

The relationships between the three major variables that control TRS are presented by location in Figures 4-6. In nearly all sites the wt. % Org-C is not limiting (>0.5 %). With the exception of the sites in and near the Nueces River S>15, so it is unlikely that sulfate is the limiting factor either. In most cases it is apparent that iron is the limiting factor. While there are a few outlying data points in the Nueces estuary system (with both high sedimentary iron and high dissolved values) overall there are low iron values in both the solid and the dissolved phase. The one location that breaks this pattern is East Matagorda Bay. There is high solid-phase and dissolved iron in all three sites. This is expected because the EMB sites tend to be finer-grained than those at other locations, and fine-grained sediments are more likely to be Fe-rich (Morse et. al. 1992). The high (>0.8) DOP values (Table 4) in nearly all sites support the iron-limited hypothesis. Mention should be made here of the differences in the CD-Fe and HCl-Fe extraction chemistries. Berner (1970) demonstrated that the HCl extraction procedure dissolves non-crystalline FeS, mackinawite, and greigite, while Cornwell

and Morse (1987) showed that the citrate dithionate method dissolves mackinawite but not all greigite. The vastly different values of DOP further support the argument of Raiswell et. al (1994) that while HCl-Fe is important on geologic timescales, CD-Fe is a better indicator of short-term processes occurring in estuary sediments.

