

1989

## Sulfur Chemistry of Louisiana Tidal Marsh Soils.

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**Sulfur chemistry of Louisiana tidal marsh soils**

**Krairapanond, Nawarat, Ph.D.**

**The Louisiana State University and Agricultural and Mechanical Col., 1989**

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Ann Arbor, MI 48106



Sulfur Chemistry  
of  
Louisiana Tidal Marsh Soils

A Dissertation

Submitted to the Graduate Faculty of the  
Louisiana State University and  
Agriculture and Mechanical College  
in Partial fulfillment of the  
requirements for the degree of  
Doctor of Philosophy

in

The Department of Marine Sciences

by  
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December 1989

To  
my lovely wife  
for  
her devotion  
and  
my parents  
and  
all hard-working Thai students

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## ABSTRACT

The amounts and profile distribution of various sulfur forms in Louisiana coastal marshes were investigated to understand sulfur cycling as related to the origin and type of tidal wetland marshes. Sampling was conducted quarterly from a *Panicum hemitomon* freshwater marsh, a *Spartina patens* brackish marsh, and a *Spartina alterniflora* salt marsh in Barataria Basin, Louisiana. Soil samples were fractionated into acid-volatile sulfides (AVS), elemental sulfur, HCl-soluble sulfur, pyrite sulfur, ester-sulfate sulfur, carbon-bonded sulfur, and total sulfur.

Seasonal changes showed a greater effect on the distribution of S fractions in brackish and salt marsh than in the freshwater marsh. Season appeared to have a pronounced effect on the distribution of acid-volatile sulfides, elemental sulfur, and pyrite sulfur. The profile distribution of acid-volatile sulfides and elemental sulfur in all marshes was similar. These sulfur forms showed the greatest abundance in the oxidized zone (<20 cm) during spring, summer, and fall. Marsh soil oxidation processes occurring during the plant growing season and a falling water level over the marsh surface resulted in a low pyrite sulfur concentration in the surface. The maximum concentration of pyrite sulfur was observed below 20 cm in all marsh types and its concentration was relatively high during winter. The presence of HCl-soluble sulfur was contributed largely from pore water sulfate, which was greater in salt marsh than in brackish and freshwater marshes, respectively. Organic sulfur, in the forms of ester-sulfate sulfur and carbon-bonded sulfur, was the major contributor to the total sulfur pool in all marsh types. Carbon-bonded sulfur was generally 2 to 3 times more abundant than ester-sulfate sulfur with less seasonal variation. Sulfur concentration (volume basis) and sulfur accumulation rates increased from freshwater marsh to salt marsh. Reduced sulfur species removed by marsh accretion or sedimentation process are likely significant in marsh energy flow. Plant activity, tidal fluctuation, and distance along a salinity gradient from the Louisiana coast seemed to have a strong influence on the distribution of sulfur.

## INTRODUCTION

Sulfur (S) is an important element of both natural and anthropogenic processes (Landers et al., 1983). Sulfur plays two key roles in wetland biological systems; it is an essential element required by all plants and organisms, and acts as a significant electron carrier in anoxic and partially anoxic ecosystems (Howarth, 1984). Because S can be present in inorganic and organic forms with oxidation states varying from -2 to +6, several important transformations in the S cycle involve changes in these oxidation states (Trudinger, 1986). It is obvious that S can undergo several biogeochemical transformation in coastal wetlands, including sulfate reduction, iron sulfides and pyrite formations, metal-trace element cycling, energy and nutrient transport, and atmospheric S emission. Each of these processes is reviewed in Chapter I. The emphasis of this literature review is placed on the biogeochemical significance and dynamics of S in coastal marshes and estuarine systems.

One important aspect of marsh composition that has received little attention is the nature and distribution of inorganic and organic forms of S as related to the origin and type of marsh material (Lowe and Bustin, 1985). Since Louisiana's coastal zone is one of the most wetland-rich regions of the world (Mitsch and Gosselink, 1986), an understanding of the distribution and dynamics of S-containing components is very important in studies of marsh development and their ecological significance including energy flow. The distribution of inorganic and organic S forms has been reported for salt marsh soils of California (Kaplan et al., 1963) and Maryland (Haering et al., 1989), and Florida marine-freshwater peats (Casagrande et al., 1977; Altschuler et al., 1983). Only one previous study has documented the seasonal cycling between inorganic and organic S forms in salt marsh soil (Luther and Church, 1988). Moreover, no attempt has been made to examine the seasonal distribution of inorganic and organic S forms in freshwater and brackish marsh soils. It is obvious that seasonal changes display a dramatic effect on the concentration, form, and profile distribution of S-containing compounds in several

coastal marsh soils (Howarth and Teal, 1979; Giblin and Howarth, 1984; Luther et al., 1986; Cutter and Velinsky, 1988; Feijtel et al., 1988; King, 1988; Luther and Church, 1988; Hines et al., 1989).

The coastal zone of the Gulf of Mexico contains 5 480 square miles or 58 % of the total coastal marshes in the United States (Alexander et al., 1986). About 69 % of this marshland occurs in Louisiana and extends inland for distances up to 50 miles. Because of the tremendous width of the marsh area along the Louisiana coast, freshwater, brackish, and salt marshes develop and represent 31, 31, and 21 % of total Louisiana marsh area, respectively (Chabreck, 1988).

In estuarine systems, S is of interest because

- 1) its role as an electron carrier and marsh energy flow, and
- 2) reduced S forms (e.g.  $\text{H}_2\text{S}$ ) can be toxic to marsh vegetation.

In Louisiana Gulf Coast marshes, it is hypothesized that

- 1) reduced S forms decrease with distance along a salinity gradient entering inland from the coast.
- 2) organic S compounds are more abundant than pyrite or other reduced inorganic S species in Barataria basin marshes.
- 3) appreciable quantities of reduced S in Louisiana marshes are accreted storing energy conserved in the reduced S species.

To test these hypotheses, the concentration and profile distribution of inorganic and organic S forms in response to seasonal changes were investigated in freshwater marsh (Chapter 2), brackish marsh (Chapter 3), and salt marsh (Chapter 4) of Barataria Basin, Louisiana. Regardless of the seasonal changes, the presence of each S form has also been compared among the three marsh types (Chapter 5). Since the chapters are manuscripts prepared for specific journals, subtle differences in format do exist.

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**CHAPTER ONE**  
**BIOGEOCHEMICAL SIGNIFICANCE AND DYNAMICS**  
**OF SULFUR IN COASTAL MARSH SOILS AND ESTUARINE SEDIMENTS**

## INTRODUCTION

Sulfur is an essential element in biological systems. In coastal wetland ecosystems, S is of interest as an electron carrier under anoxic and partially anoxic conditions (Howarth, 1984). Due to its significance to the structure and metabolism of plants and microorganisms, S is continuously being cycled between inorganic and organic forms and as a result, a variety of inorganic and organic S compounds are added to or produced in soil (Freney, 1986). Sulfur occurs in several different oxidation states in wetlands and is transformed through several pathways that are mediated by microorganisms (Mitsch and Gosselink, 1986).

The nature and distribution of the S compounds formed depend to some extent on the environmental conditions. The chemical and microbiological reactions occurring in waterlogged soils may be different from those operating in upland soils (Freney, 1986). This review chapter emphasizes the nature, distribution, and transformations of inorganic and organic S compounds present in tidal marsh soils and estuarine sediments.

## SIGNIFICANCE

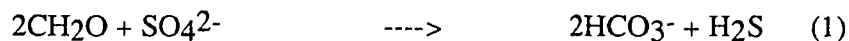
The dynamics of S is very complex because it includes aqueous, sedimentary, and atmospheric phases (Valiela, 1984). The scheme of S dynamics involving oxidation state changes is shown in Figure 1.1. Because S is an important redox element under aerobic and anaerobic conditions, S is involved in a number of important biogeochemical processes in wetland systems such as sulfate reduction, pyrite formation, metal cycling, energy and nutrient transport, and atmospheric S emissions. Each of these processes depends upon the S forms, which may have oxidation states between -2 to +6 (Luther et al., 1986).





## SULFATE REDUCTION

Sulfate reduction is the major form of microbial respiration in organic-rich sediments underlying productive marine ecosystems (Howarth and Giblin, 1983; Howarth, 1984). About 50 % of the deposited organic matter in coastal sediments has been found to be mineralized anaerobically via sulfate reduction (Jorgensen, 1982). In stands of short *Spartina alterniflora* in the Great Sippewissett marsh, Massachusetts (Howarth and Teal, 1979), and at Sapelo Island, Georgia (Howarth and Giblin, 1983), sulfate reduction annually degrades an amount of organic carbon equivalent of 70 to 90 % of estimated net primary production, respectively. Howarth and Giblin (1983) suggested that the sulfate reduction dominates decomposition in anoxic marine sediments as a result of the abundance of dissolved sulfate in seawater and higher relative energy yield for bacteria carrying out the reduction. The general reaction may be illustrated as (Kaplan et al., 1963):



According to this equation, *Desulfovibrio* bacteria utilize sulfate as a terminal electron acceptor, permitting the continued oxidation of organic carbon.

Several workers claimed that pyrite is the major short term end product of sulfate reduction (Howarth, 1979; Howarth and Teal, 1979; Howarth and Giblin, 1983; Lord and Church, 1983; Cutter and Velinsky, 1988). In contrast, Berner (1970) and King et al. (1985) found that the acid-volatile sulfides ( $\text{H}_2\text{S}$  and  $\text{FeS}$ ) and elemental S ( $\text{S}^0$ ) are the major end-products of sulfate reduction, and only 13 % is defined as pyrite ( $\text{FeS}_2$ ). It has been shown, however, that sulfate reduction does not always result in  $\text{FeS}_2$  formation, even where  $\text{FeS}_2$  forms in significant amounts; it is rather derived from the organic S pool (Nriagu and Soon, 1985). However, Thode-Andersen and Jorgensen (1989) found that the distribution of AVS,  $\text{S}^0$ , and  $\text{FeS}_2$  is dependent on the S chemistry and on the overall sulfate reduction rates. They found that in sediments with relatively low metabolic rates, only 32 to 55 % of the reduced  $^{35}\text{S}$  is recovered, whereas the  $^{35}\text{S}$  reco-

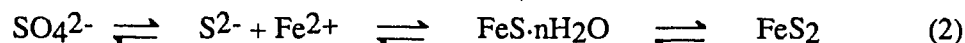
very is 63 to 92 % in the sediments with high metabolic rates. For long term S accumulation, sulfate reduction can play a key role not only in inorganic S accumulation, but also in organic S accretion (Rudd et al., 1986).

There are two possible major pathways for the incorporation of S into soils and sediments through sulfate reduction: (i) dissimilatory sulfate reduction and (ii) assimilatory sulfate reduction (Konopka et al., 1986). Dissimilatory sulfate reduction results in a significant release of  $\text{H}_2\text{S}$  (Altschuler et al., 1983). Uptake of sulfate by plants and microorganisms involves an assimilatory sulfate reduction with S-containing amino acids as the major product (Lowe and Bustin, 1985). Through this process, the reduced S is utilized in protein synthesis without a significant release of  $\text{H}_2\text{S}$  (Altschuler et al., 1983). Some microorganisms, however, cannot reduce  $\text{SO}_4^{2-}$  to organic thiol groups, but can use partially oxidized molecules such as thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) or sulfite ( $\text{SO}_3^{2-}$ ) as S sources (Konopka et al., 1986). The rates of sulfate reduction depend on the mechanisms that convey sulfate into the anaerobic environment, such as diffusion, bioturbation, and on the availability of organic matter (Valiela, 1984). King (1988) found that the temporal variability in sulfate reduction rates is correlated with seasonal changes in temperature. The reduction rates are generally maximum during summer and minimum during winter (Howarth and Teal, 1979; Howarth, 1984; King, 1988; Thode-Andersen and Jorgensen, 1989). In addition, the temporal sulfate reduction may be affected by plant growth in tidal marshes (Hines et al., 1989).

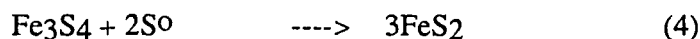
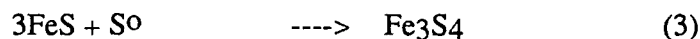
Sulfate reduction can account for up to 50 % of total marsh respiration. During dissimilatory sulfate reduction only a fraction of the energy of marsh soil organic matter is dissipated or is available to the microorganism. Seventy-five percent of the free energy (relative to completed oxidation) is conserved in reduced S compounds (Howarth and Teal, 1980; Howarth, 1984). In Louisiana's rapidly accreting salt marshes, there is the potential for significant portion of the energy to be stored or trapped.

## IRON MONOSULFIDES AND PYRITE FORMATION

The dissolved sulfides ( $\text{H}_2\text{S}$  and  $\text{HS}^-$ ), a product of sulfate reduction, may react with  $\text{Fe(II)}$  and precipitate as iron sulfides (Howarth, 1979; Luther et al., 1986) under which the conditions of early diagenesis are thought to favor the formation of amorphous iron sulfides ( $\text{FeS}$ ) and mackinawite ( $\text{FeS}_{0.9}$ ) (Goldhaber and Kaplan, 1974). Nedwell and Abram (1978) believed that sulfide mineral first precipitated would be hydrotroilite ( $\text{FeS} \cdot n\text{H}_2\text{O}$ ), which is labile under acidic conditions. After diagenesis the hydrotroilite converts to pyrite, which is a more stable mineral. The reaction can be simply represented as (Nedwell and Abram, 1978):



In the presence of elemental S ( $\text{S}^0$ ),  $\text{FeS}$  is transformed to gregite ( $\text{Fe}_3\text{S}_4$ ) and pyrite ( $\text{FeS}_2$ ) (Berner, 1970):

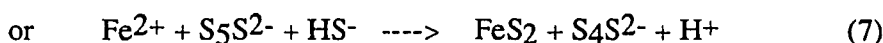
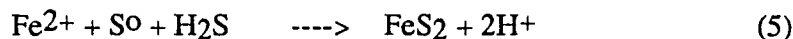


Alternatively, iron monosulfide may also be lost through oxidation to  $\text{Fe (II)}$ ,  $\text{Fe (III)}$ , and  $\text{S}^0$ , and  $\text{Fe}_3\text{S}_4$  can be dissociated to produce  $\text{FeS}$  and  $\text{FeS}_2$  (Cutter and Velinsky, 1988). In most marine systems, iron monosulfides are thermodynamically less stable than pyrite, but their formation is kinetically favored over pyrite (Berner, 1970; Goldhaber and Kaplan, 1974).

In some coastal marshes, the low availability of  $\text{Fe (II)}$  may limit the formation of iron sulfide minerals, resulting in a high sulfide concentration in the pore water and leading to depressed growth of marsh plants (DeLaune et al., 1983; Giblin and Howarth, 1984; Griffin and Rabenhorst, 1989; Haering et al., 1989; Koch and Mendelsohn, 1989). However, the low concentration of pore water  $\text{Fe (II)}$  may not limit iron sulfide formation and cannot be explained by high rates of iron sulfide formation depleting the pore water  $\text{Fe (II)}$ . It is more likely that low pore water  $\text{Fe (II)}$  concentrations are a result of lower rates of  $\text{Fe (III)}$  reduction than its exhaustion by sulfide formation and may be ac-

accompanied by the low rates of sulfate reduction in the sediments, resulting in low sulfide concentrations (Rudd et al., 1986).

The formation of pyrite can occur following the two mechanisms proposed by Goldhaber and Kaplan (1974), in which single pyrite crystals are formed rapidly through direct precipitation of Fe (II) and polysulfides ( $S_n^{2-}$ ), and framboidal pyrite is produced by a slower reaction of FeS with  $S^0$  to produce a gregite intermediate (equation 3 and 4). The direct precipitation of pyrite requires the prior oxidation of  $H_2S$  to either  $S^0$  or  $S_n^{2-}$  for reactions like the following (Berner, 1964; Goldhaber and Kaplan, 1974; Rickard, 1975; Howarth, 1979):



Rickard (1975) examined the mechanisms and kinetic of pyritization in marine sediments and showed that rapid pyritization has a second-order dependence on FeS surface area, and a first-order dependence on  $H^+$ , total dissolved sulfides ( $H_2S$  and  $HS^-$ ), and the surface area of  $S^0$ . Nonetheless, the two mechanisms of pyrite formation are likely to occur at the same time in two distinct regimes within the coastal marsh profiles (Lord and Church, 1983; Cutter and Velinsky, 1988; Feijtel et al., 1988a). The rapid pyrite formation (equation 5, 6, or 7) occurs in the upper 20 cm of marsh profile (more oxidized), displaying a larger variation in pyrite content, whereas the slow pyritization (equation 3 and 4) tends to exist below 20-cm depth of marsh profile (more reduced) with pyrite maximum content. It appears in organic-rich swamps and peats that pyrite can form through the reduction of organic oxysulfur compounds through dissimilatory sulfate reduction, which generates  $HS^-$  or organic sulfides to react with Fe (II) in the degrading tissues (Altschuler et al., 1983).

In coastal marsh areas, where the marsh plants can possibly affect the dynamic transformation of pyrite, a large percentage of sedimentary pyrite is converted to an oxi-

dized Fe mineral and sulfate by the oxidation around plant roots during the marsh plant growing season. Over the fall and winter, there is a net increase in pyrite content as the marsh plant is inactive (Howarth and Teal, 1979; Giblin and Howarth, 1984; Feijtel et al., 1988a). Oxygen diffusing into the sediment surface from tidal currents can also induce pyrite oxidation in coastal marine sediments (Troelsen and Jorgensen, 1982; Thode-Andersen and Jorgensen, 1989) and marsh soils (Giblin and Howarth, 1984; Luther and Church, 1988), releasing excess dissolved Fe (II) and  $\text{SO}_4^{2-}$  to the pore waters, and precipitating an authigenic solid Fe phase.

### SULFUR-METAL CYCLING

Sulfur is not only involved in the cycling of Fe in marsh soils and estuarine sediments (see discussion above), but it can also play an important role in retaining heavy metal and trace element in these systems. Griffin et al. (1989) noted that the mechanisms responsible for metal retention in the coastal marsh soils are mainly associated with complexation by organic S ligands and precipitation as insoluble sulfide species. A number of studies have shown that sulfides not only act to remove metals from solution, but may also hold the metals in a way that will allow their subsequent release back into the sediment-water column (Feijtel et al., 1988b).

The production of reduced S compounds during sulfate reduction has a controlling influence on the chemistry of trace metals in anoxic sediments (Berner, 1970; Goldhaber and Kaplan, 1974). Griffin et al. (1989) found that in the presence of reduced S, the extremely low solubility products of most metal sulfides predict that metal will precipitate as stable sulfide minerals in the marsh soils. Conversely, a severe metal loading beyond the capacity of sulfide precipitation appears to inhibit sulfate reduction (Capone et al., 1983).

Moore et al. (1988) found that concentrations of arsenic, copper, zinc, manganese, and iron in the pore water sediment are controlled by the solubility of metal sulfides in

the reduced zone where sulfate reduction is dominant. They further stated that the change in redox condition upon burial results in a system where the growth of diagenetic copper, zinc, and arsenic sulfides controls the distribution and partitioning of metals and arsenic in the sediment. In polluted lake sediments, Nriagu and Soon (1985) found that sulfate reduction plays a key role in the formation and retention of sedimentary S as copper and nickel sulfides. Feijtel et al. (1988*b*) have reported that the majority of the iron and manganese in coastal lake sediments is associated with sulfidic forms, particularly in the more saline marsh.

Boulegue et al. (1982) reported that the concentrations of trace elements, copper and iron, in the marsh pore waters are mainly controlled by sulfide formation. Their calculations showed that copper is strongly complexed, probably with organo-S ligands, and iron might be complexed with S species to a much lesser extent than copper. In estuarine and marsh sediments, it appears that copper and cadmium retention is largely controlled by sulfide precipitation and organic complexation, whereas zinc retention is apparently being controlled primarily by pyrite occlusion and discrete sulfide precipitation (Griffin et al., 1989). In addition, Griffin et al. (1989) found evidence of sulfide formation and pyrite coprecipitation. Other trace elements such as molybdenum entering the sediment are eventually retained in association with iron sulfides or as discrete molybdenum sulfide (Malcolm, 1985).

## ENERGY AND NUTRIENT TRANSPORTS

Sulfate reduction, which is reported to account for 50 to 90 % of total microbial respiration in salt marsh and nearshore sediments (Howarth, 1979; Howarth and Teal, 1979; Howarth and Giblin, 1983; Howarth, 1984), plays an important role in S cycling and energy flow in coastal marshes (Nedwell and Abram, 1978; Howarth and Teal, 1979, 1980; Peterson et al., 1983). Although the energy yield for anaerobic sulfate reduction is less than that for aerobic respiration, the decomposed organic matter resulted from sulfate

reduction is perhaps 12-times more prevalent in salt marsh than aerobic respiration and denitrification combined (Howarth, 1979; Howarth and Teal, 1979). For an ecosystem such as a coastal marsh, which is partially anoxic and a significant percentage of the metabolism is anaerobic, carbon cycling is no longer proportional to energy flow and therefore a carbon budget is not an adequate representation of energy flow (Howarth and Teal, 1979). Sulfate reduction, which accounts for the consumption of  $1\,800\text{ g C m}^{-2}\text{ yr}^{-1}$ , (or about equal to the net primary production in the marsh) would be more important in energy flow (Howarth and Teal, 1979). Since the reduced S compounds produced by sulfate reduction are energy-rich and biologically active, these S compounds can be closely entangled in the energy flow and food web relationships for the marsh, itself, and can be transported into estuarine ecosystems (Howarth and Teal, 1980; Peterson et al., 1983).

During sulfate reduction, large amounts of energy from the respired organic matter are stored in inorganic reduced S compounds such as soluble sulfides, iron monosulfides, pyrite, elemental S, polysulfides, thiosulfate, and polythionate (Howarth, 1984). Howarth and Teal (1980) reported that energy flow involving these inorganic S substances in the salt marsh ecosystem is as large as  $54.4\text{ M J m}^{-2}\text{ yr}^{-1}$  or equivalent to 70 % of the net primary production. When these reduced inorganic S compounds are subsequently oxidized, energy is released (Howarth, 1984). Of course, energy transported through these reduced inorganic compounds can be quite large and must be included in the energy budget of an ecosystem which contains anoxic regions (Howarth and Teal, 1980). Howarth and Teal (1979) found that the total energy export from the marsh peat to the adjacent creeks as inorganic S compounds is as much as  $18\text{ M J m}^{-2}\text{ yr}^{-1}$ , which is equal to 28 % of the total net primary production and more than twice the aboveground net production of *Spartina*.

The export of energy from the marsh peat to the coastal food webs as reduced S forms is by tidal flow (Peterson et al., 1983) and through lateral transport in pore waters



as they drain into adjacent streams at low tide (Howarth and Teal, 1980). The energy transported in these S compounds is more labile and easily used by a variety of organisms than other organic compounds such as humic acids and lignin (Howarth, 1984). It is unclear, however, how much of this energy is used and converted to organic biomass by marsh plants and the microbes of the rhizosphere (Howarth and Teal, 1980).

### ATMOSPHERIC SULFUR EMISSION

Large amounts of reduced S gases are produced by bacteria in anaerobic, sulfate-rich environments such as marine sediments and coastal marshes and mud flats, and because of the widespread occurrence of such environments, reduced S gases have been assumed to be the major biological source of atmospheric S emission (Brown, 1982). Salt marshes, for example, have high rates of sulfide production due to dissimilatory sulfate reduction (Howarth and Teal, 1979; Howarth and Giblin, 1983). Moreover, hydrogen sulfide ( $\text{H}_2\text{S}$ ) and smaller amounts of other reduced S gases such as methane thiol or mercaptan ( $\text{CH}_3\text{SH}$ ), dimethyl sulfide ( $(\text{CH}_3)_2\text{S}$ ), dimethyl disulfide ( $(\text{CH}_3)_2\text{S}_2$ ), carbonyl sulfide ( $\text{COS}$ ), and carbon disulfide ( $\text{CS}_2$ ) are also produced during the bacterial decomposition of S-containing organic materials such as proteins and amino acids (Brown, 1982).

Noggle et al. (1986) reported that  $\text{H}_2\text{S}$  is the greatest S emission flux for most of the soil types they studied and the highest S emission comes from coastal wetland soils. They also noted that the other gases released are, in order of their importance,  $\text{COS}$ ,  $\text{CS}_2$ ,  $(\text{CH}_3)_2\text{S}$ , and  $\text{CH}_3\text{SH}$ . This is in good agreement with Steudler and Peterson (1984) who indicated that coastal marshes have the highest areal gaseous S emissions with rates at least 10- to 100-fold greater than the emissions from oceans and inland soils. Steudler and Peterson (1984) estimated that  $\text{H}_2\text{S}$  and  $(\text{CH}_3)_2\text{S}$  are the predominant S gases emitted, and account for 2.2 and 1.5 g S m<sup>-2</sup> yr<sup>-1</sup> or 48 and 33 % of the total S emission from the *Spartina* marsh area, respectively. Adam et al. (1980) found  $\text{CS}_2$  emission rates

of  $13 \text{ mg S m}^{-2} \text{ yr}^{-1}$  for an intertidal marsh and  $125 \text{ mg S m}^{-2} \text{ yr}^{-1}$  from infrequently flooded marshes and cultivated histosol soils. In addition, they detected 8-times more  $\text{CS}_2$  concentrations in coastal marsh water than in ocean water.