4.2.2  C/S ratio

The C/S ratio in a "normal" marine sediment is 2.8 ± 0.8 (Berner, 1982) "Normal" is defined as a fine-grained, siliclastic sediment overlain by oxic waters of typical marine salinity. The exact boundaries for this condition are not explicitly defined. However, sediments from a wide variety of environments generally fall into this range (Goldhaber and Kaplan, 1974), (Berner, 1982). Data for the sediments examined in this study are presented in Figure 7. While many of the data points fall outside of this range, they also fall outside the range of "normal" marine sediments. When sandy sediments, sediments overlain by freshwater, and those with a high percentage of carbonate are removed from consideration, the data generally falls within the typical range. Those "normal" sediments that do fall outside of the typical range tend to have higher organic-C values, and are most likely in highly productive areas, e.g. Morse et. al. (1992) or are iron limited for pyrite formation (Morse and Berner, 1995). Also, because the sediment cores are relatively shallow, the reactions might not have gone to completion, leading to an altered C/S ratio.
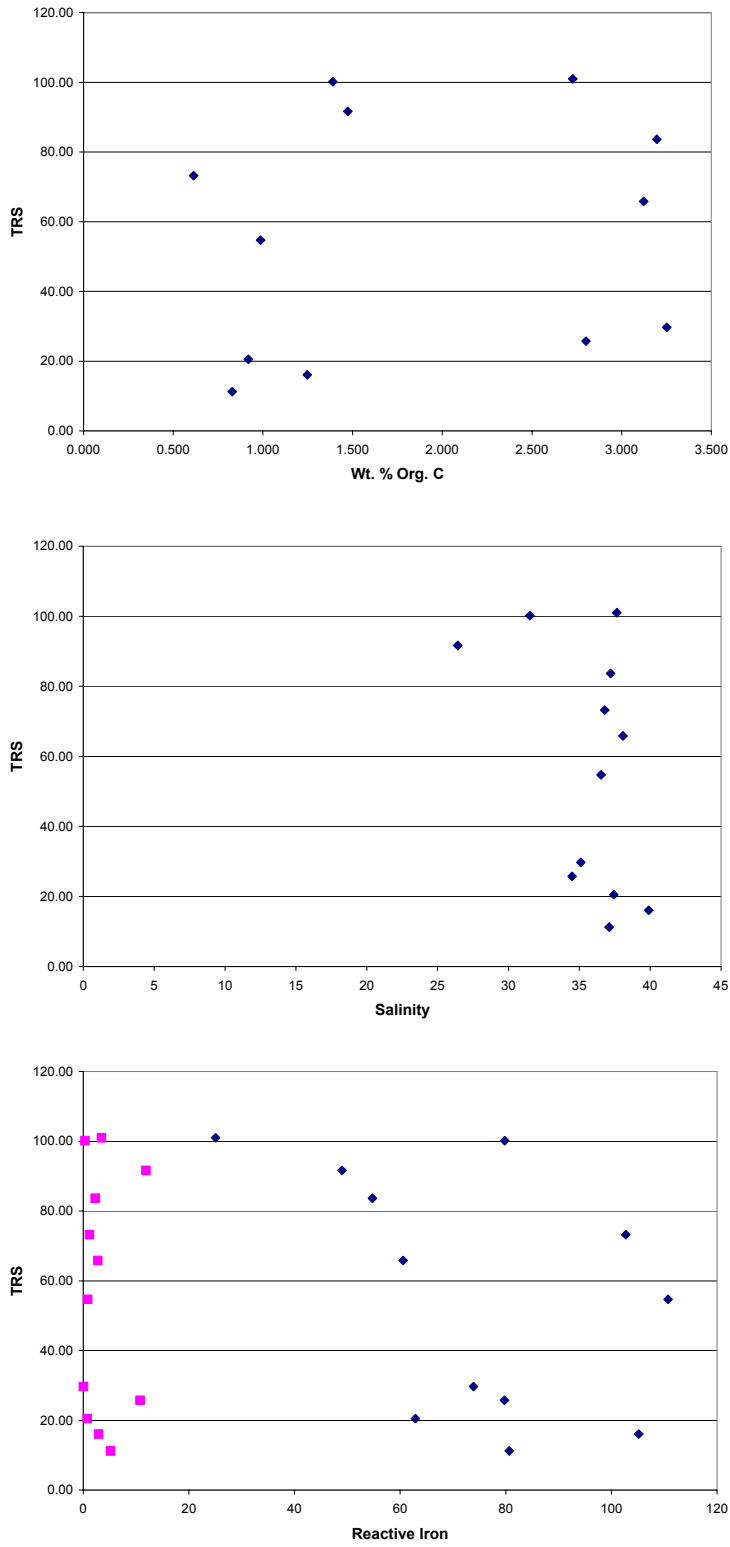
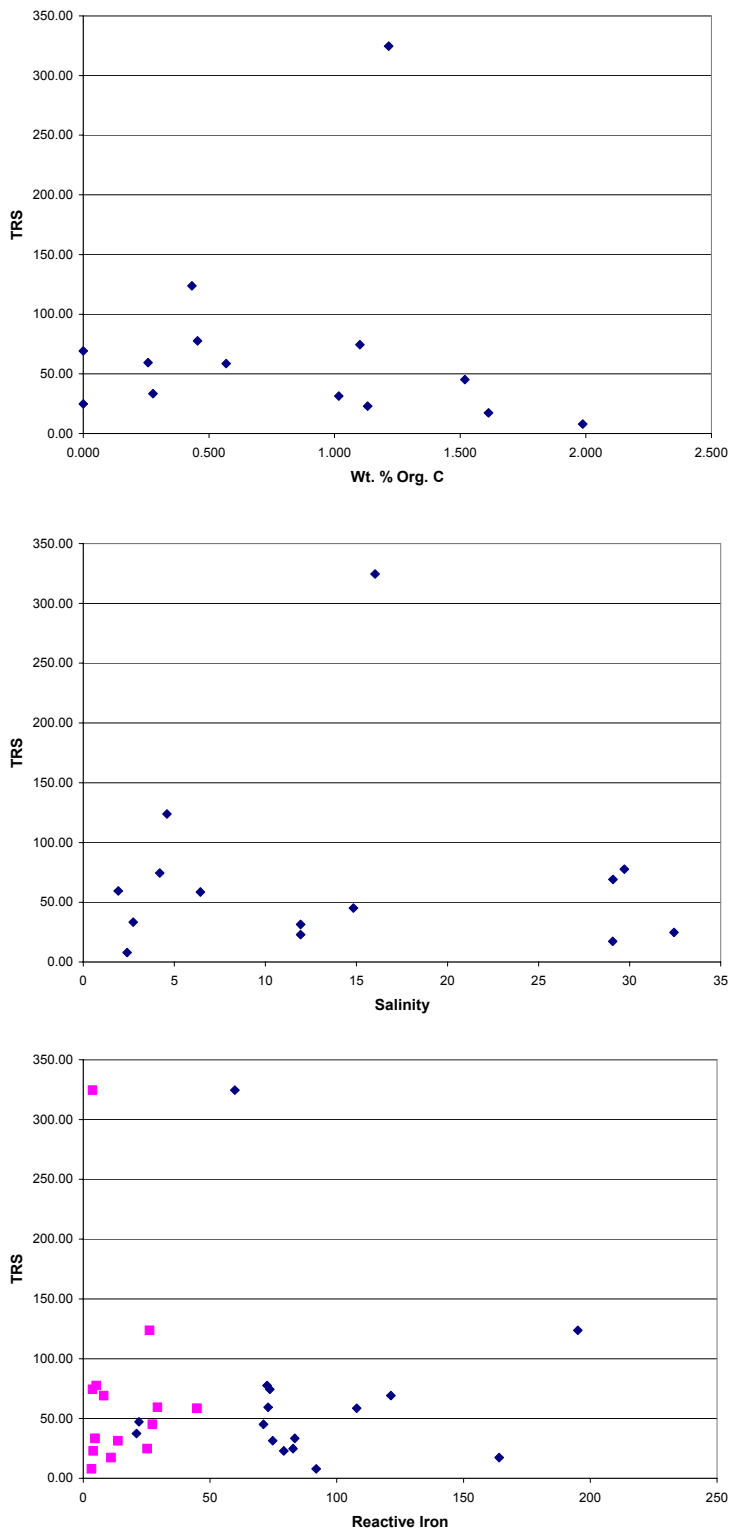Figure 4  Controls on TRS from Baffin Bay Sites
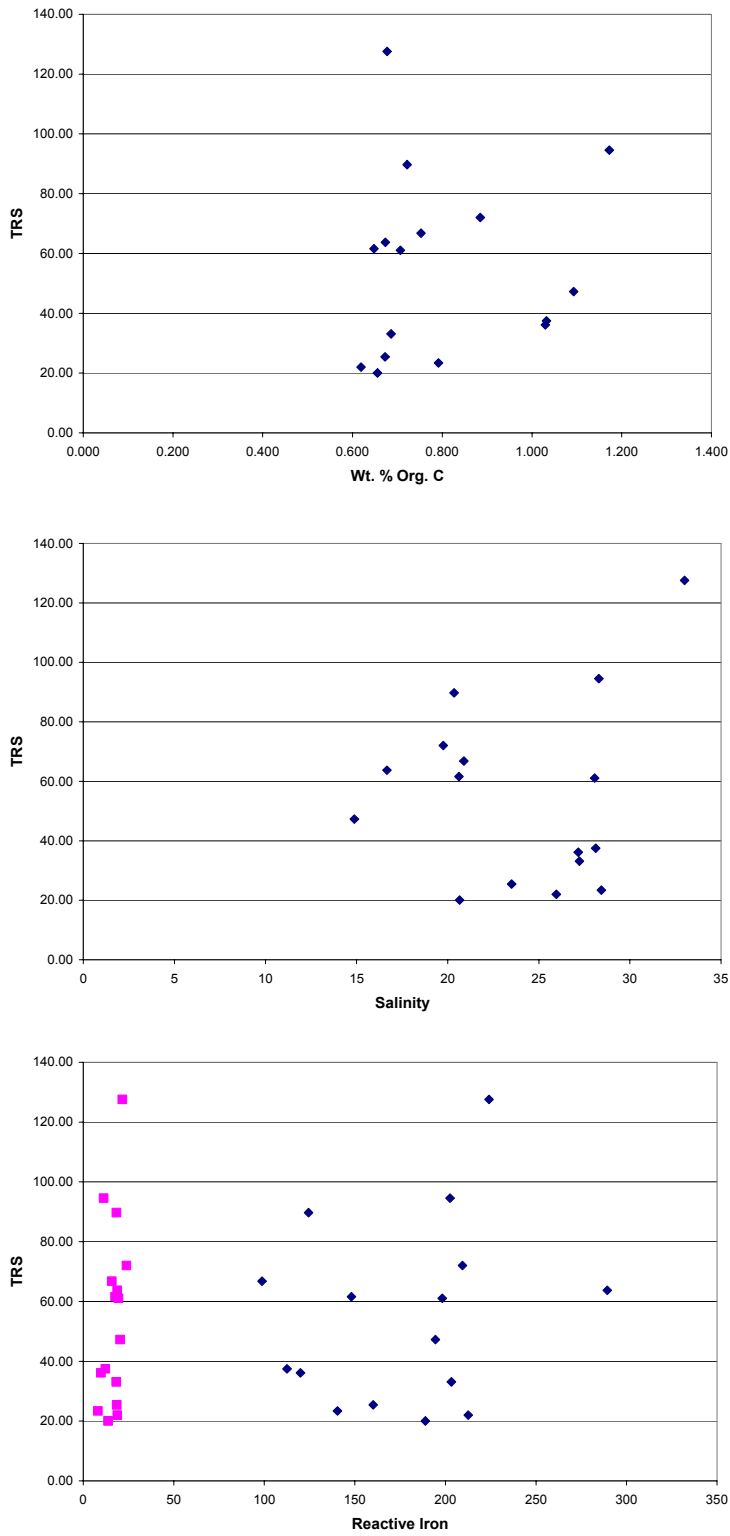
Figure 5  Controls on TRS from Neuces Sites

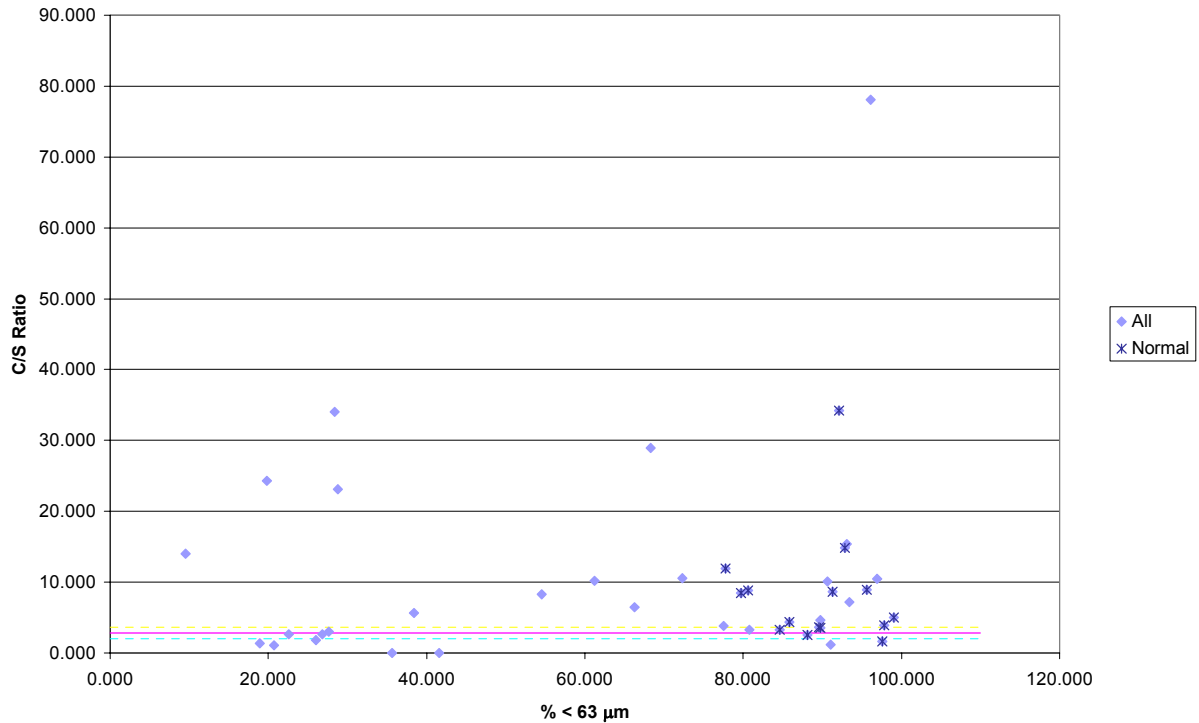Figure 6  Controls on TRS for Matagorda Bay Sites