The role of gaseous S compound is dependent upon their atmospheric lifetimes that vary from a few hours to many years (Noggle et al., 1986). The rapid tropospheric oxidation of  $\text{H}_2\text{S}$ ,  $(\text{CH}_3)_2\text{S}$ ,  $(\text{CH}_3)_2\text{S}_2$  (short-lived compounds), which are the major gases released from coastal marsh, can be expected to produce elevated atmospheric levels of sulfur dioxide ( $\text{SO}_2$ ) and sulfate aerosol ( $\text{SO}_4$ ) in the vicinity of the marsh surface (Steudler and Peterson, 1984). This could possibly be important in the locations where marshes constitute a large portion of the land area such as Louisiana, which contains one of the largest coastal marshes in the United States (Mitsch and Gosselink, 1986). The emission of  $\text{CS}_2$  and  $\text{COS}$ , which are a minor fraction (9.6 %) of total gaseous S released, may have an important role globally because they are long-lived S species with tropospheric lifetimes of 1 month and 1 year, respectively (Steudler and Peterson, 1984). The aforementioned information is an example of the complex relationship between atmospheric S and S in terrestrial systems, explaining the transport of S from the emission source (coastal marsh) to the receptor (atmosphere). The amount and rate of transfer of S gases to soil and plants, and the impact on plant production may be enormous (Noggle et al., 1986).

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**CHAPTER TWO**  
**SEASONAL SULFUR DYNAMICS IN LOUISIANA**  
**FRESHWATER MARSH SOILS**



### ABSTRACT

The profile distribution of specific sulfur forms related to the sulfur cycle were examined at a site in a Louisiana freshwater marsh. Soil samples were fractionated into acid-volatile sulfides (AVS), HCl-soluble sulfur, elemental sulfur ( $S^0$ ), pyrite sulfur ( $FeS_2$ ), ester-sulfate sulfur, carbon-bonded sulfur, and total sulfur. Inorganic sulfur constituted 14 to 30 % of total sulfur pool, with HCl-soluble sulfur present as the largest portion (77-94 %). No clear pattern of pyrite sulfur formation was observed in the upper 20 cm of soil profile throughout the year, but its concentration tended to increase with depth in every season below this zone. Pyrite sulfur represented <3 % of total sulfur and together with elemental sulfur accounted for 6 to 21 % of inorganic sulfur fraction. The elemental sulfur concentration was high in the plant root zone (<20 cm). Organic sulfur, in the forms of ester-sulfate sulfur and carbon-bonded sulfur, was a major constituent (70-86 %) of total sulfur. The conversion of ester-sulfate sulfur into carbon-bonded sulfur was greatest in spring. The transformations of sulfur from inorganic to organic and vice versa were likely to occur in spring, summer, and fall growing seasons, rather than in winter. Total soil sulfur was statistically significantly higher in spring than in other seasons.

## INTRODUCTION

Sulfur is an important component of both natural and anthropogenic processes; its importance has been known as a macronutrient required by all plants and organisms and a dominant element in acidic precipitation. Sulfur can form a number of inorganic and organic species with oxidation states varying from -2 to +6, and as a result undergoes a variety of biogeochemical transformations in the environment. As a result, the role of S has been investigated in atmospheric, aquatic, and terrestrial systems (Landers et al. 1983).

The nature of the biogeochemical cycling of S in freshwater wetlands has received little attention because S is seldom a limiting nutrient nor is it adequately abundant to have a large influence on decomposition pathways and energy flow (Urban et al. 1989). Unlike coastal marine sediments, where sulfate reduction can account for 70 to 90 % of the total microbial respiration (Howarth 1984), sulfate reduction in freshwater wetlands generally does not play a significant role in energy flow (Urban et al. 1989). Sulfate uptake and retention in freshwater wetlands has received great interest because sulfate may serve as a source of alkalinity ( $\text{HCO}_3^-$ ) to offset acid deposition (see Urban et al. 1989). Most studies have focused on the potential for wetland acidification and on the role of dissimilatory sulfate reduction as a buffer against such acidification (Jarvis et al. 1987). Other workers have calculated input-output budgets for watersheds containing peats and bogs and have generally concluded that those systems appear to retain S on an annual basis. The budgetary approach, however, provides little insight into the biogeochemical processes affecting S pools within the system themselves (Wieder et al. 1987).

An aspect of freshwater marsh substrate composition that has received little attention is the nature and distribution of inorganic and organic forms of S as they relate to the origin and type of marsh materials (Lowe and Bustin 1985). Although recent investigations have centered on the forms and diagenesis of S in freshwater systems such

as in peat (Casagrande et al. 1977; Altschuler et al. 1983; Brown 1985; Lowe and Bustin 1985; Wieder et al. 1987) and lake sediments (Landers et al. 1983; Mitchell et al. 1984; Nriagu and Soon 1985; Rudd et al. 1986), there are few data on the distribution and forms of S in coastal freshwater marshes. Due to a lack of information on S fluxes and transformations, the understanding of S dynamics (Landers et al. 1983) and marsh development (Lowe and Bustin 1985) in a natural setting has been limited. To obtain needed information, the profile distribution and the pool size of both inorganic and organic forms of S were examined in soils from a Louisiana coastal freshwater marsh over a one year period.

## MATERIALS AND METHODS

### *Study site*

Soil samples investigated in this study were obtained from a freshwater marsh located in Barataria Basin, Louisiana (29° 55' N, 90° 35' W) (Fig. 5.1). Barataria Basin is a 400 000-ha intertributary Louisiana Gulf Coast estuarine basin with well-defined vegetative units that is bounded on the east by the Mississippi River and on the west by the river's most recently abandoned channel, Bayou Lafourche. Freshwater marsh (salinity 1-5 ‰) covers 19 % of the basin. *Panicum hemitomon* Shult. is the dominant vegetation and covers about 41 % of the entire freshwater marsh system. *Sagittaria lancifolia* L. and *Eleocharis* spp. claim about 17 and 12 % of the total cover (Chabreck 1972). Clay content of freshwater marsh soils averages about 33 % and organic matter content is approximately 65 % (Bahr and Hebrard 1976). Net C accumulation in this marsh area is 224 g C m<sup>-2</sup> yr<sup>-1</sup> (Feijtel et al. 1985) and the sedimentation rate is 8.5 mm yr<sup>-1</sup> (Feijtel et al. 1988).

### *Sampling and Analysis*

Five soil cores were collected at 20 m from the bank of Lake des Allemands (within a radius of 3 m) during April 1987 through August 1988. This allows us to minimize the effect of spatial heterogeneity and to determine seasonal variation (Feijtel et al. 1988). Soil samples were obtained by twisting an aluminum core (15-cm i.d. and 50-cm height) into the marsh substrate. Little compaction resulted from this sampling method. The cores were extruded and sectioned into 3-cm intervals immediately upon return to the laboratory. Approximately 75 % of each section was rapidly sealed in a plastic bag and frozen, and was subsequently used for S fractionations. The remaining 25 % was utilized for the determination of pH, bulk density (Table 2.2), and water content. Prior to chemical analysis, the samples were thawed and thoroughly mixed, and any live roots and debris were removed.

The procedure used for the sequential extraction of S fractions shown in Fig. 2.1 is a modification of Nriagu and Soon (1985). The extractions were performed using a modified Johnson-Nishita (J-N) digestion-distillation apparatus (Johnson and Nishita 1952) (Fig. 2.2). Extractant was introduced to the boiling flask by syringe injection through a serum cap at the upper end of the condenser. This was a more convenient way to add an extractant and reduced the risk of H<sub>2</sub>S loss during acid addition (Freney et al. 1970). Sulfur species containing in each extracted S fraction are shown in Table 2.1. Fresh sample containing about 5 to 10 g of oven-dried material was used. Acid-volatile sulfides (AVS), HCl-soluble S, elemental S (S<sup>0</sup>), pyrite S (FeS<sub>2</sub>), and ester-sulfate S were extracted by the method described by Nriagu and Soon (1985). For ester-sulfate S, the extractant (HI reducing mixture) was prepared by a method outlined by Landers et al. (1983). The concentration of each S fraction was determined with the inductively coupled argon plasma spectrometry (ICP) instead of the gravimetric method used by Nriagu and Soon (1985). Carbon-bonded S was estimated by subtracting all of the other S fractions (sum) from total S. Pore water was extracted by centrifuging a 50 to 100 g

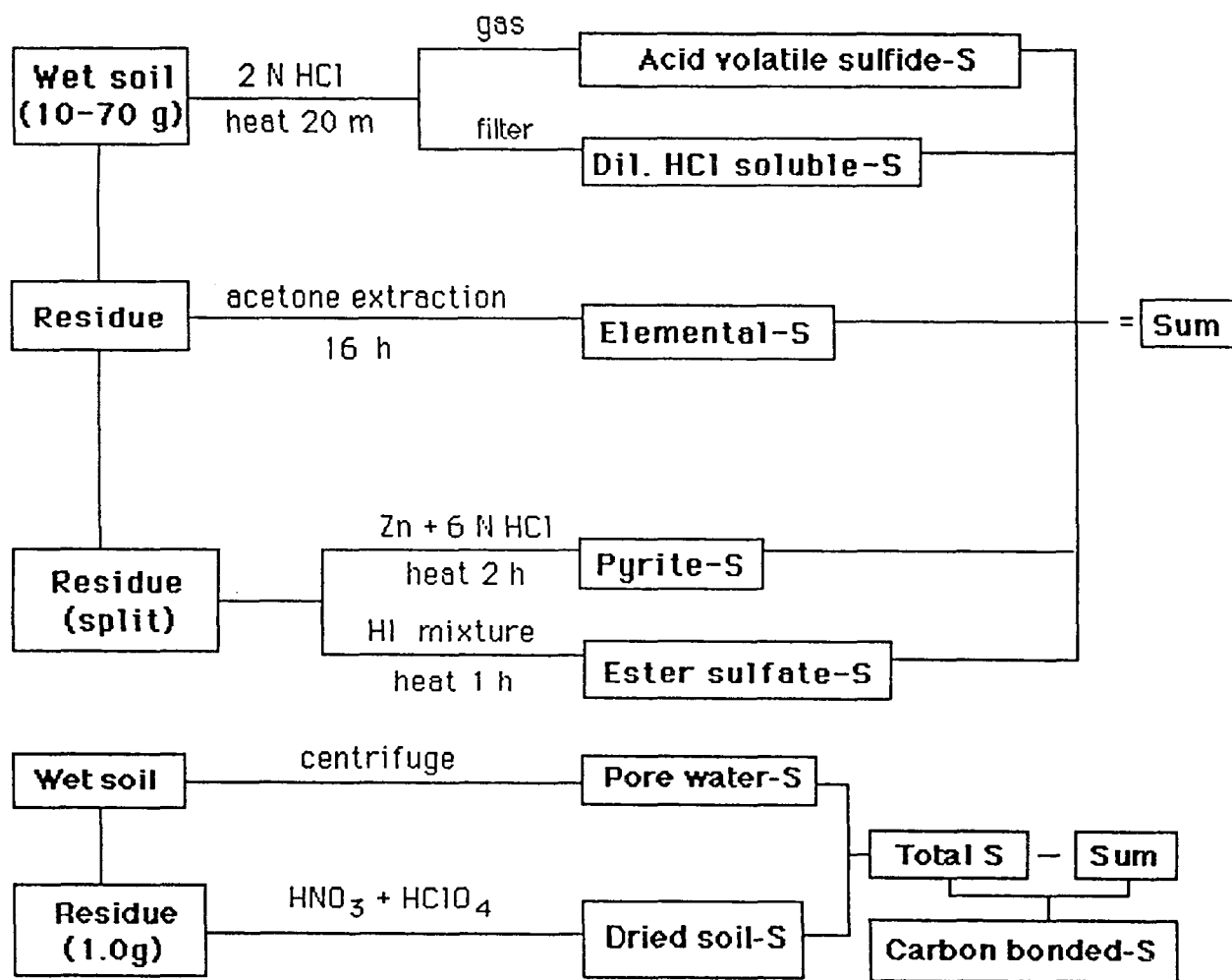


Figure 2.1. Schematic diagram showing a modified sequential procedure of Nriagu and Soon (1985) for fractionation of different forms of sulfur (S).

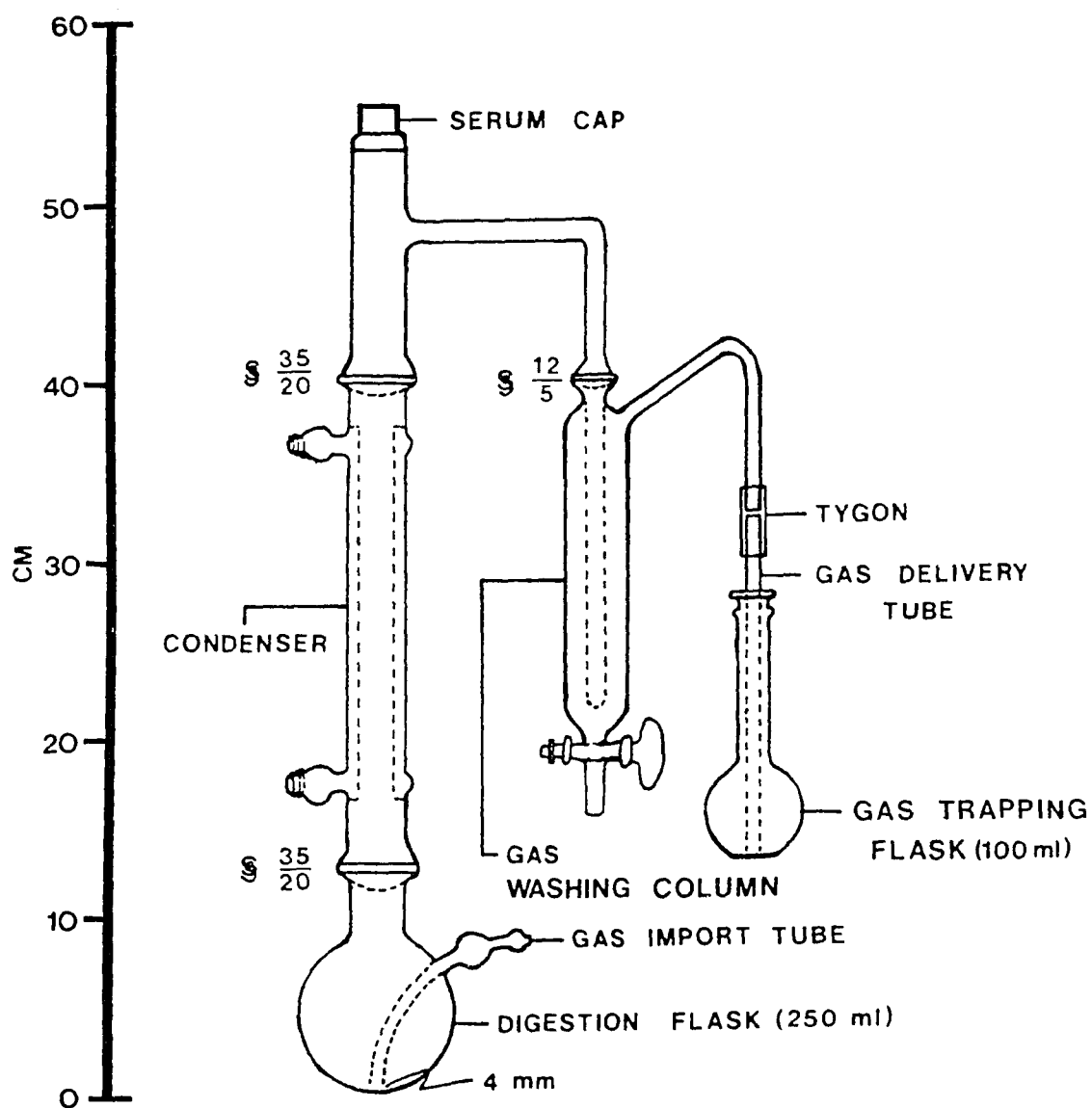


Figure 2.2. A modified Johnson-Nishita (J-N) digestion-distillation apparatus.

Table 2.1. Sulfur species contain in each S fraction.

Sulfur Fraction	Sulfur Species	Reference
Acid-volatile sulfides (AVS)	Dissolved $\text{H}_2\text{S}$ and $\text{HS}^-$ , and iron monosulfides ( $\text{FeS}$ )	Jorgensen and Fenchel (1974)
HCl-soluble S	Pore water sulfate ( $\text{SO}_4^{2-}$ ), thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ), polythionates ( $\text{S}_{3+n}\text{O}_6$ , $n = 0-3$ ), polysulfides ( $\text{S}_n^{2-}$ ), soluble organic S, and HCl-hydrolysable organic S (sulfate polysaccharides and amino acids)	Nriagu and Soon (1985)
Pyrite S	Pyrite and marcasite ( $\text{FeS}_2$ )	Nriagu and Soon (1985)
Elemental S	Elemental S ( $\text{S}^0$ )	Berner (1964)
Ester-sulfate S (Organic S not directly bonded to C)	Ester sulfates ( $-\text{C}-\text{O}-\text{S}-$ ), sulfamic acid ( $-\text{C}-\text{N}-\text{S}-$ ), and S-sulfocysteine ( $-\text{C}-\text{S}-\text{S}^*-$ )	Johnson and Nishita (1952); Freney (1986)
Carbon-bonded S (Organic S directly bonded to C)	Peptides, proteins, coenzyme, sulfolipids, aliphatic sulfones, sulfonic acids (methionine, sulfone, and cysteic acid) and heterocyclics	Johnson and Nishita (1952); Freney et al. (1970); Nriagu and Soon (1985)

fresh aliquot for 20 min at 8 000 x g (7 000 rpm, Sorvall GSA-400 rotor, DuPont Co. Wilmington, DE). The supernatant was filtered through a 0.45- $\mu$ m membrane filter. Sulfur in the filtrate was measured with ICP. The residual aliquot was oven dried at 60 °C to constant mass, ground, sieved (150-mesh size), and thoroughly mixed prior to digestion with HNO<sub>3</sub>-HClO<sub>4</sub> (Beaton et al. 1968). The digested sample was filtered through a 0.45- $\mu$ m membrane filter. Sulfur in the filtrate was determined with the ICP. The sum of pore water S and soil S fractions represented a total S. All values are reported on an oven-dried soil weight basis. Pearson's correlation coefficients and Duncan's Multiple Range Test (DMRT) were calculated with Statistical Analysis System (SAS Institute Inc. 1985). An asterisk (\*), double asterisk (\*\*), and triple asterisk (\*\*\*) are used to represent significant correlation at  $P < 0.05$ ,  $< 0.01$ ,  $< 0.001$ , respectively.

## RESULTS AND DISCUSSION

### *Acid volatile sulfides (AVS)*

Fig. 2.3 displays the depth profiles of AVS fraction. Mean concentrations of AVS ranged from 7.1 to 13.2  $\mu$ g S g<sup>-1</sup> soil and accounted for <1 % of total S (Table 2.2). AVS was the least significant component of the inorganic S pool (Fig. 2.11). The AVS values were close to the range reported for peats (Casagrande et al. 1977; Altschuler et al. 1983; Lowe and Bustin 1985; Wieder and Lang 1986) and lake sediments (Davison et al. 1985; Nriagu and Soon 1985; Rudd et al. 1986). The low concentration of AVS in this study is generally due to low interstitial sulfate of 20.7 mg L<sup>-1</sup> (Feijtel et al. 1988), which is about 30-fold less than that of a salt marsh in the same basin. Feijtel et al. (1988) also reported undersaturation of pore waters with respect to iron monosulfide (FeS) by at least two orders of magnitude over the whole sampling interval at this site.

There was no clear pattern of AVS concentration with depth observed in any sampling period, except for April 1987 when it showed a significant negative relationship



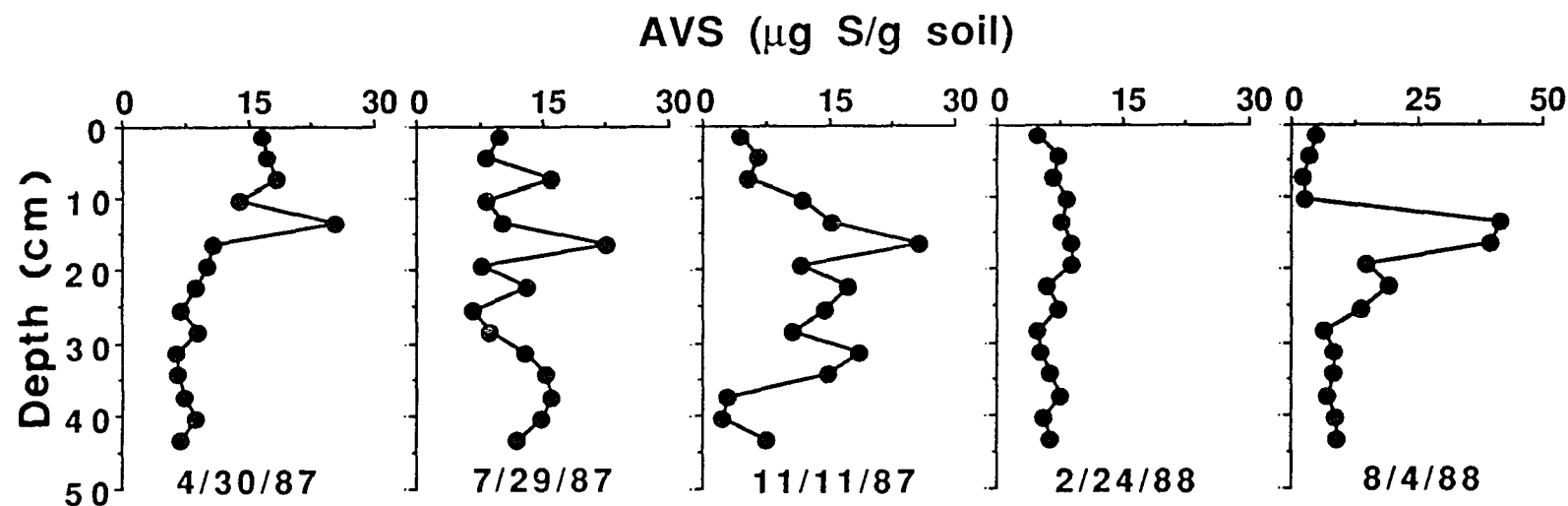


Figure 2.3. Profile distribution of acid-volatile sulfides (AVS) in freshwater marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).

with depth ( $r = -0.88^{**}$ ). On an annual basis, however, AVS concentration showed a significant increase with depth ( $r = 0.86^*$ ) in surface zone (<20 cm) and a significant decrease with depth ( $r = -0.76^*$ ) below 20-cm depth. Similar patterns are observed in a northwestern Ontario peat (Bayley et al. 1986) and in lake sediments (Davison et al. 1985; Nriagu and Soon 1985). Bayley et al. (1986) found that this observation may be a result of the dominant sulfate reduction in the surface zone. As shown in Fig. 2.3, the AVS peaks were observed in April ( $25.3 \mu\text{g S g}^{-1}$ ), July ( $22.6 \mu\text{g S g}^{-1}$ ) and November ( $25.7 \mu\text{g S g}^{-1}$ ) 1987, and August ( $41.7 \mu\text{g S g}^{-1}$ ) 1988 between 10- and 20- cm depth. Bayley et al. (1986) postulated that the peak of  $\text{H}_2\text{S}$  concentration in northwestern Ontario peat at 10- to 20- cm depth is attributed to downward diffusion of sulfate and its reduction to  $\text{H}_2\text{S}$  there.

As a result of reactions of  $\text{H}_2\text{S}$  with organic molecules, sulfate reduction can also lead to formation of organic S (Casagrande and Ng 1979). Rudd et al. (1986) indicated that the production of C-bonded S by reaction of  $\text{H}_2\text{S}$  from sulfate reduction does occur in freshwater sediments. This process was likely to occur during this study, but it was possibly less important in Louisiana freshwater marshes because only one core taken in spring showed a significant negative relationship between AVS and C-bonded S ( $r = -0.89^{**}$ ). It has also been shown with  $^{35}\text{SO}_4^{2-}$  that small amounts of organic S are formed via sulfate reduction in South Lake sediments of New York (Landers et al. 1983).

Although there was no significant difference in AVS concentration observed among the sampling periods, its concentration was relatively low in winter 1988 and relatively high in summer 1987 and 1988. The AVS concentrations in spring 1987 and fall 1987 were slightly higher than that in winter 1988. This phenomenon primarily resulted from low temperatures in winter when sulfate reduction rates (and probably microbial activity in general) are suppressed and followed by progressively increasing temperatures in spring throughout the summer and early fall when sulfate reduction

becomes more intense. Davison et al. (1985) also reported a higher sulfide accumulation during summer than in other seasons for English Lake sediments.