Figure 7 C/S Ratio vs wt % < 63 μm

4.2.3   Sedimentary environment

Figure 8 is a duplication of a graph created by Aller et. al. (1986) with the data

points from this study added.  It shows the weight ratios of S:Fe and C:Fe plotted

against each other.  This can be used to describe the depositional environment that sites

can exhibit.  As expected, only some of the data falls within the range of "normal"

sediments.   None fell within the range of iron-rich sediments, supporting the

conclusion that iron is generally the limiting factor on the Central Texas coast.  Some

of the Nueces sites plot toward the freshwater line, as is expected.  The two sites that

plot above the pyrite line both have high TRS, and little iron, explaining why they plot

so high off the scale.  Some Baffin Bay sites plot into the biogenic range, which is also

expected due to the high amount of seagrasses present in the area.  What is unusual is

that some Baffin Bay sites plotted into the freshwater range, even though those sites
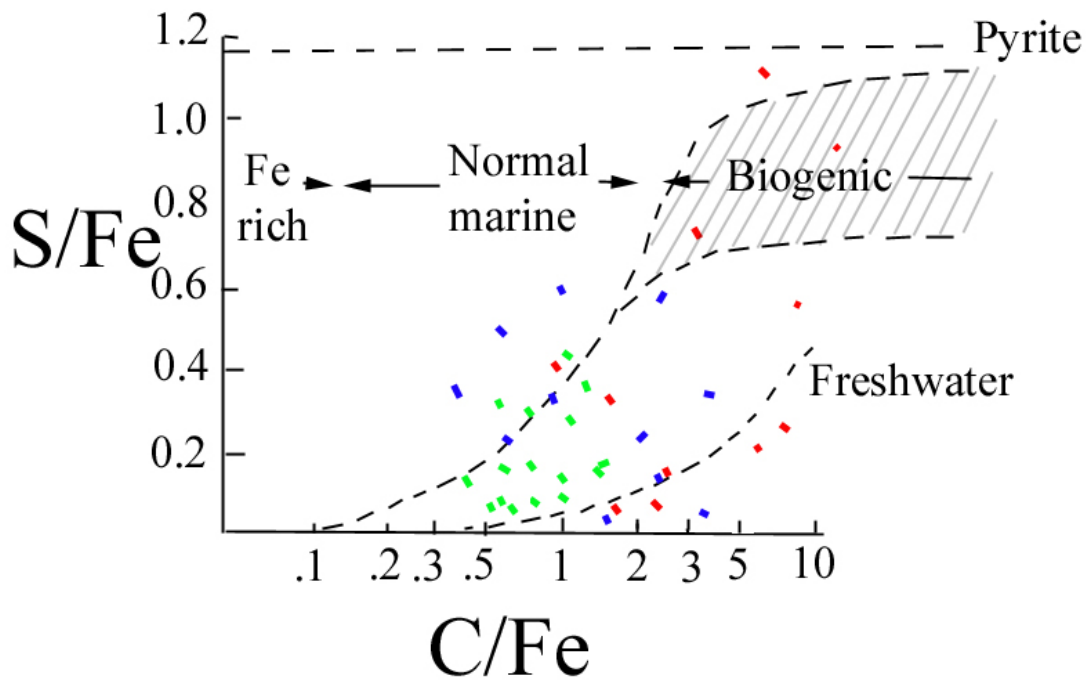
had the highest salinities.



Figure 8 Sedimentary environment

4.2.4   Seasonality

No significant difference was noted between samples of different seasons.  This was not altogether unexpected, as there wasn't a large amount of time between sampling trips.  However, if samples had also been taken in the winter one might expect to find a greater difference seasonally, as did Thamdrup et. al (1994) in Aarhus Bay, Denmark, and Rozan et. al. (2002) in Rehoboth Bay, Delaware.  This seasonal difference comes about because of changes in temperature and water flow.  This brings varying amounts of nutrients into the system, which affects productivity.  Changes in organic matter degradation and thus AVS and TRS formation follow.  Had samples been taken throughout the year a more dramatic seasonal change might have been observed.

4.2.5   Comparison to previous work in same location

As previously mentioned, much work has been done in some of the same locations of this study, namely Laguna Madre and Baffin Bay (Morse et. al., 1992), (Morse, 1999).  Overall the results from this study correlate well with what they observed.  In Upper Laguna Madre the extractable iron (both HCl and CD) and the amount of organic carbon found fell within the ranges observed previously.  The amount of TRS found was higher than that found by Morse, but that could reflect a seasonal difference or it could be a result of the fact that different depths were analyzed in each study.  The results from Baffin Bay also fit within those previously found, though they were at the high end of the range observed.  The only difference was that AVS was much greater in this study than before.  This again can be attributed to

differences in sampling depth, as the previous work was done at 20 cm core depth, after much of the AVS has reacted to TRS.