### *HCl-soluble S*

HCl-soluble S was the most important part of the inorganic S fraction in this freshwater marsh (Fig. 2.11), accounting for 77 to 94 % of inorganic S or no more than 29 % of total S (Table 2.2). There was a significant positive relationship between HCl-soluble S and depth in July 1987 ( $r = 0.80^*$ ), while a low concentration of this S fraction at <20-cm depth and a high concentration of that at >20-cm depth was not significantly different in April 1987. On the contrary, there was a significant negative relationship between HCl-soluble S and depth observed during November 1987 ( $r = -0.93^{**}$ ) and August 1988 ( $r = -0.86^*$ ) (Fig. 2.4). Although there was no negatively significant difference with depth found in February 1988, concentrations of this S form was slightly higher in surface zone (<20 cm) than at depth (>20 cm). On an annual average, the concentration of HCl-soluble S in the upper 20-cm depth was not significantly higher than that below 20-cm depth. However, HCl-soluble S was slightly higher in the upper 20 cm than below 20 cm (Fig. 2.10). This corresponded with the relatively high concentration of pore water S in the top 20 cm versus that at depth (data not shown). The major contribution to the variability in HCl-soluble S content was possibly attributed to pore water S.

With the exception of summer 1987, concentration of HCl-soluble S was correlated with that of pore water S in spring and fall 1987, and winter and summer 1988 ( $r = 0.79^*$ ,  $0.82^*$ ,  $0.94^{**}$ , and  $0.76^*$ , respectively). Pore water S was composed largely of sulfate, possibly derived from atmospheric deposition. Although no annual sulfate deposition amount has yet been reported in this area, Bahr and Hebrard (1976) found that the flushing action over this marsh surface is provided mainly by rainfall. Brown (1986) noted that peat systems play an important role in controlling the retention and release of

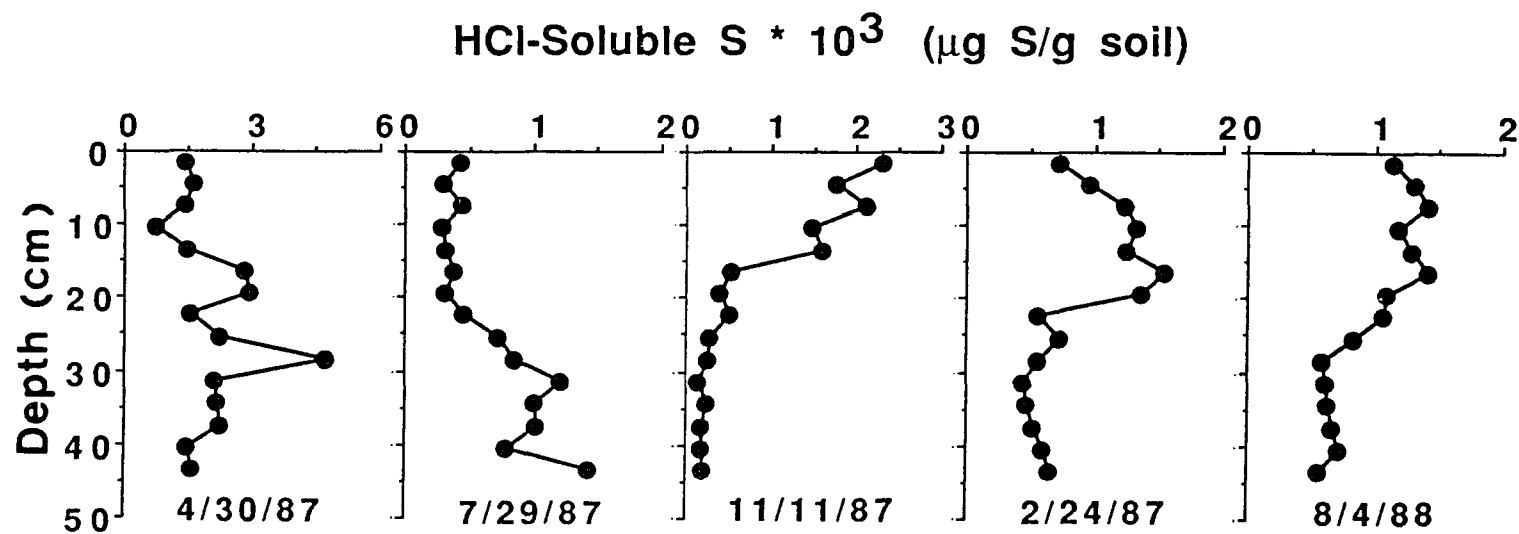


Figure 2.4. Profile distribution of HCl-soluble S (HCl) in freshwater marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).

sulfate. In addition, Ogden (1981) found a net retention of sulfate throughout the year in a permanently-waterlogged bog system in coastal Nova Scotia. It seems therefore reasonable that sulfate, as a major component of pore water S, can contribute to the HCl-soluble S fraction.

The presence of a significant inverse relationship between HCl-soluble S and AVS ( $r = -0.75^*$ ) in spring 1987 may be the result of oxidation of sulfides. Hydrogen sulfide ( $H_2S$ ) also shows a trend opposite to that of sulfate in Okefenokee freshwater peat (Casagrande et al. 1977). Nriagu and Soon (1985) reported traces of HCl-soluble S derived from the oxidation of reduced S forms in lake sediments. A significant inverse relationship between HCl-soluble S and C-bonded S ( $r = -0.86^*$ ) observed during fall 1987 suggested a transformation of S species from C-bonded S to the HCl-soluble S fraction. Nriagu and Soon (1985) noted that HCl-soluble S is likely derived from soluble and HCl hydrolysable organic S containing C-bonded S such as amino acids in some profiles of lake sediments.

#### *Elemental S ( $S^0$ )*

Concentrations of elemental S in Louisiana freshwater marsh made up 0.16 to 2.11 % of total S (Table 2.2). Lowe and Bustin (1985) reported that elemental S accounts for 0.5 to 1.4 % of total S in freshwater-derived peat. The elemental S concentration was generally 9-fold higher than that of the AVS fraction (Fig. 2.11). Although there was no significant difference in elemental S concentration found among the sampling periods, its concentration was relatively low in April 1987 and relatively high in August 1988. The maximum elemental S concentration observed in August in this study corresponds to that reported by Troelsen and Jorgensen (1982) in shallow coastal sediments. They claimed that the maximum elemental S accumulation in summer is created by a transitional oxidation of the sulfide-rich layers during the fall and winter. Urban et al. (1989) reported minor concentrations of elemental S for a *Sphagnum* bog in

northern Minnesota, while Wieder et al. (1987) found slightly higher values for Big Run Bog peat.

In general, no consistent pattern has been reported with regard to the relative abundance of elemental S fraction in freshwater peat deposits (Casagrande et al. 1977; Nriagu and Soon 1985; Urban et al. 1989). However, our data (Fig. 2.5) showed a consistent pattern of increasing elemental S concentrations in the upper 20-cm depth during fall 1987 ( $r = 0.85^*$ ), winter ( $r = 0.94^{**}$ ), and summer ( $r = 0.94^{**}$ ) 1988 and appeared to peak at 10.5 to 16.5 cm below the soil surface. In contrast, a decline in elemental S concentrations with depth below 20-cm depth was observed in fall 1987 ( $r = -0.77^*$ ), winter ( $r = -0.85^*$ ), and summer ( $r = -0.87^*$ ) 1988. Although there was no clear pattern with depth in the spring core, the concentration of elemental S in the upper 20-cm depth was almost twice as much as that below 20-cm depth (Fig. 2.10). A similar trend was observed in shallow coastal sediments (Troelsen and Jorgensen 1982). Casagrande et al. (1977) postulated that elemental S accumulation observed in peat probably arises either from the oxidation of  $H_2S$  in contact with dissolved oxygen in pore waters or from microbial sulfate reduction. In summer 1987, elemental S concentration was statistically significant lower in the oxidized zone ( $<20$  cm) than in the reduced zone ( $>20$  cm) ( $P < 0.05$ ). It is possible that oxidizing power of plant roots coupled with microorganism in the upper 20 cm during this season may be strong enough to oxidize elemental S further to sulfate or thiosulfate (Troelsen and Jorgensen 1982). Casagrande et al. (1977) reported that decreasing concentration of elemental S in the upper portion of the marsh profile may result from interactions of elemental S and  $H_2S$  (diffusing from the reduced zone) with organic matter to produce C-bonded S. Based on a significant inverse relationship between elemental S and C-bonded S ( $r = -0.76^*$ ) found in this sampling period, the above observation seems to be possible in the present study. Casagrande and Ng (1979) also presented evidence that elemental S can serve as a source of C-bonded S formed in the Okefenokee swamp peat of Florida.

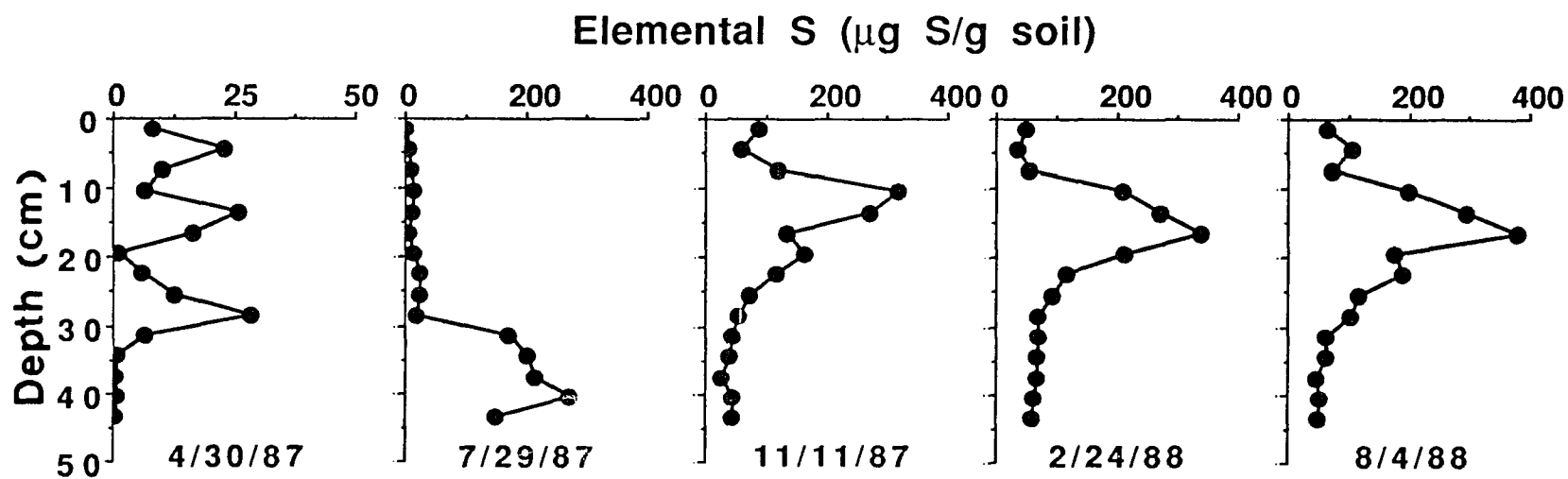


Figure 2.5. Profile distribution of elemental S ( $S^0$ ) in freshwater marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).

### *Pyrite S (FeS<sub>2</sub>)*

Pyrite S was a minor constituent of the soil S pool at this site and quite comparable to elemental S content (Fig. 2.11). Pyrite S accounted for 5 to 12 % of inorganic S or no more than 3 % of total S (Table 2.2). This is in good agreement with the previous study (Altschuler et al. 1983). Brown (1985) measured <1 % of total S in a pyrite S form in waterlogged peat. Lowe and Bustin (1985) reported that 1 and 3 % of total S in freshwater sedge and clay was present as pyrite S, respectively. Concentrations of pyrite S in the present study ranged from 84.0  $\mu\text{g S g}^{-1}$  in November 1987 to 111  $\mu\text{g S g}^{-1}$  in April 1987 (Table 2.2). Mean concentration of pyrite S was comparable to that of elemental S (Fig. 2.11). Similar concentrations of pyrite S have been reported in freshwater peats (Casagrande et al. 1977; Lowe and Bustin 1985), lake sediments (Davison et al. 1985; Nriagu and Soon 1985), and a *Sphagnum* bog (Urban et al. 1989).

In the upper 20-cm depth, pyrite S concentrations ranged from 68  $\mu\text{g S g}^{-1}$  soil in fall 1987 to 101  $\mu\text{g S g}^{-1}$  soil in summer 1987. There was no clear pattern observed during fall 1987, winter and summer 1988. This may be attributed to a high variability in seasonal pattern of the vertical redox profile in this marsh soil (Feijtel et al. 1988). Davison et al. (1985) also noted that the concentrations of pyrite S in freshwater sediments may be more dependent upon the redox conditions than the concentration of sulfate and organic C. However, pyrite S showed a significant inverse relationship with depth in summer 1987 ( $r = -0.74^*$ ), whereas a significant positive relationship between pyrite S and depth was found in spring 1987 ( $r = 0.78^*$ ) (Fig. 2.6). This observation may result from an oxidation process in the marsh soil dominated by plant roots and low water levels, inducing pyrite oxidation. This process appeared to be greater during the peak growing season (summer), rather than in the onset of growing season (spring). The increasing concentration of pyrite S with depth during winter corresponded to the highest degree of marsh soil reduction observed at this site by Feijtel et al. (1988). On an annual basis, however, concentration of pyrite S was positively correlated with depth ( $r = 0.87^*$ ),



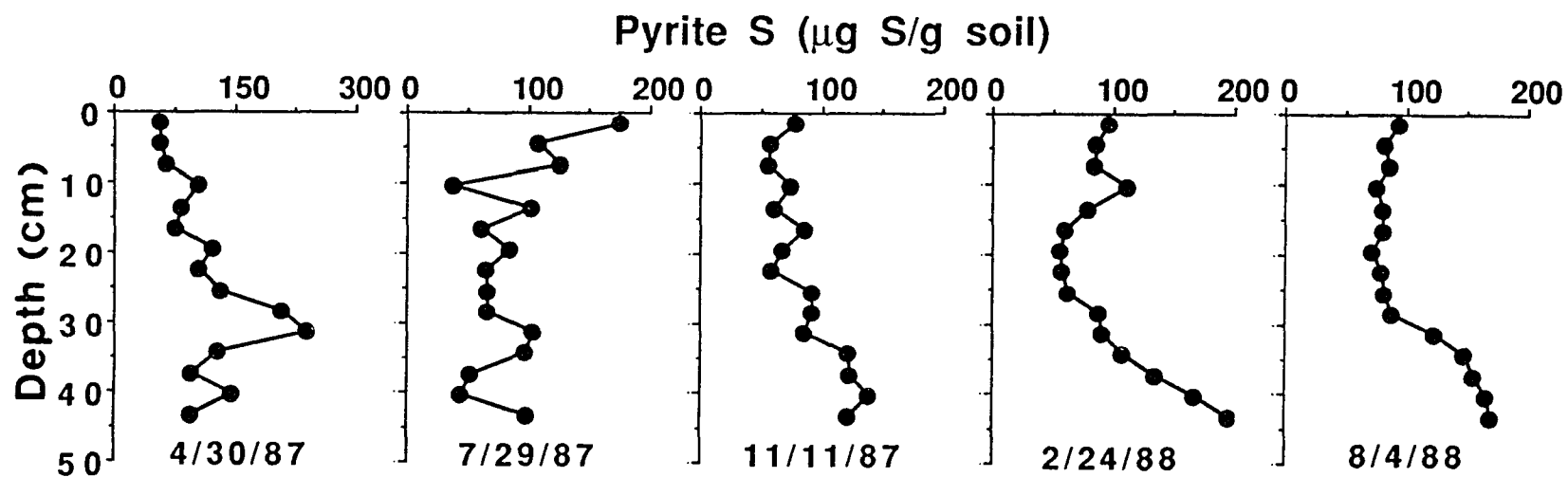


Figure 2.6. Profile distribution of pyrite S ( $\text{FeS}_2$ ) in freshwater marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).

suggesting that annual accumulation of pyrite S was greater than dissolution or oxidation of pyrite S at depth.

On an annual average, the pyrite S concentration below 20-cm depth was 2-fold higher than that found in the upper 20-cm depth (Fig. 2.10). The concentration of pyrite S ranged from  $86 \mu\text{g S g}^{-1}$  soil in summer 1987 to  $141 \mu\text{g S g}^{-1}$  soil in spring 1987. This observation was similar to the distribution of mean values which showed the lowest value of  $85 \mu\text{g S g}^{-1}$  soil in summer 1987 and the highest value of  $141 \mu\text{g S g}^{-1}$  soil in spring 1987. The observed phenomenon appeared to relate to oxidation and reduction processes which were the dominant mechanisms at this site during summer and spring seasons, respectively (Feijtel et al. 1988). Mitchell et al. (1984) established that loss of pyrite S would be favored under oxidizing conditions, whereas pyrite S formation would be favored under reducing conditions. The concentration of pyrite S showed a statistically significant increase with depth to 35-cm depth in spring ( $r = 0.98^{***}$ ) and summer ( $r = 0.84^*$ ) 1987, and remained increasing to the bottom of the cores (45 cm) during fall 1987 ( $r = 0.89^{**}$ ), winter ( $r = 0.97^{***}$ ) and summer ( $r = 0.97^{***}$ ) 1988 (Fig. 2.6). The consistent pattern of pyrite S concentration below 20-cm depth was primarily due to less seasonal variation of this S fraction at greater depth, which was characterized in this freshwater marsh soil by the absence of single crystal pyrite S particles (rapid pyritization) as opposed to framboidal pyrite (slow pyritization) (Feijtel et al. 1988). In addition, pyrite S concentration was positively correlated with depth on an annual basis ( $r = 0.88^{**}$ ). A similar pyrite S distribution has been documented for southeast English peat (Brown 1985). In the present study, the observed relationship of increasing pyrite S content with depth in every season of the year was evidence of a process of a slow pyrite formation from iron monosulfide and elemental S, previously hypothesized by Howarth (1979) in anoxic marsh sediments. The presence of a pyrite S peak at depth (31.5 cm) in spring 1987 was also indication of slower pyritization below 20 cm than in surface sections (<20 cm) (Feijtel et al. 1988). Statistically, there was no relationship between

the pyrite S fraction and AVS, elemental S, or the pore water S fractions observed in any sampling period. Nriagu and Soon (1985) postulated that the pyritization process in freshwater sediments appears to be independent of the AVS, elemental S, and pore water sulfate concentrations.

### *Ester-sulfate S*

Ester-sulfate S observed in this study ranged from 15 to 34 % of organic S fraction and accounted for 11 to 29 % of total S (Table 2.2). The ester-sulfate S pool was the second largest S constituent contributing to total S (Fig. 2.11). The values are comparable to those found by Mitchell et al. (1984) for three New York lakes sediments in which ester sulfate constituted from 22 to 33 % of total S. In freshwater-derived peat, this S fraction accounted for 12 to 21 % of total S (Lowe and Bustin 1985) and represents approximately 25 % of total S in Okefenokee swamp (Casagrande and Siefert 1977). A relatively low proportion of ester-sulfate S of 11 to 28 % of organic S was also reported for Big Run Bog peat (Wieder et al. 1987). Analyses of a wide range of agricultural soils summarized by Tabatabai (1984) have shown, however, that between 25 and 75 % (average 50 %) of organic S is present in this form.

For the five sampling periods, mean concentrations of ester-sulfate S ranged from 0.75 mg S g<sup>-1</sup> soil in April 1987 to 1.54 mg S g<sup>-1</sup> soil in July 1987. The lowest value in April 1987 corresponded to the highest level of C-bonded S in the same month (Fig. 2.7 and Table 2.2). A similar observation is reported by Mitchell et al. (1984) for New York lake sediments. These findings were indicative of S transformation from ester-sulfate S to C-bonded S which preferentially occurs in the spring season. Several earlier workers have confirmed that the conversion of ester-sulfate S to C-bonded S is mediated by plants and microorganisms (Altschuler et al. 1983; Lowe and Bustin 1985; Nriagu and Soon 1985; Wieder et al. 1987).

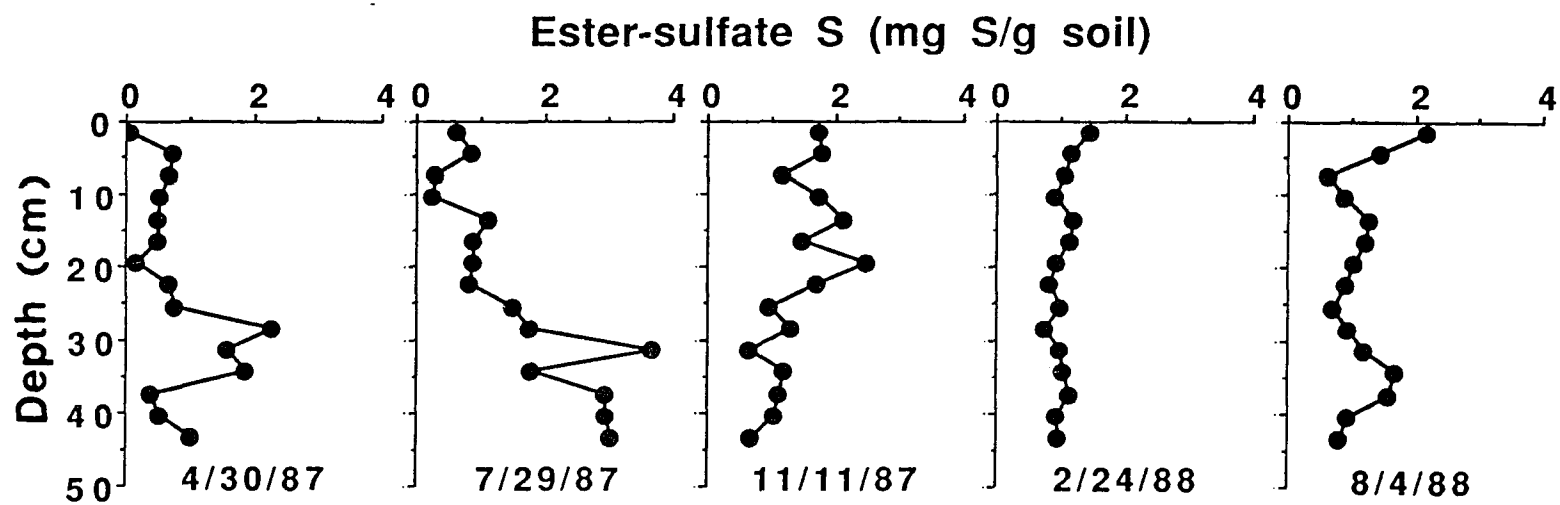


Figure 2.7. Profile distribution of ester-sulfate S in freshwater marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoints of each section (3-cm interval).

No consistent seasonal pattern of ester-sulfate S content with depth was observed in the upper 20-cm depth. Concentration of ester-sulfate S, however, showed a statistically significant positive relationship with depth below 20-cm depth during spring ( $r = 0.79^*$ ) and summer ( $r = 0.86^*$ ) of 1987, winter ( $r = 0.75^*$ ) and summer ( $r = 0.95^{***}$ ) of 1988. In contrast, a significant inverse relationship between ester-sulfate S and depth was found in fall 1987 ( $r = -0.81^*$ ) (Fig. 2.7). This corresponded to a decline in pore water S (mainly as sulfate) from  $256 \mu\text{g S g}^{-1}$  soil at 19.5-cm depth to  $49 \mu\text{g S g}^{-1}$  soil at 43.5-cm depth. McGill and Cole (1981) suggested that mineralization of ester-sulfate S molecules, mediated by extracellular aryl- and alkylsulfatases which are produced by soil microorganisms and plant roots, will occur in response to low sulfate supply. Supportive evidence of this process has also been reported for Big Run Bog peat (Jarvis et al. 1987), where decreasing ester-sulfate S with depth was accounted for by an increase in arylsulfatase activity with depth in response to low sulfate availability. They further noted that sulfatase activity may exhibit seasonal variability. Since ester-sulfate S can be hydrolyzed by sulfohydrolases, which are produced by soil microorganisms and plant roots (McGill and Cole 1981), the ester-sulfate S would be mineralized in response to a need of S for microbial community and plant growth (Maynard et al. 1984). This was consistent with our study, where concentration of ester-sulfate S observed near root zone (15-20 cm) during spring and summer was 2-fold less than that found during fall and winter, when microbial activity and plant growth were suppressed.

Although ester-sulfate S concentration did not show a significant difference between the upper 20 cm and below 20 cm, its mean concentration was slightly higher below 20-cm depth (Fig. 2.10). This observation may result from a greater amount of organic acids and humic materials in the reduced zone (>20 cm) than in the more oxidized zone (<20 cm) (Gambrell and Patrick 1978). In a waterlogged swamp-marsh environment, where organic matter is not readily degraded, an accumulation of humic and fulvic acids can be expected, and the phenolic groups in these compounds may react with

various S forms to produce ester-sulfate linkages (Casagrande and Siefert 1977). Rudd et al. (1986) claimed that ester-sulfate formation does not involve sulfate reduction, rather the reaction of sulfate with organic matter which consumes one  $H^+$  per mole of sulfate lost:



Casagrande et al. (1980) have shown that 80 % of the S associated with the fulvic acid fraction and 35 % of that with humic acid fraction in peat are in the form of ester-sulfate S. More than 40 % of organic S formed from sulfate in anaerobic freshwater peat and presented as humic materials may be assimilated into peat organic matter by esterification as well (Brown 1986).

#### *C-bonded S*

Carbon-bonded S constituted a larger portion than ester-sulfate S in all sampling periods and generally resulted in a ratio of C-bonded S to ester-sulfate S of 2.4 in the upper 20-cm depth and 3.0 below 20-cm depth. Similarly, in freshwater-mangrove peat (Casagrande et al. 1977; Altschuler et al. 1983), lake sediments (Mitchell et al. 1984; Nriagu and Soon 1985) and in the subsurface peat from Big Run Bog (Wieder et al. 1987), C-bonded S was typically 2 to 3 times more abundant than ester-sulfate S. It seems reasonable that C-bonded S would be more likely to persist in the soils than ester-sulfate S, particularly over the long term since ester-sulfate S is more labile than C-bonded S (Rudd et al. 1986). Concentration of C-bonded S varied between 2.63 mg S  $g^{-1}$  soil in November 1987 and 4.33 mg S  $g^{-1}$  soil in April 1987, representing 66 to 85 % of organic S or equivalent to 53 to 59 % of total S (Table 2.2). These high percentages demonstrate its importance as a major constituent of total S in the present study. This observation agreed well with studies of Nriagu and Soon (1985) and Rudd et al. (1986), who concurrently concluded that C-bonded S formed via sulfate reduction in lake sedi-

ments can be the most important source of S to freshwater sediments on a long term basis. About 90 % of S compounds existing in plants and microorganisms contain amino acids, such as cysteine (-C-S-H), cystine (-C-S-S-C-), and methionine (-C-C-C-) (Freney 1986). These compounds, found in marsh plants (source material for the marsh) and microorganisms (degraders of the marsh substrates), can be considered as a major source of C-bonded S in Louisiana freshwater marsh. Carbon-bonded S also accounts for between 40 and 70 % of the total S in grassland soils and consists mainly of the S amino acids, protein S, and sulfonic acids (sulfonates) (Maynard et al. 1984). A lower mean value of this S form ranging from 7 to 30 % of total S has been reported for various agricultural soils (Tabatabai 1984). Lowe and Bustin (1985) found that C-bonded S accounts on average for 65 to 83 % of total S in freshwater-derived clays and peats. Between 72 to 89 % of organic S in Big Run Bog peat is present as C-bonded S (Wieder et al. 1987).

A significant increase in concentrations of C-bonded S with depth was observed in the months of April ( $r = 0.87^*$ ) and November ( $r = 0.91^{**}$ ) of 1987, and February ( $r = 0.92^{**}$ ) and August ( $r = 0.76^*$ ) of 1988 (Fig. 2.8). A similar observation of increasing C-bonded S with depth has also been reported in sediments of some northern Ontario lakes (Nriagu and Soon 1985). Lower concentrations of C-bonded S in the upper 20-cm depth (more oxidized) than in the lower depths (more reduced) may be attributed to microbial mineralization which progressively decreases down the profile (Maynard et al. 1984). McGill and Cole (1981) suggested that the oxidation of organic molecules by heterotrophic bacteria in aerated soils results in the mineralization of S from C-bonded S. Wieder et al. (1987) also noted that C substrate availability is generally low in aerobic forest soils in comparison to that in anaerobic freshwater peat. There was a significant inverse relationship between C-bonded S and depth ( $r = -0.92^{**}$ ) only in July 1987. It is likely that high uptake of sulfate by microorganisms, and plants in particular, was responsible for the incorporation of C-bonded S into soils during this time period. The content of pore-water S in summer 1987 was as low as  $30 \mu\text{g S g}^{-1}$  soil, which was 10- to 100-fold less

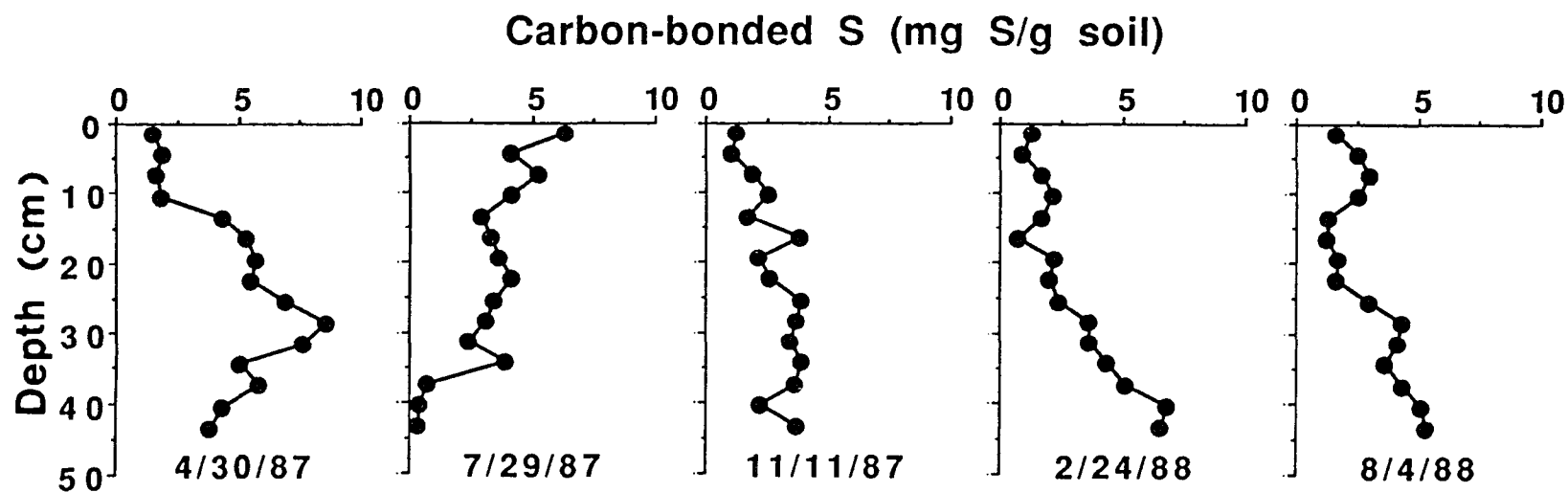
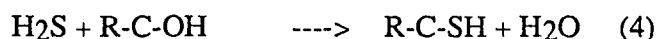


Figure 2.8. Profile distribution of C-bonded S in freshwater marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).



than that in other sampling periods, especially in the root zone (15-20 cm). Lowe and Bustin (1985) concluded that uptake of sulfate by plants and microorganisms, involving an assimilatory reduction process with S-containing amino acids as the major product, can result in a buildup of organic S, largely in C-bonded S form. While the incorporation of S-containing amino acids derived from plants and microorganisms seems a most likely source of C-bonded S in soils, it is possible that elemental S interacts with organic matter to produce C-bonded S (Casagrande and Ng 1979).

A significant negative relationship between C-bonded S and elemental S observed only in summer 1987 ( $r = -0.76^*$ ) suggested that the contribution of elemental S into C-bonded S is likely, but may be a less significant process in Louisiana freshwater marshes. As discussed previously, Casagrande and Ng (1979) have shown that some C-bonded S can actually originate from elemental S at ambient temperatures. Also, the production of C-bonded S by reaction of  $H_2S$  from sulfate reduction, which has been reported for the Florida Everglades peat (Casagrande et al. 1977) and lake sediments of northwestern Ontario (Rudd et al. 1986), could have occurred to occur in the present study as supported by a significant inverse relationship between C-bonded S and AVS observed in spring 1987 ( $r = -0.89^{**}$ ). Rudd et al. (1986) proposed a possible reaction of  $H_2S$  with hydroxyl groups of organic compounds:



### *Total S*

Mean concentrations of total S ranged from 5.11 mg S g<sup>-1</sup> soil in February 1988 to 7.63 mg S g<sup>-1</sup> soil in April 1987 (Table 2.2). Although there was no distinct variation in the depth profile observed during July and November 1987 and August 1988, a significant positive relationship between total S and depth was found in April 1987 ( $r = 0.86^*$ ) and February 1988 ( $r = 0.82^*$ ) (Fig. 2.9). On an annual basis, however, the concentration of total S was relatively low in the upper 20-cm depth (Fig. 2.10). The relatively high

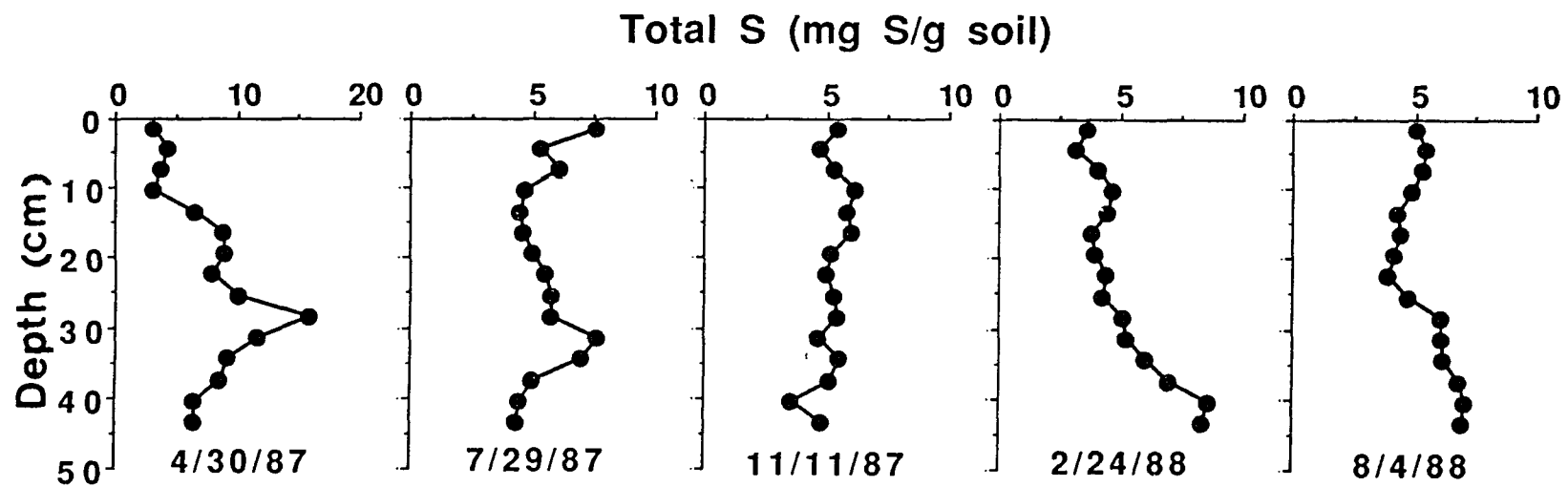


Figure 2.9. Profile distribution of total S in freshwater marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).

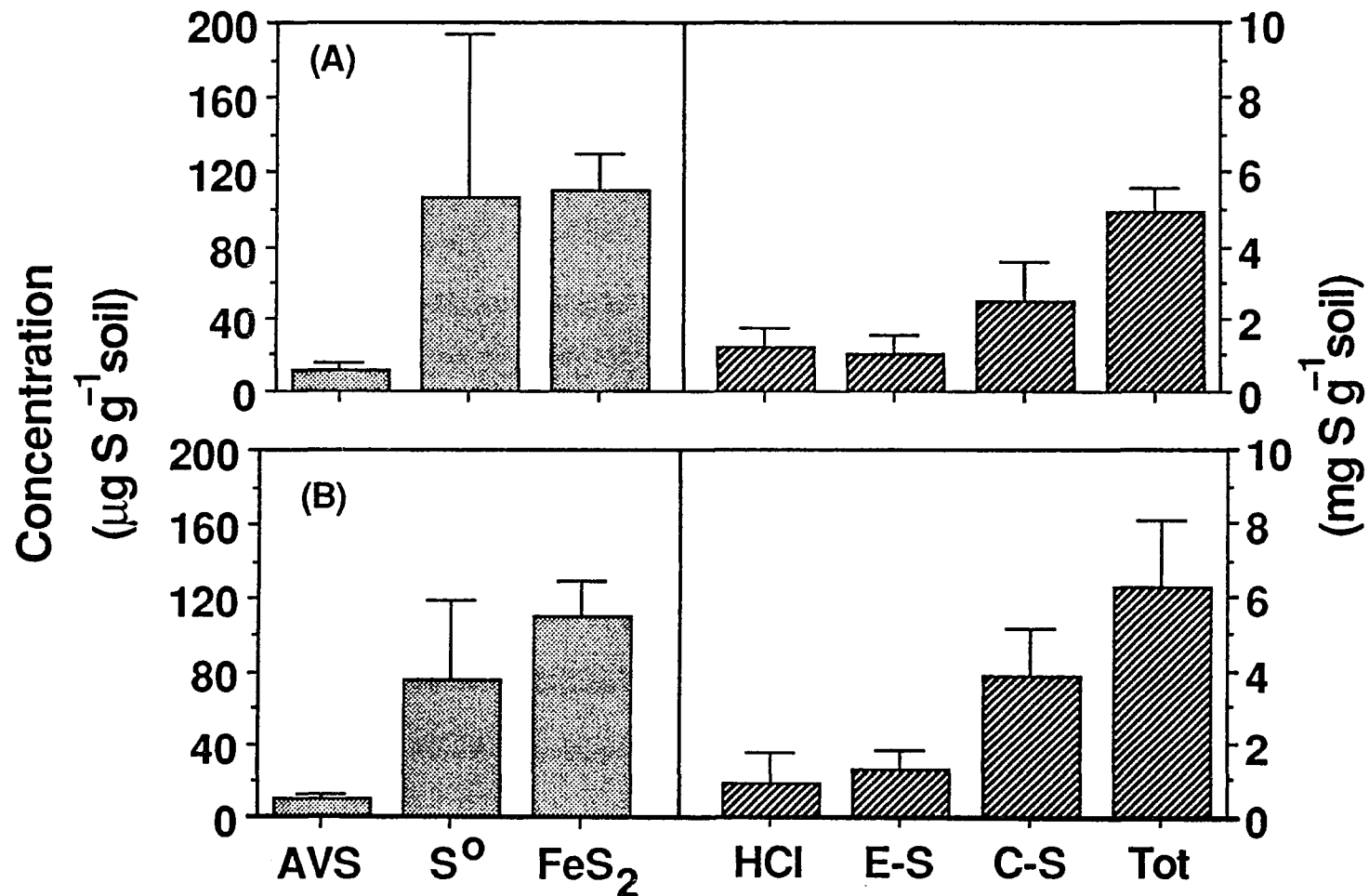


Figure 2.10. Mean concentrations of S fractions averaged over season present as acid-volatile sulfides (AVS), HCl-soluble S (HCl), elemental S ( $\text{S}^0$ ), pyrite S ( $\text{FeS}_2$ ), ester-sulfate S (E-S), C-bonded S (C-S), and total S (Tot) in the oxidized (A) and reduced (B) zone of soils collected from a freshwater marsh in Barataria Basin, LA during April 1987 through August 1988.

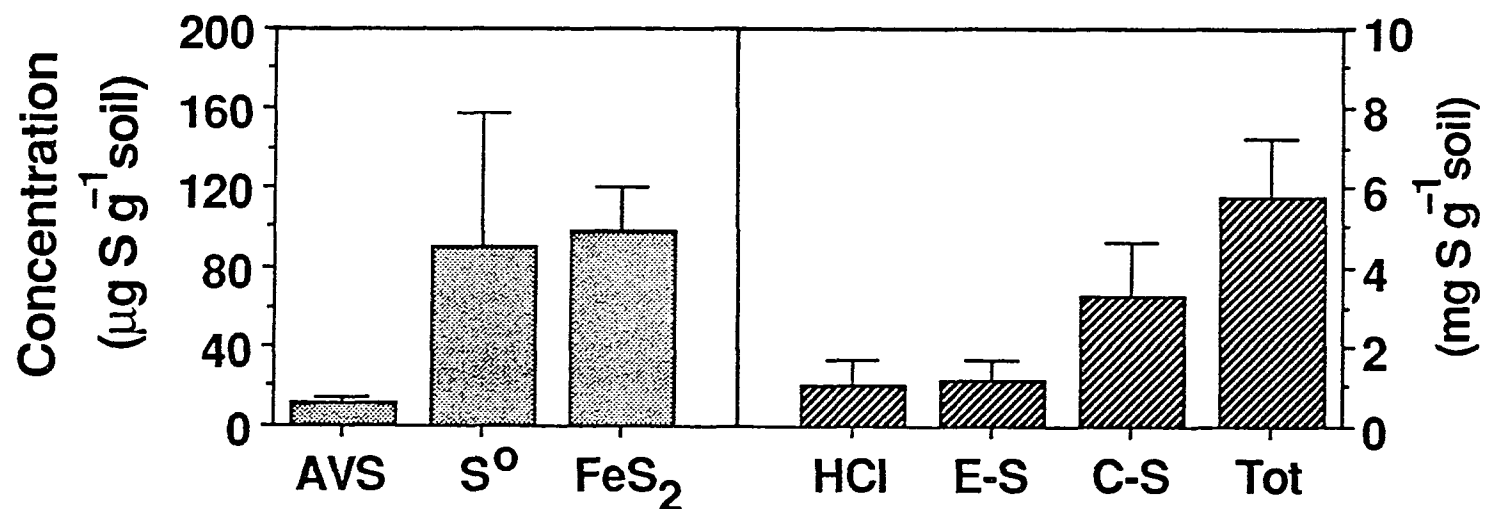


Figure 2.11. Mean concentrations of S fractions averaged over season and depth (0-50 cm, N = 15) present as acid-volatile sulfides (AVS), HCl-soluble S (HCl), elemental S ( $\text{S}^0$ ), pyrite S ( $\text{FeS}_2$ ), ester-sulfate S (E-S), C-bonded S (C-S), and total S (Tot).

content of total S at depth is similar to those reported for freshwater-derived peats (Brown 1985; Wieder et al. 1987) and lake sediments (Rudd et al. 1986). The temporal changes in the depth profile of total S were primarily due to the variability of C-bonded S. The total S was highly significantly correlated with C-bonded S during spring, summer, and winter ( $r = 0.99^{***}$ ,  $0.88^{**}$ , and  $0.95^{***}$ , respectively). Based on a Duncan's Multiple Range Test (DMRT), however, there was no significant difference in concentrations of total S averaged over depth (0-50 cm) during most of the year, except for the spring 1987 in which the concentration was greatest (Table 2.2). This may be the result of a relatively low plant S uptake and the presence of dead marsh plants in winter which will provide the major flux of organic S to the soils and thus the major source of S recycling in the spring. On an annual average, the concentration of total S in the present study was comparable to those reported by several workers for freshwater peats (Altschuler et al. 1983; Lowe and Bustin 1985; Bayley et al. 1986; Wieder and Lang 1986; Wieder et al. 1987), *Sphagnum* bog (Urban et al. 1989), and lake sediments (Mitchell et al. 1984; Nriagu and Soon 1985; Rudd et al. 1986).

Our data showed that organic S, in the forms of ester-sulfate S and C-bonded S, was the major constituent of total S in Louisiana freshwater marsh soils, accounting for 70 to 86 % of total S pool. This corresponds to previous studies in freshwater peat (Altschuler et al. 1983; Wieder and Lang 1986; Wieder et al. 1987) and lake sediments (Nriagu and Soon 1985). Also, a higher amount of organic S (>90 %) has been reported in freshwater-related materials by several workers (Casagrande et al. 1977; Brown 1985; Lowe and Bustin 1985; Bayley et al. 1986). Tabatabai (1984) found organic S was present >95 % in most agricultural soils from the temperate, humid, and semi-humid regions. It presently appears that the formation of organic S is an important pathway of long term S deposition in freshwater-derived soils and sediments and this pathway is primarily responsible for long term alkalinity production by sulfate reduction (Rudd et al. 1986).

Table 2.2. Concentrations of various S fractions averaged over depth (0-50 cm) and bulk density (mean  $\pm$  SD, N = 15), and pH range of soils taken from a freshwater marsh in Barataria Basin, LA during April 1987 through August 1988. Data in parentheses are mean values of S fractions as percent of total S.

Sampling Period	Sulfur Fraction							Soil pH	Bulk Density g cm <sup>-3</sup>
	AVS ----- $\mu\text{g S g}^{-1}$ soil	Elemental S $\mu\text{g S g}^{-1}$ soil	Pyrite S -----	HCl-soluble S ----- $\text{mg S g}^{-1}$ soil	Ester-sulfate S $\text{mg S g}^{-1}$ soil	C-bonded S -----	Total S -----		
Spring (4/30/87)	11.8a $\pm$ 4.5 (0.21)	10.6a $\pm$ 9.5 (0.16)	107a $\pm$ 52 (1.59)	1.97a $\pm$ 0.94 (28.1)	0.75a $\pm$ 0.62 (10.6)	4.33a $\pm$ 2.23 (59.3)	7.63a $\pm$ 3.33	5.3-6.4	0.11a $\pm$ 0.03
Summer (7/29/87)	12.3a $\pm$ 4.3 (0.23)	74.5a $\pm$ 95.6 (1.67)	92.2a $\pm$ 43.9 (1.40)	0.66a $\pm$ 0.37 (11.2)	1.54a $\pm$ 1.10 (29.1)	3.17a $\pm$ 1.69 (56.5)	5.52b $\pm$ 1.06	6.8-7.2	0.15a $\pm$ 0.06
Fall (11/11/87)	10.6a $\pm$ 5.8 (0.21)	115a $\pm$ 86 (1.75)	84.0a $\pm$ 27.1 (1.96)	0.94a $\pm$ 0.79 (15.1)	1.53a $\pm$ 0.62 (27.1)	2.63a $\pm$ 1.03 (53.9)	5.16b $\pm$ 0.63	5.9-6.5	0.13a $\pm$ 0.04
Winter (2/24/88)	7.1a $\pm$ 1.3 (0.15)	125a $\pm$ 93 (1.91)	96.1a $\pm$ 41.3 (2.64)	0.91a $\pm$ 0.38 (19.1)	1.05a $\pm$ 0.17 (22.2)	2.73a $\pm$ 1.93 (54.0)	5.11b $\pm$ 1.61	6.0-6.6	0.11a $\pm$ 0.02
Summer (8/4/88)	13.2a $\pm$ 2.3 (0.27)	140a $\pm$ 98 (2.11)	111a $\pm$ 44 (2.78)	1.02a $\pm$ 0.33 (19.4)	1.17a $\pm$ 0.41 (22.1)	2.83a $\pm$ 1.40 (53.4)	5.38b $\pm$ 1.02	6.2-6.8	0.11a $\pm$ 0.02

Any two mean values having a common letter are not significant difference at the 5 % level of significance based on a Duncan's Multiple Range Test (DMRT)

Inorganic S constituted 14 to 30 % of total S with HCl-soluble S accounting for 77 to 94 % of the inorganic S fraction. Pyrite S and elemental S, which were the second largest inorganic S fraction, made up 6 to 21 % of inorganic S pools. Similar results are also observed in freshwater peats (Casagrande et al. 1977; Lowe and Bustin 1985; Wieder and Lang 1986). Inorganic S species are only trace constituents in peat from a valley mire in S. E. England (Brown 1985) and *Sphagnum* bog in northern Minnesota (Urban et al. 1989), accounting for <2 % of total S. Recent investigations in freshwater marsh soils (this study), peat (Casagrande and Ng 1979; Casagrande et al. 1979; Altschuler et al. 1983), and lake sediments (Nriagu and Soon 1985; Rudd et al. 1986) have shown that inorganic S species may be converted to organic S forms. The transience of pyrite due to its susceptibility to oxidation is also well documented in marsh systems (Howarth 1984; Feijtel et al. 1988). Thus, although inorganic S species are not important pools of S in Louisiana freshwater marsh and elsewhere (see previous discussion), they may be important as short-term end products in a dynamic S cycle.

## CONCLUSIONS

Organic S, in the forms of ester-sulfate S and C-bonded S, was a major constituent (70-86 % ) of total S. Carbon-bonded S was the most important fraction contributing 53 to 59 % of the total S pool. Inorganic S, of which 77 to 94 % was accounted for by HCl-soluble S, made up 14 to 30 % of total S. Pyrite S and elemental S, together, consisted 6 to 21 % of the inorganic S fraction. Acid-volatile sulfides (AVS) was the minor constituent, representing <1 % of total S. The presence of an elemental S maximum and a lower concentration of pyrite S in the surface section (0-20 cm) than at depth (>20 cm) during the plant growing season suggested that oxidation in the plant root region was appreciable. Transformations of S from inorganic species to organic species and vice versa were evident in the active plant growing season. Sulfur constituents in Louisiana freshwater marsh soil exhibit seasonal fluctuations along the depth profile

which are related to various abiotic and biotic processes in soil. To understand S dynamics in marsh systems more clearly, it is necessary to consider the effects of temporal and spatial variability and plant activity on the distribution of various S forms. Further studies on those factors which affect S fluxes and transformations will lead to a fuller assessment of the importance of soil S in nutrient cycling and the development of marsh systems.