4.2.6   Comparison to previous work in other locations

Many other studies have been done in estuaries similar to the one studied here, and generally similar results were found.  Thamdrup et. al (1994) studied the Aarhus Bay in Jutland, Denmark.  Though water depth was greater (~16 m) and the water temperature cooler (10-15 °C) they also found no seasonal relationship for AVS or $FeS_2$.  They did, however, find a seasonal relationship in the overall Fe and Mn cycle, including an effect of bioturbation.  They also found higher amounts of Fe in the sediment using CD extraction.

Another study, performed by Rozan et. al (2002) studied Fe, S and P cycling in Rehoboth Bay, Delaware.   They found that the seasonal change in redox conditions was the driving factor in the Fe and S cycle.  In the summer, because of high organic matter decomposition, the pH of the water dropped to 6.5, making $H_2S$ (as opposed to $HS^-$) the dominant sulfide species.  This reacts with $FeS_{aq}$ faster than the $HS^-$, increasing the speed of pyrite formation.  While pH was not examined in the present study, this could explain the lack of seasonality observed, because in the Delaware study the pH did not rise again until winter.

# 5.  CONCLUSION

While the heterogeneity of locations along the Central Texas coast makes it difficult to make a definitive statement about the controls on TRS in this area, it is generally true that the sites are iron limited.  Low reactive iron concentrations and high degrees of pyritization (DOPs) support this argument.  Exceptions exist for low-salinity (sulfate-limited) or very fine-grained (organic matter limited) sites.  The work done agrees well with other studies done in the same and similar locations, and is useful in expanding our understanding of the estuarine sulfur cycle.

## REFERENCES

Aller, R. C., Mackin, J. E., Cox R.T. (1986). Diagenesis of iron and sulfur in Amazon inner shelf muds: apparent dominance of iron reduction and implications for the genesis of ironstones. *Continental Shelf Research* **6**(1-2), 263-89.

Behrens, E. W. (1969). Hurricane effects on a hypersaline bay. *Lagunas Costeras, un Simposio. Mem. Simp. Intern. Lagunas Costeras.* UNAM-UNESCO, Nov. 28-30, 1967. Mexico, D.F., 301-312.

Berner, R. A. (1970). Sedimentary pyrite formation. *Americal Journal of Science* **268**, 1-23.

Berner, R. A. (1982). Burial of organic carbon and pyrite sulfur in the modern ocean: its geochemical and environmental significance. *American Journal of Science* **282**(4), 451-73.

Boesen, C. and Postma D. (1988). Pyrite formation in anoxic environments of the Baltic. *Americal Journal of Science* **288**, 575-603.

Brendel, P. J. and Luther G. W. I. (1995). Development of a gold amalgam voltammetric microelectrode for the determination of dissolved Fe, Mn, $O_2$, and S(-II) in porewaters of marine and freshwater sediments. *Environmental Science and Technology* **29**(3), 751-61.

Canfield, D. E., Raiswell, R., Westrich, J.T., Reaves, C.M., Berner, R.A. (1986). The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chemical Geology* **54**(1-2), 149-55.

Cooper, D. C. and Morse J. W. (1996). The chemistry of Offatts Bayou, Texas: a seasonally high sulfidic basin. *Estuaries* **19**(3), 595-611.

Cornwell, J. C. and Morse J. W. (1987). The characterization of iron sulfide minerals in anoxic marine sediments. *Marine Chemistry* **22**(2-4), 193-206.

Goldhaber, M. B. and Kaplan I. R. (1974). The sulfur cycle. in Goldberg, E. D. (ed) *The Sea*. New York, John Wiley & Sons. **5**, 569-655.

Jørgensen, B. B. (1978). A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments: measurement with radiotracer techniques. *Geomicrobiology Journal* **1**, 11-28.

Lin, S. (1990). Environmental controls on sulfate reduction and iron sulfide mineral formation. Ph.D, College Station. Texas A&M University.

Martens, C.S. and Klump J. V. (1984). Biogeochemical cycling in an organic-rich coastal marine basin 4. An organic carbon budget for sediments dominated by sulfate reduction and methanogenesis. *Geochimica et Cosmochimica Acta* **48**, 1987-2004

Morse, J. W. (1999). Sulfides in sandy sediments: new insights on the reactions responsible for sedimentary pyrite formation. *Aquatic Geochemistry* **5**(1), 75-85.