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**CHAPTER THREE**  
**SEASONAL DYNAMICS OF INORGANIC AND ORGANIC SULFUR**  
**CONSTITUENTS IN LOUISIANA GULF COAST BRACKISH MARSH SOILS**

### **Abstract**

The profile distribution of specific sulfur forms associated with the sulfur cycle were investigated at a site in a Louisiana brackish marsh. Soil samples were fractionated into acid-volatile sulfides (AVS), HCl-soluble sulfur, elemental sulfur, pyrite sulfur, ester-sulfate sulfur, carbon-bonded sulfur, and total sulfur. Inorganic sulfur composed 9 to 20 % of total sulfur, with HCl-soluble sulfur representing 63 to 92 % of the inorganic sulfur fraction. The presence of pyrite sulfur was greater in fall and winter than in spring and summer. When compared to sulfur in the pyrite form, elemental sulfur was less abundant, but it showed greater seasonal variation. Pyrite sulfur and elemental sulfur together accounted for 8 to 33 % of the inorganic sulfur pool. Organic sulfur, in the forms of ester-sulfate sulfur and carbon-bonded sulfur, was the most dominant pool in all sampling periods, consisting 80 to 91 % of total sulfur. The conversion of ester-sulfate sulfur to carbon-bonded sulfur was greatest in spring. Transformations of sulfur from inorganic to organic and vice versa appeared to be greater in spring and summer than in fall and winter. Organic sulfur, composed largely of carbon-bonded sulfur, was responsible for much of the variation of total sulfur. The concentrations of total sulfur in spring was a statistically significantly difference from other seasons.

## Introduction

Tidal marshes commonly occur in coastal areas and along tidal rivers on the Atlantic and Gulf Coasts of the United States. Between the freshwater and marine ends of these marshes is situated perhaps the most interesting environmental unit; the brackish marsh area. The brackish marsh can be thought of as a transition zone on a hydraulic gradient where nutrient export or import occurs (Feijtel *et al.*, 1985). It is obvious, however, that this marsh system represents an intermediate zone (mixing zone) of the estuarine ecosystem in several aspects other than salinity and temperature (Bahr and Hebrard, 1976). One aspect that has received little attention is the composition of the brackish marsh substrate, particularly the nature and distribution of inorganic and organic S forms as they relate to the origin and type of marsh substrate materials (Lowe and Bustin, 1985).

The dynamics of sulfur (S) include aqueous, sedimentary, and atmospheric phases and, as a result, the S cycle is very important (Landers *et al.*, 1983). In organic-rich sediments underlying productive plant ecosystems, S is involved in sulfate reduction, pyrite formation, metal cycling, energy transport, and atmospheric S emissions (see Luther *et al.*, 1986). Each of these processes depends upon the formation of one or more intermediate oxidation states of S (Luther and Church, 1988). Since S can form a number of inorganic and organic species with oxidation states varying from -2 to +6, it can undergo a variety of biogeochemical transformations in the natural environment (Luther *et al.*, 1986). Due to its importance, several studies have placed considerable emphasis on the chemical constituents of S in marine and coastal marine environments (see Nriagu and Soon, 1985). Although there have been a number of studies dealing with the forms, distribution, and isotopic composition of S in sediments from those systems (Kaplan *et al.*, 1963; Berner, 1964, 1970; Nedwell and Abram, 1978; Howarth, 1984; Haering *et al.*, 1989), they generally did not detail the effect of temporal changes on the inorganic and, particularly, the organic S compounds. In addition, little information has

been reported for brackish marsh sediments. The only study on the distribution of inorganic and organic S forms in brackish-related materials is by Lowe and Bustin (1985). Although they did not examine the effect of seasonal changes on the distribution of S forms, they related the S distribution to peat origin and degree of decomposition, and eventually concluded that increases in the degree of decomposition of peat is associated with increasing S content.

Due to the lack of information on the nature and distribution of inorganic and organic S forms, the understanding of S fluxes and transformations as related to origin and type of material has been limited (Landers *et al.*, 1983; Lowe and Bustin, 1985). To obtain needed information on the distribution of S forms, we therefore examined the S profile distribution in soils taken from a Louisiana Gulf Coast brackish marsh. To determine temporal changes and the possible effect of plant growing seasons on the profile distribution of S forms, both inorganic and organic S forms were quantified over a one year period.

## Materials and Methods

### *Study area*

Samples for this study were collected from a brackish marsh located in Barataria Basin, Louisiana (29° 28' N, 90° 10' W) (Figure 5.1). Barataria Basin is a 400 000-ha intertributary Louisiana Gulf Coast estuarine basin with well-defined vegetative units that is bounded on the east by the Mississippi River and on the west by the river's most recently abandoned channel, Bayou Lafourche. Brackish and intermediate marshes (salinity 5-10 ‰) together cover approximately 20 % of the basin. *Spartina patens* (Ait.) Muhl. is the dominant vegetation and covers about 46 % of the entire brackish marsh area. *Distichlis spicata* (L.) Greene. and *Spartina alterniflora* Loisel. comprise 29 and 9 % of the total vegetative cover of the area, respectively (Chabreck, 1972). Clay content of brackish marsh soil ranges from 17 to 30 % and organic C is about 28 % (Bahr



and Hebrard, 1976). Net carbon accumulation in this marsh area is  $296 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Feijtel *et al.*, 1985) and the sedimentation rate is  $9.5 \text{ mm yr}^{-1}$  (Feijtel *et al.*, 1988), which is in between that of freshwater and salt marshes in Barataria Basin.

### *Sampling and Analysis*

Five soil cores were collected at 20 m from the bank of Little Lake within a radius of 3 m in a time series during April 1987 through August 1988. This allowed us to minimize the spatial heterogeneity and to assess seasonal variation (Feijtel *et al.*, 1988). Soil samples were obtained by twisting an aluminum core (15-cm i.d. and 50-cm height) into marsh substrate. Little compaction resulted from this sampling method. The cores were extruded and sectioned into 3-cm intervals immediately upon return to the laboratory. Approximately 75 % of each section was rapidly sealed in a plastic bag and then frozen, and was subsequently used for S fractionations. The remaining 25 % was utilized for the determinations of pH, bulk density (Table 3.1), and water content. Prior to chemical analysis, the samples were thawed and thoroughly mixed and any live roots and debris were removed.

The procedure used for the sequential extraction of S fractions shown in Figure 2.1 is a modification developed by Nriagu and Soon (1985). The extractions were performed using a modified Johnson-Nishita (J-N) digestion-distillation apparatus (Johnson and Nishita, 1952) (Figure 2.2). Extractant was introduced to the boiling flask by syringe injection through a serum cap at the upper end of the condenser. This was a more convenient way to add an extractant and reduced the risk of  $\text{H}_2\text{S}$  loss during acid addition (Frenay *et al.*, 1970). Sulfur species containing in each extracted S fraction are shown in Table 2.1. Fresh sample containing about 5 to 10 g of oven-dried material ( $60^\circ\text{C}$ ) was used. Acid-volatile sulfides (AVS), HCl-soluble S, elemental S ( $\text{S}^0$ ), pyrite S ( $\text{FeS}_2$ ), and ester-sulfate S were extracted by the method described by Nriagu and Soon (1985). For ester-sulfate S, the extractant (HI reducing mixture) was prepared by a

method outlined by Landers *et al.* (1983). The concentration of each S fraction was determined with inductively coupled argon plasma spectrometry (ICP) instead of the gravimetric method used by Nriagu and Soon (1985). Carbon-bonded S was estimated by subtracting from total S all of the other S fractions (sum). Pore water was extracted by centrifuging a 50 to 100 g fresh aliquot for 20 min at 8 000 x g (7 000 rpm, Sorvall GSA-400 rotor, DuPont Co., Wilmington, DE). The supernatant was filtered through a 0.45- $\mu$ m membrane filter. Sulfur and iron in the filtrate was measured with ICP. The residual aliquot was oven dried at 60 °C to constant mass, sieved (150-mesh size), and thoroughly mixed prior to digestion with HNO<sub>3</sub>-HClO<sub>4</sub> (Beaton *et al.*, 1968). The digested sample was filtered through a 0.45- $\mu$ m membrane filter. Sulfur in the filtrate was determined with ICP. The sum of pore water S and soil S fractions represented total S. All values are reported on an oven-dried soil weight basis. Pearson's correlation coefficients and Duncan's Multiple Range Test (DMRT) were calculated with Statistical Analysis System (SAS Institute Inc., 1985). An asterisk (\*), double asterisk (\*\*), and triple asterisk (\*\*\*) were used to represent significant correlations at  $P < 0.05$ ,  $< 0.01$ ,  $< 0.001$ , respectively.

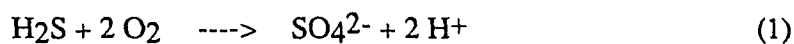
## Results and Discussion

### *Acid-volatile sulfides (AVS)*

The AVS fraction appeared to be the least significant S constituent in Louisiana brackish marsh soils (Figure 3.9) and represented <1 % of total S (Table 3.1). Similar contributions of this S form to the total S pool have been reported for Connecticut coastal sediments (Berner, 1970) and marine-mangrove swamp of southern Florida (Casagrande *et al.*, 1977). In the present study, concentrations of AVS ranged between 19.8 and 48.5  $\mu$ g S g<sup>-1</sup> soil in February 1988 and November 1987, respectively, which agreed well with those reported for brackish-derived peat and clay by Lowe and Bustin (1985) and other coastal marsh (Nedwell and Abram, 1978).

Depth profiles of AVS concentrations varied from one season to another (Figure 3.1). There was a significant negative relationship between AVS concentration and depth observed in July 1987 ( $r = -0.79^{***}$ ) and February 1988 ( $r = -0.81^{***}$ ). On the contrary, the AVS concentration showed a significant increase with depth in August 1988 ( $r = 0.76^{**}$ ). An unusual depth profile was found in summer 1987 in which AVS decreased with depth. Also, inconsistent patterns with depth were observed in April and November 1987. Perhaps this finding may be attributed to the inconsistent seasonal pattern of the vertical redox profile complemented by high variability in interstitial iron (II), which may affect hydrogen sulfide ( $H_2S$ ) production (Feijtel *et al.*, 1988). Higher rainfall and water levels during spring and summer may partly contribute to the variation in redox conditions and thus explain for this observation. Cutter and Velinsky (1988) postulated that the abundance and distribution of iron sulfide ( $FeS$ ) appears to be a sensitive indicator of redox condition in marsh sediments. Since iron monosulfide is the initial product of the reaction of sulfide ion ( $S^{2-}$ ) and iron (II), the variation in  $H_2S$  and  $Fe$  (II) certainly affect the abundance of iron sulfide and hydrogen sulfide *per se*.

Several workers (Giblin and Howarth, 1984; Cutter and Velinsky, 1988; Luther and Church, 1988) have also noted that the dynamics of AVS is controlled to some extent by the temperature and the production of oxygen via photosynthesis by marsh plants, particularly during the spring and summer. A significant increase in AVS concentration with depth found in spring (up to 30 cm,  $r = 0.73^{**}$ ) and fall 1987 (up to 25 cm,  $r = 0.89^{***}$ ), and summer 1988 (throughout the profile,  $r = 0.76^{**}$ ) was believed primarily due to the greater oxidation of sulfide and iron monosulfide or by plant uptake. During these growing seasons, the marsh surface (<20 cm) became more oxidized and sulfides were converted to sulfate (equation 1) or to various partially oxidized compounds like elemental S ( $S^0$ ), sulfite ( $SO_3^{2-}$ ), thiosulfate ( $S_2O_3^{2-}$ ) (equation 2), polysulfides ( $S_n^{2-}$ ), or polythionates ( $S_{3+n}O_6$ ,  $n = 0-3$ ) (Giblin and Howarth, 1984):



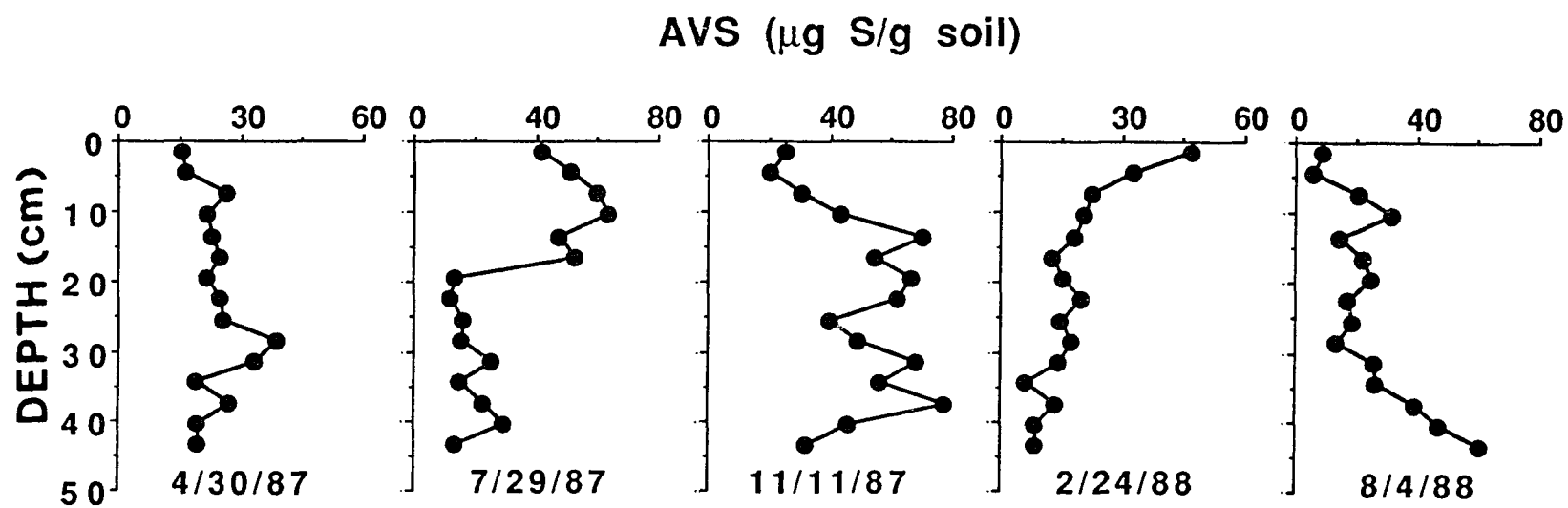
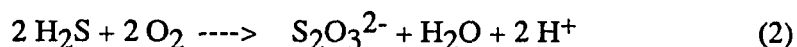


Figure 3.1. Profile distribution of acid-volatile sulfides (AVS) in brackish marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).



Loss of iron monosulfides may also occur through oxidation to iron (II), iron (III), and elemental S, particularly in the surface oxidized zone (15-20 cm) (Cutter and Velinsky, 1988). Due to the aforementioned mechanisms, the concentration of AVS under study was 1- to 2-fold lower in the surface section (<20 cm) than in the deeper profile (>20 cm) which showed a significant increase with depth (previously mentioned) during the plant growing seasons (except summer of 1987). This corresponds to a report on undersaturation of pore waters with respect to iron monosulfides up to a depth of 20 cm at this site by Feijtel *et al.* (1988).

In winter 1988, AVS concentration showed a significant decrease with depth ( $r = 0.81^{***}$ ). The declining AVS concentration with depth can result from a dramatic decrease in the rate of sulfate reduction due to low winter temperatures (Luther and Church, 1988) in the reduced zone (>20 cm) coupled with low sulfide uptake in the root zone (<20 cm) when plants are metabolically inactive (Howarth and Teal, 1979). Upward diffusion of sulfides from the reduced layer may induce losses of sulfides at depth (Nedwell and Abram, 1978). Whitcomb *et al.* (1989) have shown that sulfide, which diffuses from a reducing soil environment to oxygen-enriched surface waters and sediments, can be rapidly chemically oxidized to elemental S in Louisiana Gulf Coast brackish and salt marshes. In the present study, a negative relationship between AVS and elemental S was evident in fall 1987 ( $r = -0.63^*$ ) and winter 1988 ( $r = -0.54^*$ ).

Although there was no significant difference in AVS concentration among the five sampling periods, the mean value was relatively low in winter 1988 and tended to be high in summer and fall 1987 (Table 3.1). This finding can be explained by differences in the rate of sulfate reduction. Howarth and Teal (1979) found that sulfate reduction rates show a pronounced seasonal trend which is not controlled entirely by temperature, but also by the availability of organic substrates. They further concluded that the higher fall rates than those of summer and spring are probably caused by the pulse of readily

available substrate as the marsh plants mature and die, starting in August. In this manner, the anoxic microbial community in the marsh receives its organic substrates from dead roots and rhizomes and perhaps from the excretion of dissolved organic compounds from living roots and rhizomes; processes which are related to the seasonal activities of the marsh plants (Howarth and Teal, 1979). On an annual basis, AVS concentration in the upper 20 cm was not significantly higher than that below 20-cm depth.

#### *HCl-soluble S*

In the present study, HCl-soluble S was the most important pool of inorganic S (Figure 3.9), representing 63 to 92 % of inorganic S (Table 3.1). Mean concentrations of this S fraction ranged from 0.75 mg S g<sup>-1</sup> soil in July 1987 to 4.04 mg S g<sup>-1</sup> soil in April 1987. This corresponds to the variations in pore water sulfate concentration. Nriagu and Soon (1985) claimed that this S phase includes pore water sulfate and sulfate from oxidation of reduced S. It is likely that the HCl-soluble S fraction in the present study may be derived largely from pore water sulfate. The mean value of pore water sulfate comprised 77 % of the HCl-soluble S fraction. Statistically, a significant relationship between HCl-soluble and pore water sulfate was found in every sampling period ( $r = 0.90^{***}$ ,  $0.64^{**}$ ,  $0.74^{**}$ ,  $0.71^{**}$ , and  $0.50^*$ , respectively), apparently supporting the significance of the pore water sulfate contribution to HCl-soluble S. Other evidence showing contributions to this S form were from the C-bonded S and AVS fractions. A significant inverse correlation between HCl-soluble S and C-bonded S was shown in November 1987 ( $r = -0.49^*$ ), July 1987 ( $r = -0.50^*$ ), and August 1988 ( $r = -0.50^*$ ). Some HCl-soluble S is possibly derived from soluble and HCl hydrolysable organic S containing C-bonded S such as amino acids (Nriagu and Soon, 1985). A similar relationship between HCl-soluble S and AVS was observed in April 1987 ( $r = -0.54^*$ ), suggesting the oxidation of dissolved sulfides and sulfide minerals to sulfate during the onset of the growing season. Under laboratory conditions, however, some of this sulfide

could have been oxidized to sulfate by bacteria during storage or during experimental manipulation of the samples, but this error would be relatively small (Berner, 1964; Nriagu and Soon, 1985).

Depth profiles of HCl-soluble S are shown in Figure 3.2. The concentration of HCl-soluble S was decreasing with depth during spring 1987 ( $r = -0.64^{**}$ ) and summer 1987 ( $r = -0.84^{***}$ ), and winter 1988 ( $r = -0.63^{*}$ ). Considering only the surface zone (<30 cm), a significant decrease with depth was observed in all sampling periods ( $r = -0.86^{***}$ ,  $-0.91^{***}$ ,  $-0.91^{***}$ ,  $-0.98^{***}$ , and  $-0.71^{**}$ , respectively). The concentrations of HCl-soluble S reached minima of 2.40, 0.31, 0.24, 0.55, and 0.43 mg S g<sup>-1</sup> soil in April, July, and November 1987, and February and August 1988, respectively, between 20- to 30-cm depth. Howarth and Teal (1979) and Howarth and Giblin (1983) have also reported a similar decline in sulfate concentrations with depth (0-30 cm) in both the tall and short *Spartina* sites. Diminishing sulfate concentrations with depth are probably caused by the greater rates of sulfate reduction at depth (Howarth and Giblin, 1983) and may also influenced by uptake of sulfate by plant roots or microorganisms involving an assimilatory reduction process with S-containing amino acids as the major product (Lowe and Bustin, 1985).

Below 20- to 30-cm depth, the concentrations of HCl-soluble S tended to increase significantly with depth during spring ( $r = 0.81^{***}$ ), summer ( $r = 0.89^{***}$ ), and fall ( $r = 0.68^{**}$ ) of 1987, and summer 1988 ( $r = 0.83^{***}$ ). These increasing patterns were likely due to the faster rate of pore water sulfate exchange than sulfate depletion. Howarth and Teal (1979) postulated that even under sulfate reducing conditions sulfate concentrations still remain high because sulfate is regularly and rapidly resupplied to the coastal marsh peat by infiltration, particularly at high tide. The concentration of HCl-soluble S, on an annual average, was 1.5-fold higher in the upper 20 cm than below 20-cm depth (Figure 3.8) similar to distributions of pore water sulfate in the surface section (<20 cm) which was 1.7-fold higher than that at depth (>20 cm). A likely explanation here is the presence

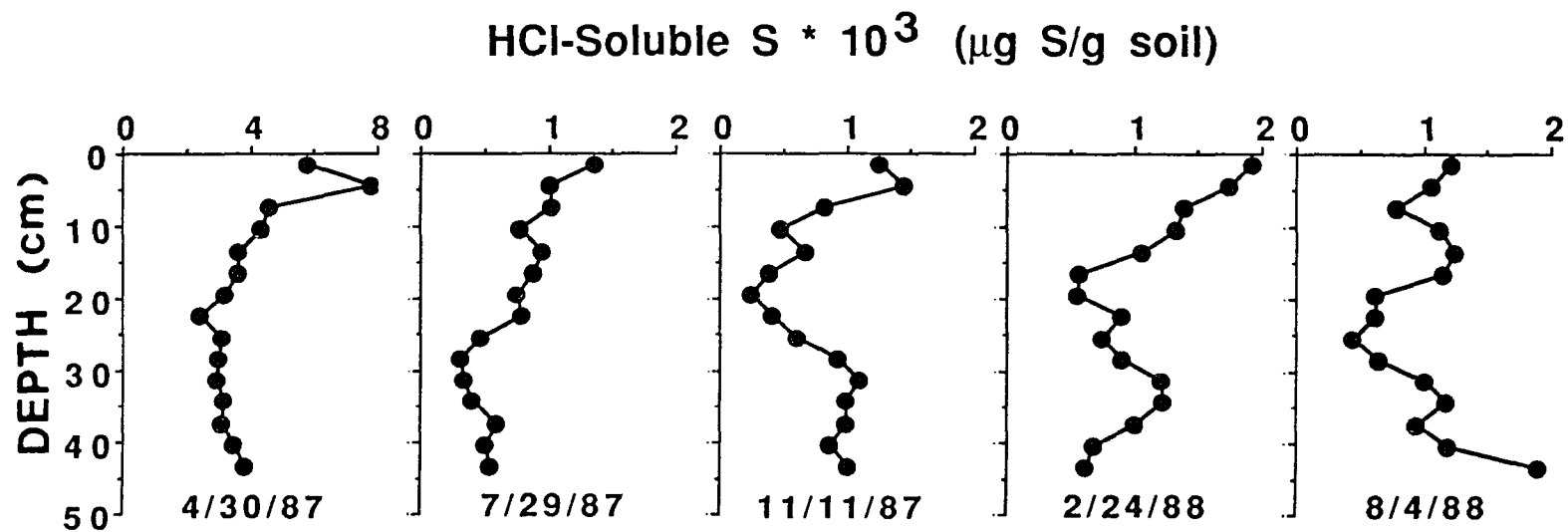


Figure 3.2. Profile distribution of HCl-soluble S (HCl) in brackish marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).



of more oxidizing condition in the upper 20 cm and more reducing condition below 20-cm depth. A study from the Great Marsh of Delaware also showed that an excess of sulfate in the upper zone (0-15 cm) apparently results from the more oxidizing condition as a result of plant root activity (Luther and Church, 1988). Howarth and Giblin (1983) noted that the accretion or depletion of sulfate is also controlled by the rate of sulfate reduction, the rate of reoxidation of reduced S compounds, diffusing out of a reducing zone, to sulfate, and the rate of pore water exchange.

#### *Elemental S ( $S^0$ )*

Elemental S comprised 0.6 to 8.7 % of the inorganic S or 0.1 to 1.0 % of total S (Table 3.1). Similar results have been reported in coastal marine sediments of Connecticut (Berner, 1970) and southern California (Kaplan *et al.*, 1963). A slightly higher percent of this S form, ranging between 1.1 and 3.6 % of total S, was present in brackish-derived materials (Lowe and Bustin, 1985). Concentrations of elemental S in the study was between 21.6 and 145  $\mu\text{g S g}^{-1}$  soil and were comparable to those observed by Troelsen and Jorgensen (1982) in shallow coastal sediments but approximately 10-fold less than those in the Great Marsh sediment (Cutter and Velinsky, 1988).