Morse, J. W., Cornwell, J. C., Arakaki, T., Lin, S., and Huerta-Diaz, M. (1992). Iron sulfide and carbonate mineral diagenesis in Baffin Bay, Texas. *Journal of Sedimentary Petrology* **62**(4), 671-80.

Morse, J. W., Berner, R. A (1995). What determines sedimentary C/S ratios?. *Geochimica et Cosmochimica Acta* **59**(6), 1073-7.

Poulton, S. W. and Canfield D. E. (2005). Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. *Chemical Geology* **214,** 209-221.

Raiswell, R., Canfield, D. E. and Berner, R.A. (1994). A comparison of iron extraction methods for the determination of degree of pyritisation and the recognition of iron-limited pyrite formation. *Chemical geology* **111**, 101-10.

Reeburgh, W. S. (1967). Improved interstitial water sampler. *Limnology and Oceanography* **12**(1), 163-5.

Rickard, D. and Morse J. W. (2005). Acid volatile sulfide (AVS). *Marine Chemistry* **97**(3-4), 141-197.

Rozan, T. F., Taillefert, M., Trouwborst, R.E., Glazer, B.T., and Ma, S. (2002). Iron-sulfur-phosphorus cycling in the sediments of a shallow coastal bay: Implications for sediment nutrient release and benthic macroalgal blooms. *Limnology and Oceanography* **47**(5), 1346-1354.

Thamdrup, B. Fossing, H., Jørgensen, B.B. (1994). Manganese, iron, and sulfur cycling in a coastal marine sediment, Aarhus Bay, Denmark. *Geochimica et Cosmochimica Acta* **58**(23), 5115-5129.

**APPENDIX A**

Results from the microelectrode profiles are summarized in Table 6. Two different sulfur values are presented based on two different calibration slopes for $Mn^{2+}$. As can be seen, iron is generally limited in the Baffin Bay sites, with the sulfide concentration much higher than that of iron. The opposite is true for the Matagorda Bay sites, with iron in much higher concentration than sulfide. No apparent pattern exists in the Nueces sites.

Integrated sulfate reduction rates are presented in Table 7. No data are presented for the Nueces sites due to difficulties in processing cores. Duplicate cores for SRR were taken in the fall to ensure reproducibility of the method. Values obtained agree well with those found by Lin (1990). A difficulty arises, however, when values from different sites are compared to each other as not all cores were measured to the same depth. It was attempted to measure cores from the same site to the same depth, with some success.

At almost all sites the SRR increased in the fall as compared to the summer. At 9MH, the SRR was fairly high. This supports the high sedimentation rate hypothesis mentioned previously. However, the amount of organic carbon decreases from summer to fall, leading one to expect the SRR to decrease, not increase. At the EMB sites, both sulfate concentration and organic carbon remained the same, while the SRR increased. A possible explanation for this is a change in the sedimentation rate.