Figure 3.3 shows the distribution of elemental S with depth. There was a negatively correlated relationship with depth in November 1987 ( $r = -0.62^*$ ), February 1988 ( $r = -0.73^{**}$ ), and August 1988 ( $r = -0.63^*$ ). No clear pattern was observed in April and July of 1987. The lowest concentration of elemental S was found in April 1987, whereas the greatest value was observed in August 1988. This corresponds to the study of Feijtel *et al.* (1988) for this brackish marsh in which reducing conditions were greatest in the spring and oxidation process dominated during the summer. The explanation for comparable elemental S concentrations in the early summer 1987 and in winter 1988 is uncertain. Tidal fluctuation from prevailing storms inducing redox changes may have

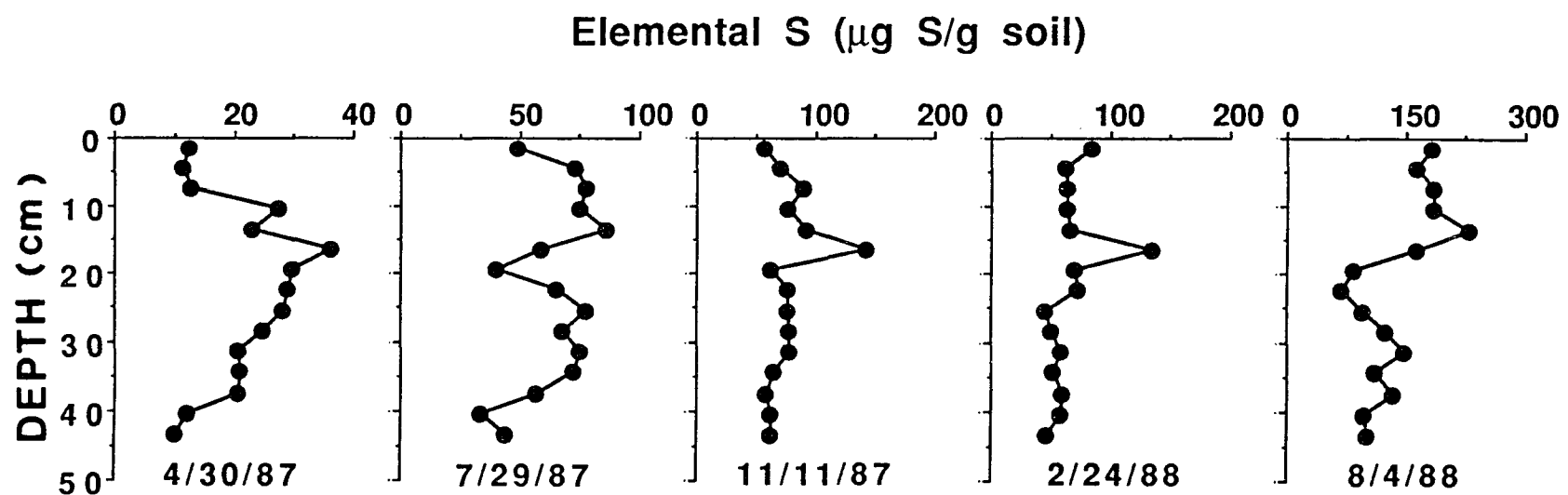
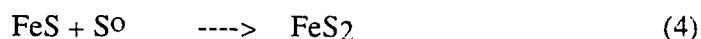
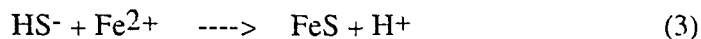
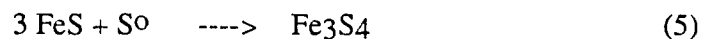


Figure 3.3. Profile distribution of elemental S ( $\text{S}^0$ ) in brackish marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).

been responsible for the unexpected low concentration of elemental S in early summer. In contrast, low water levels in winter, allowing more oxidizing conditions in the marsh profile, may result in high elemental S content even though the oxidizing power of plant roots was low. The second greatest mean concentration of elemental S was found in fall. Elemental S was seemingly derived from the oxidation of AVS in the same season as evidenced by a significant inverse relationship between AVS and elemental S ( $r = -0.63^*$ ). Fall was the highest production period of AVS in the present study (as discussed previously). Elemental S is believed to be formed only by the oxidation of dissolved  $H_2S$  and iron sulfide (AVS) (Troelsen and Jorgensen, 1982; Cutter and Velinsky, 1988). Troelsen and Jorgensen (1982) suggested that the seasonal transition from a more oxidized condition (summer) to a more reduced condition (winter) can also lead to the accumulation of elemental S during the fall. In summer 1988, a significant negative relationship found between elemental S and pyrite ( $FeS_2$ ) ( $r = -0.56^*$ ) indicated that elemental S may be utilized in pyrite formation as shown in equation (3) and (4) (Berner, 1970; Goldhaber and Kaplan, 1974; Altschuler *et al.*, 1983):



Further oxidation removes elemental S as does the formation of greigite ( $Fe_3S_4$ ) and pyrite, shown in equation (5) and (6) (Goldhaber and Kaplan, 1974; Cutter and Velinsky, 1988):



Elemental S can be further oxidized to sulfate by bacteria using ferric ion or nitrate (Troelsen and Jorgensen, 1982). This appeared to occur in the present study as indicated by significant inverse correlations not only between elemental S and HCl-soluble S ( $r =$

-0.59\*) but also between elemental S and pore water sulfate ( $r = -0.62^*$ ) in spring 1987. Casagrande *et al.* (1977) found an inverse correlation between elemental S and sulfate in the Florida Everglades peat, suggesting the oxidation of elemental S to sulfate.

Concentrations of elemental S appeared to peak at 13.5 to 16.5 cm below the marsh surface. The greatest abundance was found in the mid summer 1988 and early fall 1987, when oxygen is largely introduced through plant roots during photosynthesis. The reduced abundance of this S form during early spring 1987 may be partially due to the variation in the initial content of AVS fraction and the oxidizing conditions during this period. Elemental S can undergo biologically mediated oxidation to sulfate and thiosulfate via the oxidizing power of marsh grass roots (Howarth and Teal, 1979; Cutter and Velinsky, 1988). In the present study, elemental S was increasing toward its maximum concentration in the upper 20 cm in all sampling periods, except for winter 1988 when the concentration of elemental S showed a sharp peak at 16.5 cm from the marsh surface. Whitcomb *et al.* (1989) found that elemental S can be formed from the chemical oxidation of sulfide diffusing from the reducing soil into oxygenated surface soil in Louisiana brackish marsh. This could explain why the concentration of elemental S in the top 20 cm was relatively high. The elemental S content at depth (>20 cm) showed a significant negative relationship with depth in April, July, and November of 1987 ( $r = -0.96^{***}$ ,  $-0.75^{**}$ , and  $-0.86^{***}$ , respectively), whereas there was no significant relationship with depth observed in February and August 1988. On an annual basis, however, elemental S exhibited a declining trend with depth ( $r = -0.83^{**}$ ). Troelsen and Jorgensen (1982) have also documented a decrease in the elemental S pool below an oxidized zone of shallow coastal sediments and concluded that it is due to the greater reducing conditions at increasing depth.

### *Pyrite S (FeS<sub>2</sub>)*

Pyrite S in the present study was the second most abundant inorganic S pool (Figure 3.9) and composed 7.3 to 27.4 % of the inorganic S or 1.5 to 2.6 % of total S pool (Table 3.1). Similarly, Lowe and Bustin (1985) reported the presence of pyrite in brackish-derived peat and clay at about 1.2 to 1.9 % of total S. Several previous studies have also documented comparable amounts of pyrite in coastal marsh sediments (Berner, 1970; Nedwell and Abram, 1978), and marine-mangrove sediments (Casagrande *et al.*, 1977; Altschuler *et al.*, 1983). These results, however, are in marked contrast to other workers who have concluded that pyrite is much more abundant and comprises most of the S pool in marsh sediments (Kaplan *et al.*, 1963; Berner, 1964; Howarth and Teal, 1979; Howarth, 1984; Cutter and Velinsky, 1988). It is likely that low iron (II) availability limits the amount of pyrite formed in some environments. Pyritization limited by the availability of iron (II) was evident in some marshes (Lord and Church, 1983; Howarth, 1984; Haering *et al.*, 1989). In the present study, low pyrite content apparently corresponded with a low content of dissolved iron of  $<1 \mu\text{g Fe g}^{-1}$  soil. In addition, Feijtel *et al.* (1988) found that only 34 % of the total iron flux in this brackish marsh occurs in the pyrite form.

The depth profiles of pyrite S is shown in Figure 3.4. In general, concentrations of pyrite S did not show a clear pattern in April, July, and November 1987, but there was a significant negative relationship with depth found in February 1988 ( $r = -0.65^{**}$ ) and a significant positive relationship with depth in August 1988 ( $r = 0.86^{***}$ ). Although pyrite concentration did not show a significant difference in all sampling periods (Table 3.1), its concentration was relatively low in summer. This corresponded somewhat to the dominance of oxidation processes during summer at this site (Feijtel *et al.*, 1988), resulting in pyrite oxidation. The concentration of pyrite S in summer 1988 was significantly negatively correlated with that of elemental S in the same season ( $r =$

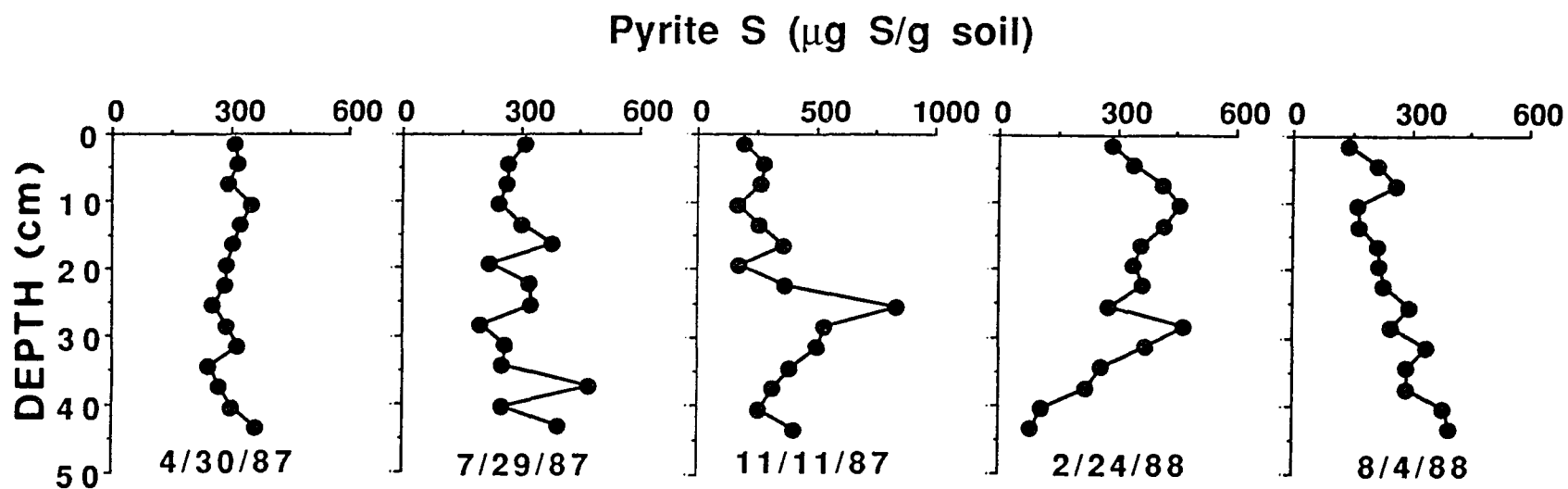


Figure 3.4. Profile distribution of pyrite S ( $\text{FeS}_2$ ) in brackish marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).

-0.56\*), suggesting that pyrite oxidation produces some elemental S. The greatest abundance of elemental S present in this period supports this possibility. Howarth and Teal (1979) postulated that elemental S may be an intermediate product of pyrite oxidation, but large amounts of elemental S generally do not build up in the marsh peat because it has a very fast turnover rate in seawater. In addition, they found that pyrite concentration varied from one season to another as well. In the present study, however, the seasonal variation in pyrite S content is more understandable in view of oxidized and reduced zones.

Pyrite S in the upper marsh sediment (<20 cm) showed more temporal variation than in the deep sediment (>20 cm) although its mean concentration was significantly lower ( $P < 0.02$ ) (Figure 3.8). The presence and absence of a shallow pyrite S maxima (<20 cm) varied from one sampling period to another, indicating rapid rates of pyrite formation (Howarth and Teal, 1979; Lord and Church, 1983; Cutter and Velinsky, 1988). Howarth (1979) and Howarth and Teal (1979) claimed that pyrite can form rapidly in the surface sediment whenever soluble sulfides are present and pyrite is supersaturated, but iron monosulfides are undersaturated. This is in good agreement with a previous study at this site by Feijtel *et al.* (1988) who indicated that pore water is supersaturated with respect to pyrite and undersaturated in respect to iron monosulfides up to a depth of 20 cm. On an average, the greatest abundance of pyrite S in the oxidized zone (<20 cm) observed in winter resulted primarily from low oxidation processes due to the depressed activity of marsh plants. This is similar to a study of Giblin and Howarth (1984) who found a net increase in pyrite content in winter.

Low pyrite S concentration in the upper 20 cm during plant growing seasons is possibly caused by the oxidation of marsh soil by plant roots which will convert a large amount of sedimentary pyrite to an oxidized iron mineral (Giblin and Howarth, 1984). Some other studies (Howarth and Teal, 1979; Luther and Church, 1988) also showed that pyrite is oxidized in marsh sediments by the growth of *Spartina* in the upper 25 cm.

Luther and Church (1988) found that excess dissolved iron and sulfate are released to the pore waters of a Delaware salt marsh when pyrite oxidation occurs. Feijtel *et al.* (1988) found the greatest abundance of dissolved iron during summer when marsh plants are most productive. This finding was in accord with the present study where the lowest concentrations of pyrite S were observed in summer.

In this brackish marsh, Feijtel *et al.* (1988) have reported supersaturation of both pyrite and iron monosulfides in pore waters below 20-cm depth. Under this circumstance, iron monosulfides can form first even though they are less stable than pyrite, and once formed, they only slowly react with elemental S to form pyrite (Howarth and Teal, 1979) (see equation 3 and 4). This finding, accompanied by the deeper pyrite S maxima (below 20 cm) observed in all five sampling periods in this study, lead to the conclusion that pyrite is forming slowly (Goldhaber and Kaplan, 1974; Cutter and Velinsky, 1988). This conclusion was evidently supported by the presence of a framboidal pyrite, indicative of slow pyrite formation when elemental S reacts with iron sulfide (Berner, 1964; Goldhaber and Kaplan, 1974), rather than the presence of single crystal pyrite particles when pyrite forms rapidly below 20-cm depth at this site (Feijtel *et al.*, 1988). Lord and Church (1983) also reported similar evidence in a Delaware marsh.

The pyrite concentration below 20-cm depth in which anaerobic conditions dominated (Feijtel *et al.*, 1988) showed a significant increase with depth in April ( $r = 0.60^*$ ) and July ( $r = 0.61^*$ ) 1987, and August 1988 ( $r = 0.86^{***}$ ). In contrast, a significant decrease with depth was found in November 1987 ( $r = -0.95^{***}$ ) and February 1988 ( $r = -0.77^{**}$ ). The decline in pyrite S content with depth in the fall was somewhat ambiguous. Nevertheless, the decrease in elemental S at corresponding depth ( $r = -0.86^{***}$ ) may be responsible for this. It is likely that this phenomenon is partially accounted for by faunal activity. Howarth and Giblin (1983) found that the absence of any clear increases in pyrite below the root zone of marsh plants results from the mixing of the deeper reduced sediment to the more oxidized surface zone by fiddler crabs.



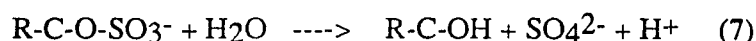
During the winter, it is not surprising that pyrite S concentration tended to diminish with depth (>25 cm). Although sulfate reduction becomes the predominant biogeochemical process during the less productive winter season, the rate of sulfate reduction appears to subside considerably as a result of low temperatures (Luther and Church, 1988). Thus, iron (II) is gradually precipitated to form pyrite during the winter (Cutter and Velinsky, 1988). This can also explain the lowest concentration of pyrite S present below 20-cm depth in winter ( $277 \mu\text{g S g}^{-1}$  soil). The greatest abundance was found in fall season ( $422 \mu\text{g S g}^{-1}$  soil). Howarth and Teal (1979) found a greater net accumulation of pyrite in the fall than in the spring and summer because either the rate of sulfate reduction is so much higher or the roots have less oxidizing power as the marsh plants mature and die starting in August.

It may be noted that the pyritization process in this Louisiana brackish marsh appeared to be dependent on the concentration of the other S fractions, for instance, AVS, pore water sulfate, and elemental S. Our data has partially supported the previous conclusion on pyrite formation in Louisiana brackish marsh (Feijtel *et al.*, 1988) in that pyrite formation occurs in two distinct processes: (i) fast reaction of iron (II) with polysulfides at the marsh surface (<15-20 cm), and (ii) slow reaction of elemental S with iron sulfide intermediate at greater depth (>15-20 cm).

#### *Ester-sulfate S*

In the present study, ester-sulfate S was the second largest component of total S (Figure 3.9), representing 13 to 48 % of organic S or 10 to 44 % (average 26 %) of total S (Table 3.1). Similar amounts of this S form were observed in brackish-derived materials (Lowe and Bustin, 1985) and in marine-mangrove peat (Casagrande and Siefert, 1977). A lower amount of 11 to 28 % of organic S is present in waterlogged peat as ester-sulfate S (Wieder *et al.*, 1987).

The profile distribution of ester-sulfate S with depth is shown in Figure 3.5. There was no significant pattern with regard to the abundance of this S form occurred in April and November of 1987. A significant relationship between ester-sulfate S and depth was found in February 1988 ( $r = 0.52^*$ ). This relationship was inconsistent between the two summer seasons. The ester-sulfate S was significantly correlated with depth in July 1988 ( $r = 0.76^{**}$ ), whereas a significant inverse correlation with depth was found in August 1987 ( $r = -0.81^{***}$ ). The discrepancy in ester-sulfate S trends from one sampling period to another may be governed by mineralization and formation processes involving the availability of sulfate. McGill and Cole (1981) suggested that S mineralization from ester-sulfate molecules is mediated by extracellular aryl- and alkylsulfatases, which are produced by microorganisms and plant roots, and occurs in response to low sulfate supply. The hydrolysis of the ester-sulfate S to release inorganic sulfate is shown in equation (7) (Freney, 1986). These enzymes, however, exhibit seasonal variability (Jarvis *et al.*, 1987).



Our data (Table 3.1) suggested that the mineralization of ester-sulfate S to inorganic sulfate (HCl-soluble S) occurred primarily in early spring. In contrast, the lowest abundance of HCl-soluble S was coupled with the greatest abundance of ester-sulfate S in summer 1987 indicating the formation of ester-sulfate S. Luther *et al.* (1986) found an indication of S transformation from inorganic to organic species during warmer, more productive seasons, and from organic to inorganic species during cooler, less productive seasons. It is likely, however, that the increase in ester-sulfate S was complemented largely by the decrease in C-bonded S during summer 1987 ( $r = -0.86^{***}$ ) in which the amount of C-bonded S was lowest. McGill and Cole (1981) suggested that available supplies of C-bonded S could repress the mineralization of ester-sulfate S. Wieder *et al.* (1987) also found a decrease in C-bonded S along with increases in ester-sulfate S during 125-day incubation and concluded that it is a result of a microbial

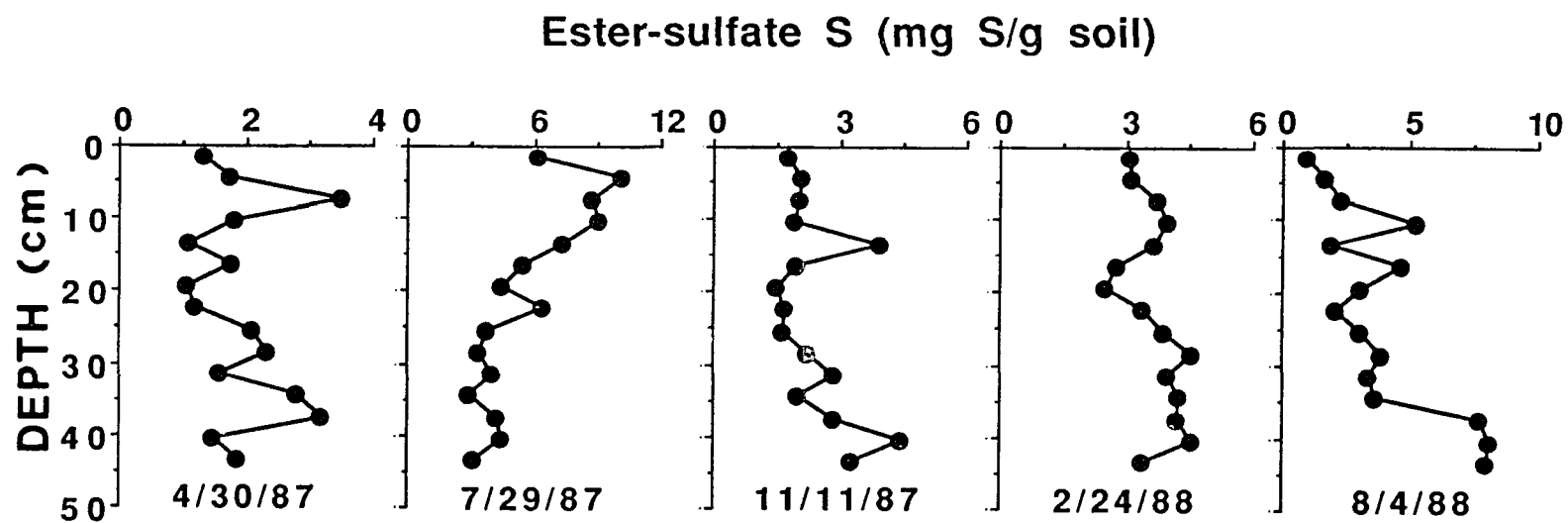


Figure 3.5. Profile distribution of ester-sulfate S in brackish marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoints of each section (3-cm interval).

demand for S which was sufficiently met by the mineralization of S from C-bonded S. As shown in Table 3.1, with the exception of summer 1987, the proportion of total S present in ester-sulfate S forms was relatively lower in spring and fall 1987. This may be due to a greater S mineralization of ester-sulfate S in the presence of active plants rather than inactive plants. In this manner, ester-sulfate S can be mineralized by extracellular periplasmic sulfohydrolases produced by soil microorganisms and plant roots in response to a need for S (Maynard *et al.*, 1984).

In comparison to the concentration of ester-sulfate S at depth (>20 cm), the mean concentration in the top 20 cm was significantly lower in all sampling periods ( $P < 0.05$ ). The increase in the concentration of ester-sulfate S with depth observed in *Spartina* marsh soils coincides with an observed pattern of decreasing arylsulfatase activity with depth (Oshrain and Wiebe, 1979). The increasing ester-sulfate S content with depth, however, may largely result from a greater amount of large organic acids and humic materials produced by anaerobic degradation of organic matter at depth, than the production of these substrates by aerobic degradation at the surface (<20 cm) (Casagrande and Siefert, 1977). Casagrande *et al.* (1980) have demonstrated that 35 % of S associated with humic acid and 80 % of that with fulvic acid in waterlogged peat are present in ester-sulfate S form.

A significant inverse relationship between ester-sulfate S and depth found in July 1987 ( $r = 0.71^*$ ) may be due to higher availability of sulfate at the top 20 cm than below 20-cm depth ( $P < 0.01$ ). Jarvis *et al.* (1987) have reported an increase in arylsulfatase activity with depth corresponding to a decrease in sulfate with depth, and believed that it may be a reflection of relatively high sulfate availability near the peat surface than at depth.

### *C-bonded S*

C-bonded S was the largest constituent of total S in the present study (Figure 3.9); its concentrations ranged from 5.73 to 14.3 mg S g<sup>-1</sup> soil. This S fraction accounted for 52 to 87 % of organic S or about 48 to 71 % of total S (Table 3.1). These estimates are in good agreement with the amounts of C-bonded S present in grassland soils (40-70 % of total S), which is believed to consist mainly of the S amino acids, proteins, and sulfonic acids (sulfonates) (Maynard *et al.*, 1984). A narrow range of 65 to 75 % of total S present in this form was reported for brackish-derived materials (Lowe and Bustin, 1985), whereas a higher proportion of 72 to 89 % of organic S in Big Run Bog peat was C-bonded S (Wieder *et al.*, 1987).