Table 6: Microelectode Profile Descriptions

| Site | Season | Core Depth (mm) | Average S(µM) | Range lowS (µM) | Range highS (µM) | Depth of Maximum (mm) | Average S(µM) | Range lowS (µM) | Range highS (µM) | Shape | Average Fe2+(µM) | Range lowFe2+(µM) | Site | Season | Range highFe2+(µM) | Depth of Maximum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EMB-A | Summer | 60 | 0.577 | 0 | 1.347 | 4 | 10.400 | 0 | 24.283 | | 250.625 | 0 | EMB-A | Summer | 456.129 | 12 |
| | Fall | 100 | 0.869 | 0 | 1.976 | 75 | 15.672 | 0 | 35.629 | | 719.418 | 73.021 | | Fall | 1583.992 | 100 |
| EMB-C | Summer | 90 | 0.037 | 0 | 0.287 | 65 | 0.676 | 0 | 5.175 | | 22.823 | 0 | EMB-C | Summer | 198.510 | 12 |
| | Fall | 100 | 0.779 | 0 | 10.515 | 0 | 10.744 | 0 | 100.538 | | 868.328 | 77.724 | | Fall | 1456.783 | 10 |
| EMB-F | Summer | 100 | - | - | - | - | - | - | - | sulfide | 762.244 | 434.521 | EMB-F | Summer | 1146.647 | 45 |
| | Fall | 100 | 1.808 | 0 | 11.224 | 0 | 32.599 | 0 | 202.389 | | 1326.277 | 317.052 | | Fall | 1670.669 | 40 |
| 9MH | Summer | 100 | 8.243 | 0 | 15.530 | 25 | 120.054 | 0 | 280.038 | | - | - | 9MH | Summer | - | iron below |
| | Fall | 100 | 35.520 | 1.3244 | 151.872 | 100 | 639.589 | 23.880 | 2738.475 | | 287.591 | 0 | | Fall | 1647.555 | 16 |
| ULM | Summer | 50 | 51.721 | 37.628 | 207.451 | 12 | 932.602 | 678.4926 | 3740.650 | | - | - | ULM | Summer | - | iron below |
| | Fall | 90 | 35.223 | 0 | 56.026 | 65 | 635.120 | 0 | 1010.229 | | 656.561 | 0 | | Fall | 6651.184 | 20 |
| Bay | Summer | 100 | - | - | - | - | - | - | - | sulfide | 71.554 | 0 | Bay | Summer | 1333.269 | 90 |
| | Fall | 100 | 1.570 | 0 | 4.457 | 35 | 28.307 | 0 | 80.359 | | 584.454 | 0 | | Fall | 3854.812 | 55 |
| Mouth | Summer | 100 | 16.048 | 0 | 28.311 | 65 | 289.373 | 0 | 510.496 | | 176.671 | 0 | Mouth | Summer | 389.270 | 16 |
| | Fall | 100 | 13.034 | 0 | 25.163 | 90 | 235.027 | 0 | 453.731 | | 1404.491 | 0 | | Fall | 2951.919 | 70 |
| River | Summer | 100 | 1.556 | 0 | 10.071 | 95 | 28.051 | 0 | 181.592 | | 1030.308 | 0 | River | Summer | 1955.535 | 95 |
| | Fall | 100 | 1.599 | 0 | 4.538 | 70 | 28.829 | 0 | 81.826 | | 1640.900 | 840.426 | | Fall | 2357.963 | 14 |

Table 7  Sulfate Reduction Rate

| Sample ID | Depth Range Measured | SRR mmoles-sulfate-reduced/ m2-sed/day) |
|---|---|---|
| BB 9/04 - A | 0-11 cm | 1.64 |
| BB 9/04 - B | 0-11 cm | 2.74 |
| 9MH 9/04 - A | 0-17 cm | 3.99 |
| 9MH 9/04 - B | 0-17 cm | 3.28 |
| 9MH11/04 | 0-17 cm | 5.55 |
| ULM 9/04 | 0-5 cm | 1.18 |
| ULM 11/04 | 0-9 cm | 15.58 |
| EMB A 9/04 - A | 0-7 cm | 2.76 |
| EMB A 9/04 - B | 0-7 cm | 2.54 |
| EMB A 11/04 | 0-15 cm | 7.55 |
| EMB C 9/04 - A | 0-11 cm | 23.10 |
| EMB C 9/04 - B | 0-9 cm | 6.64 |
| EMB C 11/04 | 0-7 cm | 2.79 |
| EMB F 9/04 - A | 0-19 cm | 5.87 |
| EMB F 9/04 - B | 0-19 cm | 5.14 |
| EMB F 11/04 | 0-15 cm | 6.92 |

**VITA**

Name:  Heather Thomson

Address: MS 3146 Texas A&M University  College Station, TX 77840

E-mail address: featherfish81@neo.tamu.edu

Education:
        Texas A&M University, College Station, TX
            M.S. in Oceanography August, 2006
        Lehigh University, Bethlehem, PA
            B. S. in Chemistry, May 2003
            Minor in Political Science, May 2003

Leadership Experience:
        Aggie Christian Grads, Secretary/Treasurer, September 2005-present

        Kappa Kappa Psi, Honorary Band Service Fraternity. Parliamentarian,
        September 2002-May 2003

        Reformed University Fellowship, Secretary, September 2001 – May 2003

        MVCA Camp Musconetcong, Counselor, Long Valley, NJ, Summers 1999 and
2000

Research Experience:
        Texas A&M University, Research Assistant, College Station, TX, June 2003 –
present

        Lehigh University, Research Assistant, Bethlehem, PA, September 2002-May
2003

        University of Queensland and Long Island University, Student, Queensland,
        Australia, June 2002

Activities:
        Oceanography Graduate Council (Member of Executive Board)
        Aggie Christian Grads (member of Leadership Team)