In the present study, the ratio of C-bonded S to ester-sulfate S was 2.8 and is quite similar to that reported for marine-mangrove peat (Casagrande *et al.*, 1977; Altschuler *et al.*, 1983) and subsurface of Big Run Bog peat (Wieder *et al.*, 1987), where C-bonded S is typically 2 to 3 times more abundant than ester-sulfate S. It seems reasonable that C-bonded S would be more likely to persist in high organic sediments than does ester-sulfate S. Carbon-bonded S would be mineralized as a result of C oxidation to provide energy (biological mineralization), whereas mineralization of ester-sulfate S would be mediated by extracellular or periplasmic sulfohydrolases (biochemical mineralization) in response to a need for S, not C (McGill and Cole, 1981; Maynard *et al.*, 1984). Bettany *et al.* (1973) postulated that C-bonded S is more resistant to mineralization than ester-sulfate S because C-bonded S is more likely to be incorporated into the strongly humic core by mechanisms such as quinone-thiol reactions, whereas a significant part of the ester-sulfate S fraction would be associated with the active side chain of organic acid components.

The profile distribution of C-bonded S is shown in Figure 3.6. As a major contribution of total S, C-bonded S showed a significant correlation with total S in all sampling periods, with the exception of July 1987 ( $r = 0.81^{***}$ ,  $0.93^{***}$ ,  $0.99^{***}$ , and  $0.54^*$ , res-

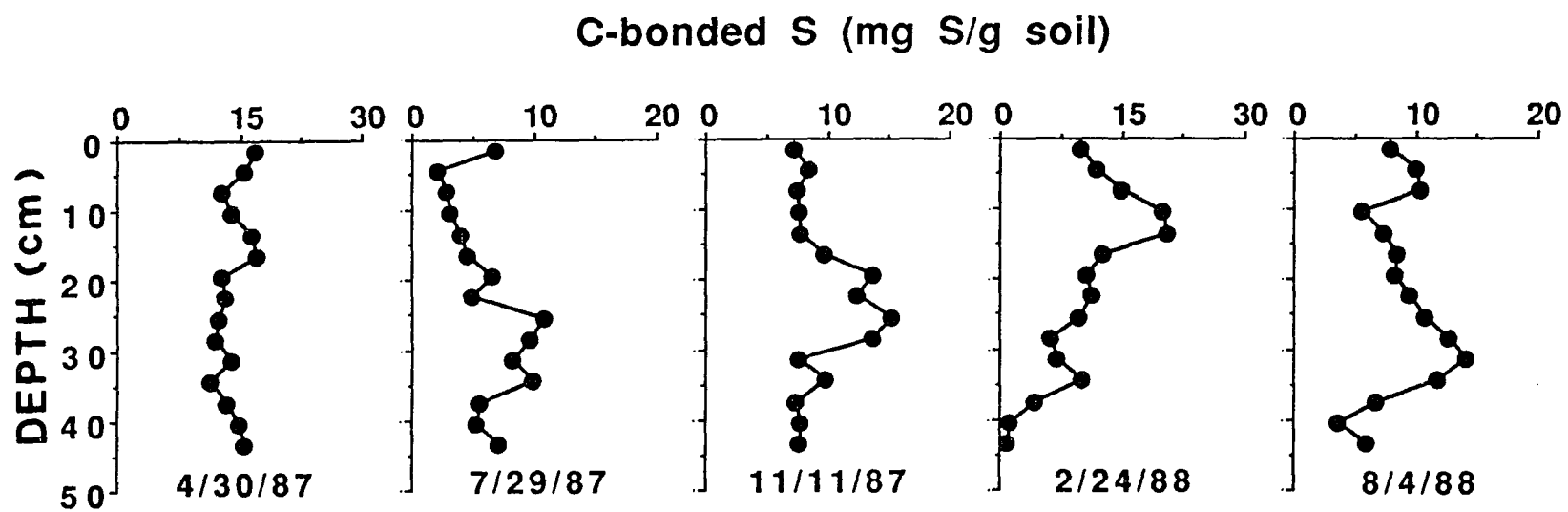


Figure 3.6. Profile distribution of C-bonded S in brackish marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).

pectively). The insignificant relationship between this S fraction and total S observed in summer 1987 may be due to the transformation of C-bonded S to ester-sulfate S. This resulted in a decrease in the proportion of C-bonded S and conversely a dramatic increase of ester-sulfate S fraction ( $r = -0.86^{***}$ ) (Table 3.1). In contrast, the transformation of ester-sulfate S to C-bonded S occurred significantly during growing season as indicated by a negative correlation between these pools in spring ( $r = -0.50^*$ ) and fall ( $r = -0.50^*$ ) 1987, and summer 1988 ( $r = -0.55^*$ ) rather than in winter. Nriagu and Soon (1985) found that the more labile ester-sulfate S is diagenetically converted to the C-bonded S form. Lowe and Bustin (1985) claimed that uptake of sulfate by plants and microorganisms, involving an assimilatory reduction process with S-containing amino acids as the major product, seemed to be more intense during the plant growing season. They further stated that the accumulation of C-bonded S by this pathway will be limited to some degree by the initial sulfate level in the environment. This corresponds to the presence of low concentration of C-bonded S in summer 1987 (Table 3.1) when pore water sulfate was much lower than in other periods ( $P < 0.01$ ).

While it was apparent that S-containing amino acids derived from plants and microorganisms was the most likely source of C-bonded S in the present study, another possibility is that AVS and elemental S interact with organic matter to produce C-bonded S. Nriagu and Soon (1985) noted that a large fraction of organic S is probably formed in situ by the reaction of the sedimentary organic matter with the reduced S species such as  $H_2S$ , polysulfides, and elemental S. In the present study, a significant negative relationship between C-bonded S and AVS fractions found in summer 1987 ( $r = -0.69^{**}$ ) and summer 1988 ( $r = -0.54^*$ ) support the hypothesis above. It has been shown that  $H_2S$  can be incorporated into peat organic matter, especially the humic acid fraction, at ambient temperature to produce organic S (Casagrande *et al.*, 1979). During the winter season, C-bonded S was significantly inversely correlated with elemental S ( $r = -0.68^{**}$ ).

Casagrande and Ng (1979) experimentally found that a portion of organic S can form in marsh sediment as the result of interaction of elemental S with organic matter.

Although concentrations of C-bonded S did not show a significant difference among the sampling periods, the C-bonded S concentrations were slightly higher in winter, early spring, and fall when biodegradation was relatively lower than in summer. During period of low microbial activity, C-bonded S showed maximum values at 13.5- to 15.5-cm from the marsh surface. This finding illustrates that organic materials derived from the death of plant blades, roots, and rhizomes were experiencing slower decomposition rates during winter and early spring. The onset of active *S. patens* in spring may also enhance the content of organic matter and thus C-bonded S in the upper 20 cm via assimilatory processes (Lowe and Bustin, 1985). In contrast to winter and spring when marsh plants were quite inactive, concentrations of C-bonded S in fall and summer 1987, and summer 1988 were significantly correlated with depth and attained maxima between 25.5- and 31.5-cm depth ( $r = 0.63^*$ ,  $0.61^*$ , and  $0.59^*$ , respectively). During these growing seasons, the roots of marsh plants seemed to penetrate deeper into the sediment (25-30 cm) when compared to those of inactive plants. Once decomposed, organic substrates, derived largely from dead roots, rhizomes, and perhaps microorganisms living around the root zones, could result in high content of C-bonded S within the root zone and probably in the deeper sediment (25-30 cm). A decrease with depth, and the fact that lowest abundance of C-bonded S below 20-cm depth was found in winter, was likely due to a lack of organic input from belowground production. Since the marsh plants are generally mature and began senescence in August (Howarth and Teal, 1979), most of the organic substrates would be decomposed before the winter comes. Because the levels of C-bonded S varied distinctively when plants were active and inactive, the annual averaged concentration of this S form in the surface zone and in the deeper profile showed a significant difference (Figure 3.8,  $P < 0.02$ ). Temporal variation in plant growth and production may influence the occurrence of this S form, greatly.



### *Total S*

Mean total S concentration varied significantly from 12.7 mg S g<sup>-1</sup> in July 1987 to 20.5 mg S g<sup>-1</sup> in April 1987 (Table 3.1). The total S concentration was comparable to several earlier studies for brackish-derived materials (Lowe and Bustin, 1985) and marsh sediments (Kaplan *et al.*, 1963; Howarth and Teal, 1979; Altschuler *et al.*, 1983; Cutter and Velinsky, 1988). Nonetheless, Casagrande *et al.* (1977) and Haering *et al.* (1989) have reported higher levels of total S. Based on a Duncan's Multiple Range Test (DMRT), the total S content was not significantly different during summer, fall, and winter, but it showed a significant difference in spring (Table 3.1). The greatest contribution to total S in the spring was from inorganic sulfate in the form of HCl-soluble S ( $r = 0.84^{***}$ ) or pore water sulfate ( $r = 0.82^{***}$ ) rather than organic ester-sulfate S or C-bonded S (Table 3.1). This suggested that the availability of dissolved sulfate was highest this season, and that no significant uptake of sulfate via plant assimilation occurred (Lowe and Bustin, 1985).

The distribution pattern of total S with depth is shown in Figure 3.7. The relationship between total S and depth showed a significant negative correlation in spring ( $r = -0.53^*$ ) and summer ( $r = -0.50^*$ ) 1987, and winter 1988 ( $r = -0.75^{**}$ ). In contrast, concentration of total S in summer 1988 was positively correlated with depth ( $r = 0.68^{**}$ ). No clear pattern was observed in fall 1987. Organic S, particularly C-bonded S, made up most of the S in all sampling periods under study except for summer 1987 ( $r = 0.81^{***}$ ,  $0.93^{***}$ ,  $0.99^{***}$ , and  $0.54^*$ , respectively). The absence of a significant correlation between C-bonded S and total S during the summer 1987 resulted from the incorporation of S (mainly sulfate) into ester-sulfate S rather than C-bonded S as occurred during other seasons. Our data, however, were similar to other studies that have concluded that organic S is responsible for much of the variation in total S found in mangrove sediments (Casagrande *et al.*, 1977; Altschuler *et al.*, 1983), brackish sedge and clay (Lowe and Bustin, 1985), peat (Wieder *et al.*, 1987), and tidal marsh sediments (Haering *et al.*,

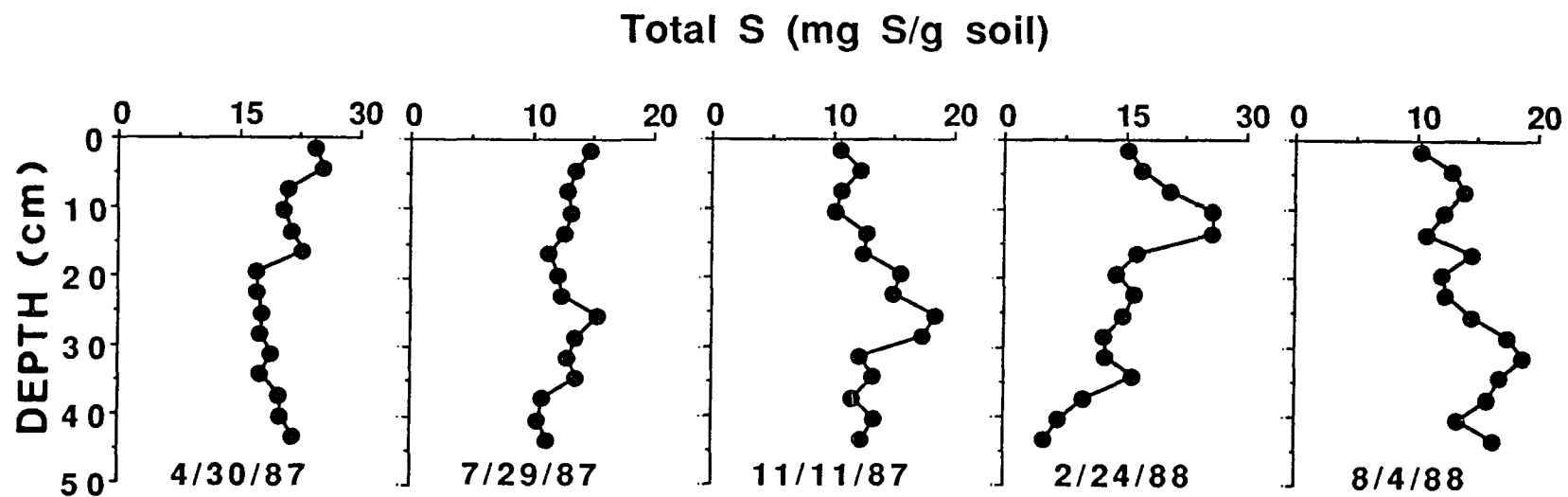


Figure 3.7. Profile distribution of total S in brackish marsh soils collected from Barataria Basin, LA during April 1987 through August 1988. Data points are plotted at the midpoint of each section (3-cm interval).

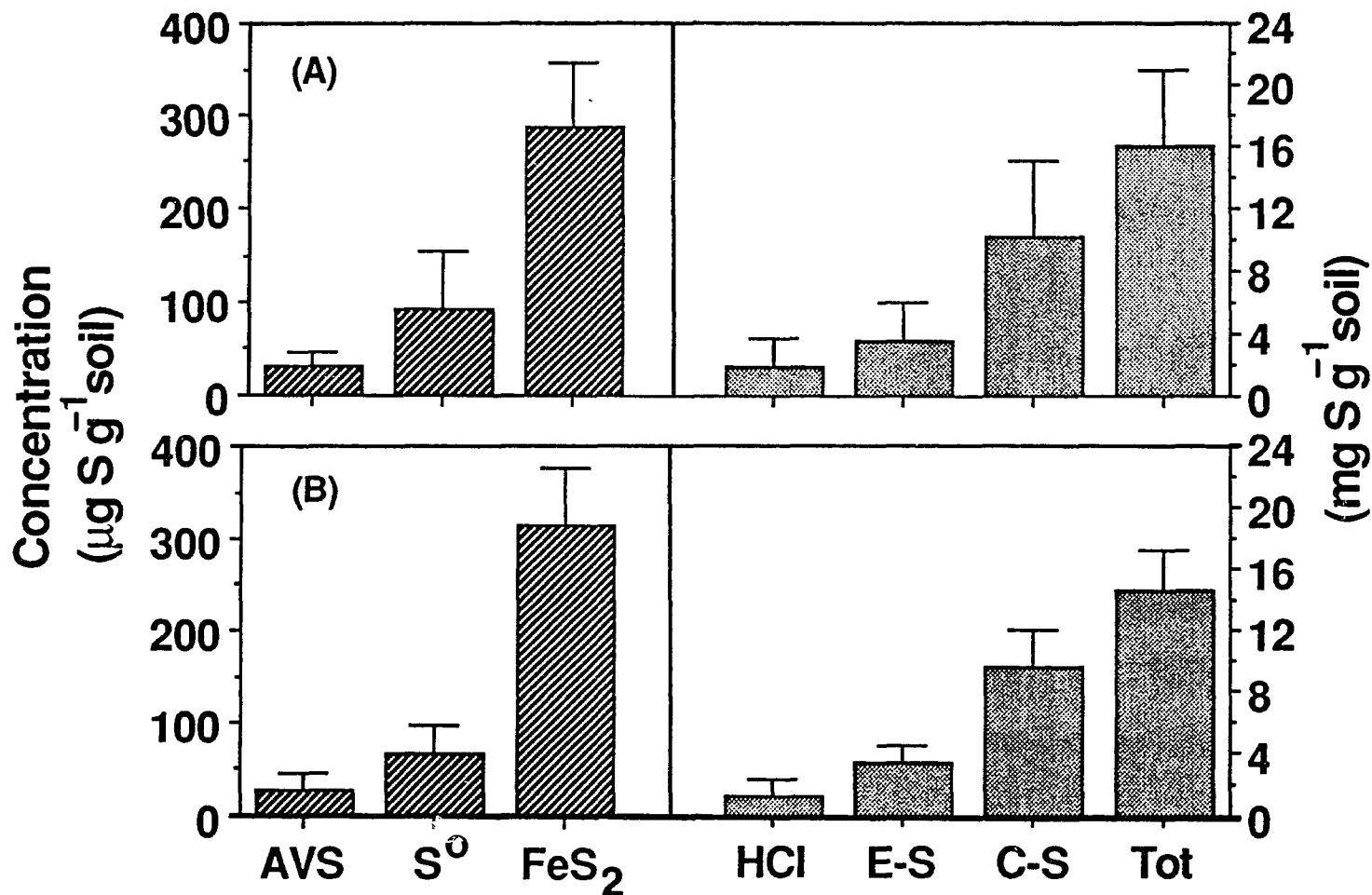


Figure 3.8. Mean concentrations of S fractions present as acid-volatile sulfides (AVS), HCl-soluble S (HCl), elemental S ( $\text{S}^0$ ), pyrite S ( $\text{FeS}_2$ ), ester-sulfate S (E-S), C-bonded S (C-S), and total S (Tot) in the oxidized (A) and reduced (B) zones of soils collected from a brackish marsh in Barataria Basin, LA during April 1987 through August 1988.

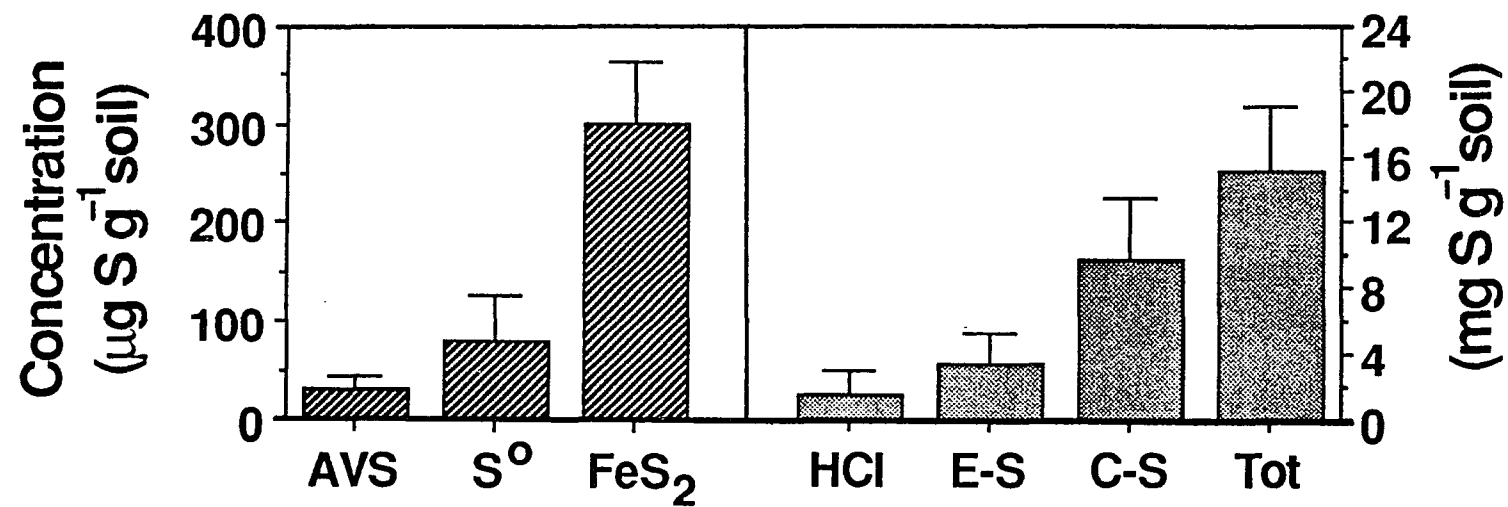


Figure 3.9. Mean concentrations of S fractions averaged over season and depth (0-50 cm, N = 15) present as acid-volatile sulfides (AVS), HCl-soluble S (HCl), elemental S (S<sup>0</sup>), pyrite S (FeS<sub>2</sub>), ester-sulfate S (E-S), C-bonded S (C-S), and total S (Tot).

Table 3.1. Concentrations of various S fractions average over depth (0-50 cm) and bulk density (mean  $\pm$  SD, N = 15), and pH range of soils taken from a brackish marsh in Barataria Basin, LA during April 1987 through August 1988. Data in parentheses are mean values of S fractions as percent of total S.

Sampling Period	Sulfur Fraction						Soil pH	Bulk Density g cm <sup>-3</sup>	
	AVS	Elemental S	Pyrite S	HCl-soluble S	Ester-sulfate S	C-bonded S			Total S
	----- μg S g <sup>-1</sup> soil	----- μg S g <sup>-1</sup> soil	----- μg S g <sup>-1</sup> soil	----- mg S g <sup>-1</sup> soil	----- mg S g <sup>-1</sup> soil	----- mg S g <sup>-1</sup> soil			----- mg S g <sup>-1</sup> soil
Spring (4/30/87)	23.3a ± 6.1 (0.12 )	21.6c ± 8.3 (1.47 )	304a ± 32 (0.11)	4.04a ± 1.37 (18.5)	1.90a ± 0.74 (10.3 )	14.3a ± 1.81 (69.5 )	20.5a ± 3.0	6.9-7.1	0.10a ± 0.02
Summer (7/29/87)	35.3a ± 18.7 (0.24 )	60.7bc ± 21.1 (2.38)	296a ± 72 (0.48)	0.75b ± 0.29 (5.60)	5.88a ± 2.29 (43.5 )	5.73a ± 2.67 (47.8)	12.7b ± 1.3	7.4-7.8	0.16a ± 0.07
Fall (11/11/87)	48.5a ± 17.6 (0.38)	96.8ab ± 35.6 (2.62)	338a ± 172 (0.73)	0.82b ± 0.34 (6.47)	2.36a ± 0.87 (18.6 )	9.28a ± 2.77 (71.1)	13.2b ± 2.3	6.6-7.5	0.20a ± 0.09
Winter (2/24/88)	19.8a ± 9.7 (0.13 )	73.0bc ± 24.1 (2.12)	327a ± 112 (0.88)	1.10b ± 0.42 (7.63)	3.60a ± 0.62 (29.3)	10.8a ± 5.7 (60.0 )	15.2b ± 5.6	6.9-7.2	0.20a ± 0.07
Summer (8/4/88)	23.6a ± 14.6 (0.17)	145a ± 45 (1.79)	244a ± 75 (1.02)	1.02b ± 0.37 (8.72)	3.67a ± 2.37 (27.2 )	8.73a ± 2.84 (62.5)	14.2b ± 2.4	6.4-7.2	0.16a ± 0.06

Any two mean values having a common letter are not significant difference at the 5 % level of significance based on a Duncan's Multiple Range Test (DMRT)

1989). These studies reported that organic S accounts for 50 to 70 % of total S. These results, however, were in contrast to other studies in coastal marsh sediments (Kaplan *et al.*, 1963; Howarth and Teal, 1979; Cutter and Velinsky, 1988) where pyrite was much more abundant than organic S. Howarth (1984) and Haering *et al.* (1989) believed that a low iron availability can limit the amount of pyrite formed in some environments, where organic S was the dominant form (see previous discussion).

It is obvious in the present study that ester-sulfate S and C-bonded S were predominant S forms, consisting 80 to 91 % of total S. This suggested that organic S would be more likely to be incorporated into marsh sediments in the long term than inorganic S, which made up to 20 % of total S pool. The HCl-soluble S was the largest inorganic S constituent, composing 71 to 92 % of the inorganic S. Pyrite S and elemental S together represented 8 to 33 % of inorganic S. These inorganic S species including the AVS fraction, seemed not to accumulate, but were very dynamic S constituents. Transformations and dynamic changes S pools were relatively high during the spring and summer growing season than in the fall and winter, where the marsh plants were metabolically inactive. In this manner, the variation in major S constituents in the top 20 cm resulted in a higher content of total S in the upper zone than that at depth (>20 cm) ( $P < 0.006$ ). A better understanding these processes in relation to the relative abundances of each S pool would certainly improve our understanding of S cycling in brackish marsh sediments.

### Conclusion

The major constituent of the total S pool in this study was organic S present in the forms of ester-sulfate S and C-bonded S. These two fractions accounted for 80 to 91 % of total S with C-bonded S the most dominant portion (52-87 %). The HCl-soluble S was the most abundant inorganic S form, making up 63 to 92 %. Pyrite S and elemental S together constituted 8 to 33 % of inorganic S, which was <4 % of total S. Acid-volatile sulfides were the least significant component of the S pool, representing <1 %. The

major transformations of S forms appeared to occur during the spring and summer rather than in the fall and winter. Plant activity and rainfall, which can influence redox processes in marsh sediments, seem to affect the S translocations and transformations between aerobic and anaerobic zones in the present study as well. Our results suggest that S cycling in the brackish marsh, where there is a transition of influence from fresh to salt waters, may be more complicated and more variable than the true freshwater and salt marsh systems. To understand more about S dynamics in this environments, it is necessary to gain more information on the temporal and spatial variability of various S forms related to plant activity and sources of S from the surroundings.

#### **Acknowledgements**

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**CHAPTER FOUR**  
**SEASONAL DISTRIBUTION OF SULFUR FRACTIONS**  
**IN LOUISIANA SALT MARSH SOILS**

### ABSTRACT

The profile distribution of specific S forms related to the sulfur cycle were examined at a site in a Louisiana salt marsh. Soil samples were fractionated into acid-volatile sulfides (AVS), HCl-soluble sulfur, elemental sulfur, pyrite sulfur, ester-sulfate sulfur, carbon-bonded sulfur, and total sulfur. Inorganic sulfur constituted 16 to 36 % of total sulfur, with pyrite sulfur representing <2 %. Pyrite sulfur content in marsh soil was relatively high in winter. Pyrite sulfur and elemental sulfur together accounted for 4 to 24 % of inorganic sulfur fraction. Between 74 and 95 % of inorganic sulfur was present as the HCl-soluble sulfur form. A negative significant correlation between acid-volatile sulfides and elemental sulfur observed in summer suggested the transformation of sulfides to elemental sulfur. Organic sulfur, in the forms of ester-sulfate sulfur and carbon-bonded sulfur, predominated in all sampling periods, comprising 64 to 84 % of total sulfur. The conversion of ester-sulfate sulfur into carbon-bonded sulfur was more likely to occur in winter than in other seasons. Carbon-bonded sulfur accounted for 53 to 89 % of the organic sulfur. Organic sulfur was the major contributor to the variation of total sulfur in all seasons studied. Total sulfur concentration showed a statistically significant increase with depth in every season and no significant difference was found during the plant growing seasons of spring, summer, and fall.

## Introduction

Biogeochemical transformations of sulfur (S) in salt marsh ecosystems are of interest from a variety of perspectives. Sulfur is an important redox element, existing in a wide range of oxidation states from -2 to +6. Sulfur can thus enter into a variety of biogeochemical processes (Luther et al. 1986a). Sulfur is involved in sulfate reduction, pyrite formation, metal cycling, energy transport, and atmosphere S emissions (see Luther et al. 1986b). Each of these processes depends upon the formation of one or more intermediate oxidation states of S, which may be in inorganic or organic forms (Luther and Church 1988).

Studies of inorganic and organic S forms in salt marsh systems have been very limited, although considerable attention has been paid to the chemical constituents of S in marine and coastal marine environments (see Nriagu and Soon 1985). The only report of seasonal distribution and forms of S in salt marsh was by Cutter and Velinsky (1988), who examined the S cycling in soils collected from a Delaware salt marsh. Although they did not examine the pools of organic S, they provided information on the depth profile of inorganic S forms according to seasonal changes. Some other previous works dealing with S constituents in such substrates (Kaplan et al. 1963; Berner 1964, 1970; Nedwell and Abram 1978; Howarth 1984; King 1988; Haering et al. 1989) generally did not detail the organic S compounds. Due to the lack of this information, the understanding of S fluxes and transformations has been restricted (Landers et al. 1983).

To obtain needed information on the seasonal distribution of S forms, we examined their profile distributions in soils taken from a Louisiana salt marsh. Owing to temporal changes and possible introduction of oxygen via photosynthesis by marsh grasses on distribution of S forms, both inorganic and organic S fractions were quantified over a one year period.

## Materials and Methods

### STUDY AREA

Samples examined in this study were obtained from a salt marsh located in Barataria Basin, Louisiana (29° 15' N, 90° 9' W) (Fig. 5.1). Barataria Basin is a 400 000-ha intertributary Louisiana Gulf Coast estuarine basin with well-defined vegetative units that is bounded on the east by the Mississippi River and on the west by the river's most recently abandoned channel, Bayou Lafourche. Salt marsh (salinity >10 ‰) covers approximately 14 % of the Basin. *Spartina alterniflora* Loisel. is the dominant vegetation and covers about 63 % of the entire salt marsh system. Three other grasses—*Juncus roemerianus* Scheele., *Distichlis spicata* (L.) Greene., and *Spartina patens* (Ait.) Muhl.—claim about 15, 10, and 8 % of the total cover, respectively (Chabreck 1972). A large part of the C surplus of 150 to 250 g C m<sup>-2</sup> yr<sup>-1</sup> contributed by this tidal salt marsh is thought to be exported into the Gulf of Mexico (Feijtel et al. 1985). DeLaune et al. (1983) reported that total sulfide contents as high as 250 µg S g<sup>-1</sup> soil may limit growth of *S. alterniflora* in this area by preventing nitrogen uptake and root development. Tidal exchanges supply salt marshes with a high mineral input, including nutrients and dissolved salts, and results in a high sedimentation rate of 10.5 mm yr<sup>-1</sup> (Feijtel et al. 1988).

### SAMPLING AND Analysis

Five soil cores were collected at 15 m from the streamside within a radius of 3 m during April 1987 through June 1988. This allowed us to minimize the effects of spatial heterogeneity and to determine seasonal variation (Feijtel et al. 1988). Soil samples were obtained by twisting an aluminum core (15-cm i.d. and 50-cm height) into the marsh substrate. Little compaction resulted from this sampling method. The cores were extruded and sectioned into 3-cm intervals immediately upon return to the laboratory. Approximately 75 % of each section was rapidly sealed in a plastic bag and then frozen, and was

subsequently used for S fractionations. The remaining 25 % was utilized for the determinations of pH, bulk density (Table 4.1), and water content. Prior to chemical analysis, the samples were thawed and thoroughly mixed, and any live roots and debris were removed.

The procedure used for the sequential extraction of S fractions shown in Fig. 2.1 is a modification of Nriagu and Soon (1985). The extractions were performed using a modified Johnson-Nishita (J-N) digestion-distillation apparatus (Johnson and Nishita 1952) (Fig. 2.2). Extractant was introduced to the boiling flask by syringe injection through a serum cap at the upper end of the condenser. This was a more convenient way to add an acid and reduced the risk of H<sub>2</sub>S loss during acid addition (Freney et al. 1970). Sulfur species containing in each extracted S fraction are shown in Table 2.1. Fresh sample containing about 5 to 10 g of oven-dried material (60 °C) was used. Acid-volatile sulfides (AVS), HCl-soluble S, elemental S (S<sup>0</sup>), pyrite S (FeS<sub>2</sub>), and ester-sulfate S were extracted by the method described by Nriagu and Soon (1985). For ester-sulfate S, the extractant (HI reducing mixture) was prepared by a method outlined by Landers et al. (1983). The concentration of each S fraction was determined with inductively coupled argon plasma spectrometry (ICP) instead of gravimetric method used by Nriagu and Soon (1985). Carbon-bonded S was estimated by subtracting all of the other S fractions (sum) from total S. Pore water was extracted by centrifuging a 50 to 100 g fresh aliquot for 20 min at 8 000 x g (7 000 rpm, Sorvall GSA-400 rotor, DuPont Co., Wilmington, DE). The supernatant was filtered through a 0.45-μm membrane filter. Sulfur in the filtrate was measured with ICP. The residual aliquot was oven dried at 60 °C to constant mass, ground, sieved (150-mesh size), and thoroughly mixed prior to digestion with HNO<sub>3</sub>-HClO<sub>4</sub> (Beaton et al. 1968). The digested sample was filtered through a 0.45-μm membrane filter. Sulfur in the filtrate was determined with ICP. The sum of pore water S and soil S fractions represented total S. All values are reported on an oven-dried soil weight basis. Pearson's correlation coefficients and Duncan's



Multiple Range Test (DMRT) were calculated with Statistical Analysis System (SAS Institute Inc. 1985). An asterisk (\*), double asterisk (\*\*), and triple asterisk (\*\*\*) are used to represent significant correlations at  $P < 0.05$ ,  $< 0.01$ , and  $< 0.001$ , respectively.

## Results and Discussion

### ACID-VOLATILE SULFIDES (AVS)

Depth profiles of the AVS fraction in Louisiana salt marsh soils are shown in Fig. 4.1. The concentrations of AVS ranged from  $5.9 \mu\text{g S g}^{-1}$  soil in April 1987 to  $45.5 \mu\text{g S g}^{-1}$  soil in February 1988, accounting for  $< 1\%$  of total S (Table 4.1). Although, on the average, the AVS concentration in the present study was relatively low, its range was consistent with previous work observed in this salt marsh (DeLaune et al. 1983) and elsewhere (Nedwell and Abram 1978). Howarth and Teal (1979) found that the concentrations of sulfides and iron monosulfides in salt marsh sediments tend to remain relatively low, generally  $< 16 \mu\text{g S g}^{-1}$  soil. For the five sampling periods, AVS peaks found in the surface section ( $< 20$  cm) corresponded to deeper pyrite S maxima observed below 20-cm depth (Fig. 4.4). This phenomenon, which also occurred in a Delaware salt marsh (Cutter and Velinsky 1988), could be explained by the fact that pore waters should become saturated with respect to iron monosulfides such as mackinawite or gregite at a lower concentration of dissolved hydrogen sulfide (at shallower depths) than that of pyrite (Howarth 1979; Cutter and Velinsky 1988).

The highest concentration of AVS was observed in winter 1988, whereas the lowest AVS concentrations was present in spring and summer 1987. King (1988) suggested that at the onset of the plant growing period (early spring) or when the plant is inactive (winter) AVS concentration are expected to be higher than those during late spring and summer as a result of less AVS oxidation by plant roots. Furthermore, some researchers also noted that the dynamics of AVS is controlled to some extent by the temperature and the injection of oxygen via photosynthesis by marsh plants during the spring and summer

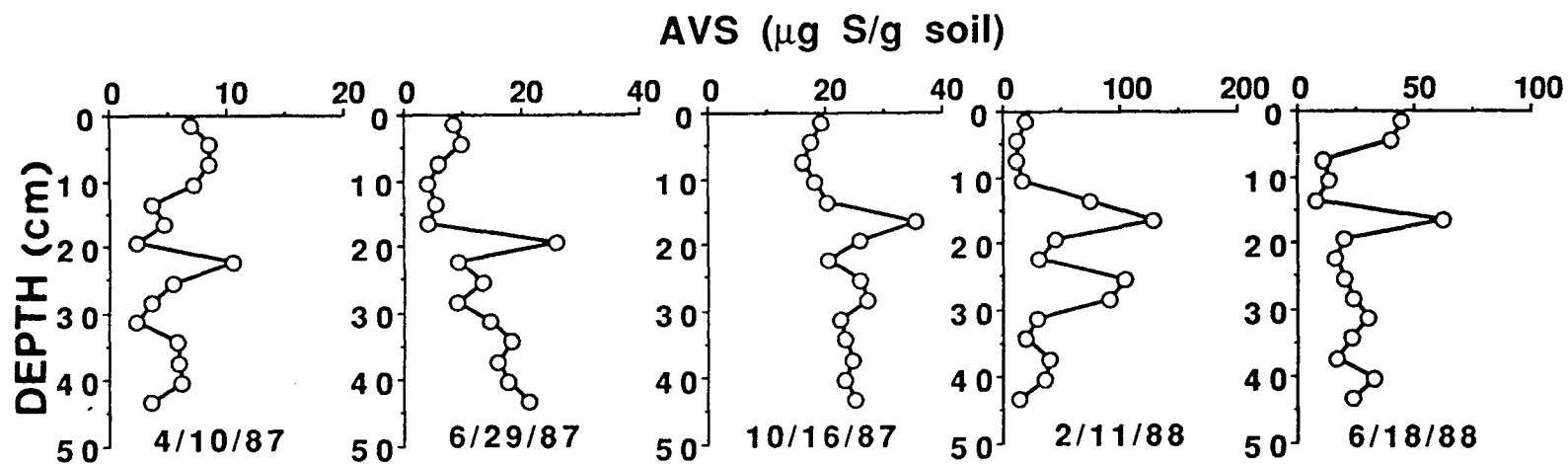


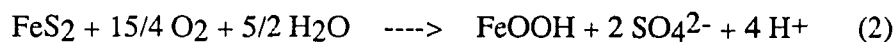
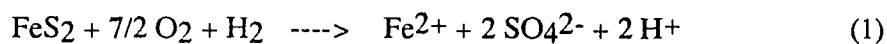
Figure 4.1. Profile distribution of acid-volatile sulfides (AVS) in salt marsh soils collected from Barataria Basin, LA during April 1987 through June 1988. Data points are plotted at the midpoint of each section (3-cm interval).

(Giblin and Howarth 1984; Cutter and Velinsky 1988; Luther and Church 1988). In the surface section (<20 cm), AVS concentration showed a significant decrease with depth in April ( $r = -0.83^*$ ) and June ( $r = -0.85^*$ ) of 1987, and June 1988 ( $r = -0.91^{**}$ ). In summer 1987, concentration of AVS in the upper 20-cm depth was lower than that below 20-cm depth ( $P < 0.003$ ). During the growing seasons, the marsh soil in the 0- to 15-cm zone becomes oxidized, converting free sulfide and sulfide minerals to thiols and sulfate (Luther et al. 1986b; Luther and Church 1988). King (1988) reported that a low sulfide content near the soil surface of a South Carolina salt marsh results from the oxidation of sulfide or direct uptake by plant roots. As evidenced by low pH (4.5-6.6) and low soil water content (63-73 %) (this study), high Eh values ( $> +300$  mV) and high levels of dissolved sulfate (Feijtel et al. 1988), the upper zone (<20 cm) of this marsh site was apparently under strong oxidizing conditions during the plant growing season. Similar period of oxidation have been reported for salt marshes of Barataria Basin, Louisiana (Feijtel et al. 1988), and in the Great marsh of Delaware (Luther and Church 1988).

Below the presence of AVS peaks (>20 cm), these marsh soils are usually under anaerobic conditions coupled with sulfate reduction (Feijtel et al. 1988). Significant increases in AVS concentrations with depth was found in June 1987 ( $r = 0.92^{**}$ ) and June 1988 ( $r = 0.81^*$ ). Data observed in February 1988 showed that the distribution of AVS tends to decrease with depth (>20 cm). Upward diffusion of sulfides from the reduced zone (Nedwell and Abram 1978) and/or a dramatic decrease in the rate of sulfate reduction during the winter (Luther and Church 1988) may result declining in AVS concentrations with depth. Losses of sulfides at depth can result from oxidation by plant roots coupled with either iron and manganese oxides (King 1988) or if there is no readily decomposable energy source for microbial activity (sulfate reducers).

### HCl-SOLUBLE S

HCl-soluble S was the most important pool of inorganic S in this salt marsh, accounting for 74 to 95 % of inorganic S or no more than 34 % of total S (Table 4.1) and comparable to ester-sulfate S (Fig. 4.9). However, this S fraction was relatively low in summer 1987 and winter 1988, representing only 11.6 and 14.9 % of total S, respectively. The highest AVS concentration occurred in spring 1987. Profile distribution of HCl-soluble S is shown in Fig. 4.2. On an annual basis, there was a significant relationship between HCl-soluble S and depth found below 20-cm depth ( $r = 0.82^*$ ). The increase in HCl-soluble S with depth was primarily due to the significant increase in pore water S with depth ( $r = 0.93^{**}$ ). The high concentrations of pore water S (data not shown) consisted of high concentrations of pore water sulfate, which resulted from seawater flushing at this marsh site influenced by strong southern winds. Due to the importance of pore water sulfate to pore water S, highly significant correlation between HCl-soluble S and pore water S was found during the winter, spring, and summer seasons ( $r = 0.90^{**}$ ,  $0.88^{**}$ ,  $0.94^{**}$ , respectively). Nriagu and Soon (1985) suggested that pore water sulfate is a major contributor to HCl-soluble S fraction in marine sediments. In addition, the highest value of HCl-soluble S (April 1987) may have been complemented by an increase in pore water sulfate due to the oxidation of pyrite. Feijtel et al. (1988) reported a sharp increase of interstitial sulfate in this salt marsh during the early spring as a result of the oxidation of pyrite to sulfate through oxygen advection driven by falling water levels over the marsh surface and by oxygen addition through plant roots. The oxidation of pyrite to sulfate could occur according to either equation (1) or (2) (Giblin and Howarth 1984):



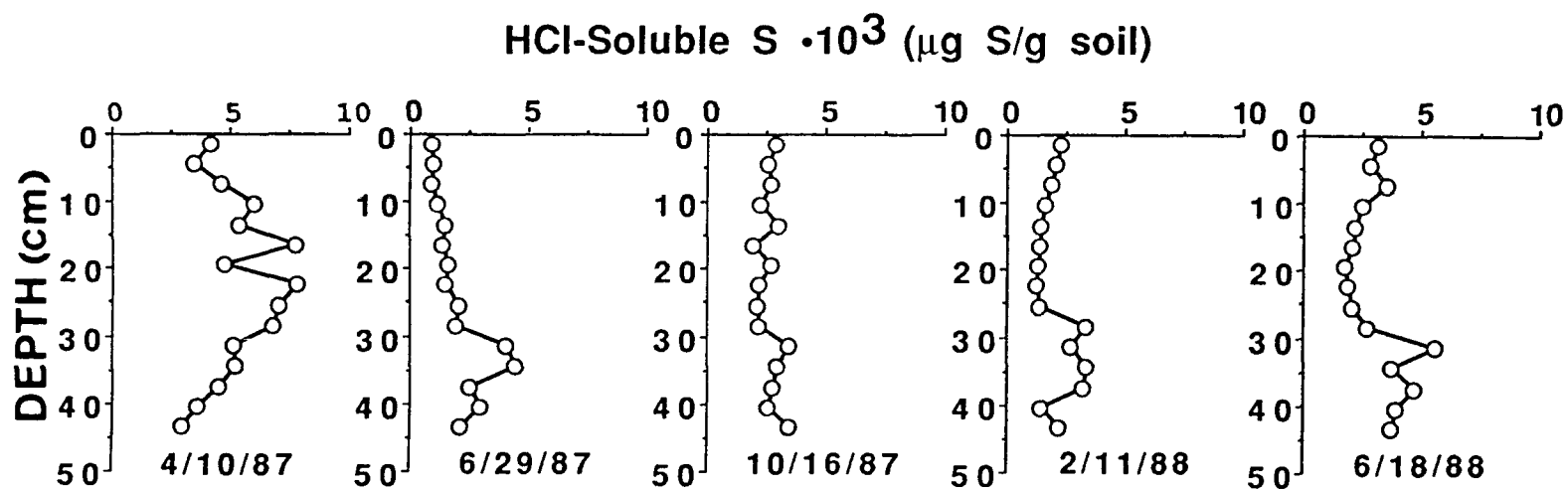


Figure 4.2. Profile distribution of HCl-soluble S in salt marsh soils collected from Barataria Basin, LA during April 1987 through June 1988. Data points are plotted at the midpoint of each section (3-cm interval).

### ELEMENTAL S (S<sup>0</sup>)

The concentrations of elemental S in this Louisiana salt marsh accounted for up to 3 % of total S (Table 4.1). In marsh soil samples, the mean elemental S concentration was 10-fold higher than that of AVS (Fig. 4.9). A significant negative correlation between elemental S and AVS ( $r = -0.86^*$ ) found in June 1987 and may have resulted from the predominance of oxidation processes in the plant root zone. The oxidation of dissolved H<sub>2</sub>S and FeS (AVS fraction) under natural condition can lead to the formation of elemental S (Goldhaber and Kaplan 1974; Cutter and Velinsky 1988). A similar observation was reported from the Great marsh of Delaware, where the marsh is apparently more oxidized during spring and summer because of increasing plant activity (Luther and Chruch 1988). The reason for fluctuations in elemental S abundance which appeared in the early fall, without showing a significant relationship with AVS fraction, was unclear. King (1988) noted that plant uptake coupled with evapotranspiration can induce variations in the oxidizing capacity in the soil profiles of salt marshes.

The five profiles of elemental S shown in Fig. 4.3 indicate that this S form reaches maximum concentrations within the upper 20-cm depth, which is the oxidized zone of these salt marsh soils (Feijtel et al. 1988). On an annual average, the concentration of elemental S showed a significant increase with depth in the upper 20-cm depth ( $r = 0.77^*$ ), whereas a significant decrease with depth was found below 20-cm depth ( $r = -0.76^*$ ). Also, the mean value average over season of elemental S found in the oxidized surface zone (<20 cm) was higher than that in the reduced deeper profile (>20 cm) ( $P < 0.02$ ) (Fig. 4.8). Qualitatively, this finding is similar to those observed by Cutter and Velinsky (1988) in Delaware salt marsh, although the concentrations of elemental S they reported are approximately 10-fold higher. However, the elemental S concentrations found in Louisiana salt marsh are comparable to those reported by Troelsen and Jorgensen (1982) in shallow coastal sediments. They also found that elemental S con-

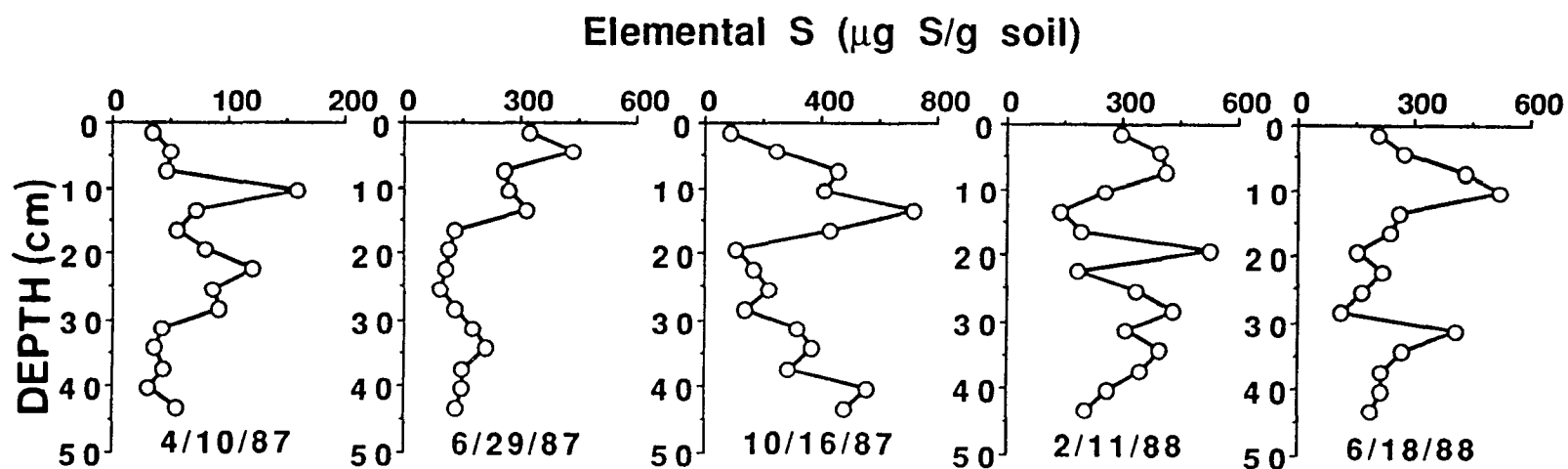


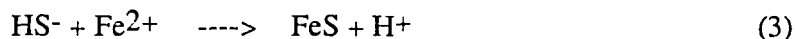
Figure 4.3. Profile distribution of elemental S ( $S^0$ ) in salt marsh soils collected from Barataria Basin, LA during April 1987 through June 1988. Data points are plotted at the midpoint of each section (3-cm interval).

centrations approach maxima in the oxidized surface layer (<5 cm) and decrease in the deeper layer.

The ambiguity in increasing elemental S concentrations in the month of October 1987 from  $107 \mu\text{g S g}^{-1}$  at 20-cm depth to  $560 \mu\text{g S g}^{-1}$  at 40-cm depth differed distinctly from the temporal changes observed at other times. Troelsen and Jorgensen (1982) suggested that the observed fluctuations in the fall season may be primarily to the seasonal transition from a more oxidized condition (summer) to a more reduced condition (winter), leading to the accumulation of elemental S during the fall, which is not a high AVS production period.

#### PYRITE S ( $\text{FeS}_2$ )

Pyrite S existed as a minor component of the S fractions in most of the soils studied, accounting for <2 % of total S (Table 4.1) and comparable to elemental S (Fig. 4.9). Howarth (1984) and Haering et al. (1989) suggested that pyrite accumulation is related to the availability of an iron source. In more reduced sediments (>15 cm), where pyrite forms slowly by the conversion of iron monosulfide ( $\text{FeS}$ ) to pyrite, the availability of Fe (II) limits the rate of pyritization (Lord and Church 1983). As proposed by Altschuler et al. (1983), Fe (II) initially forms mackinawite ( $\text{FeS}_{0.9}$ ) and is secondarily converted to pyrite by interaction with elemental S as shown in equation (3) and (4):



This is supported by a study of DeLaune et al. (1983), who reported low dissolved iron concentrations on the order of  $0.003 \text{ mg L}^{-1}$  in Louisiana salt marsh soils. Only 23 % of the total iron flux in this area studied by Feijtel et al. (1988) occurs in the form of pyrite. Comparable amounts of pyrite S, accounting for <2 % of total S, are observed in Connecticut coastal sediments (Berner 1970). This finding provides evidence that the temporal variability in total S content in this salt marsh is not primarily due to the



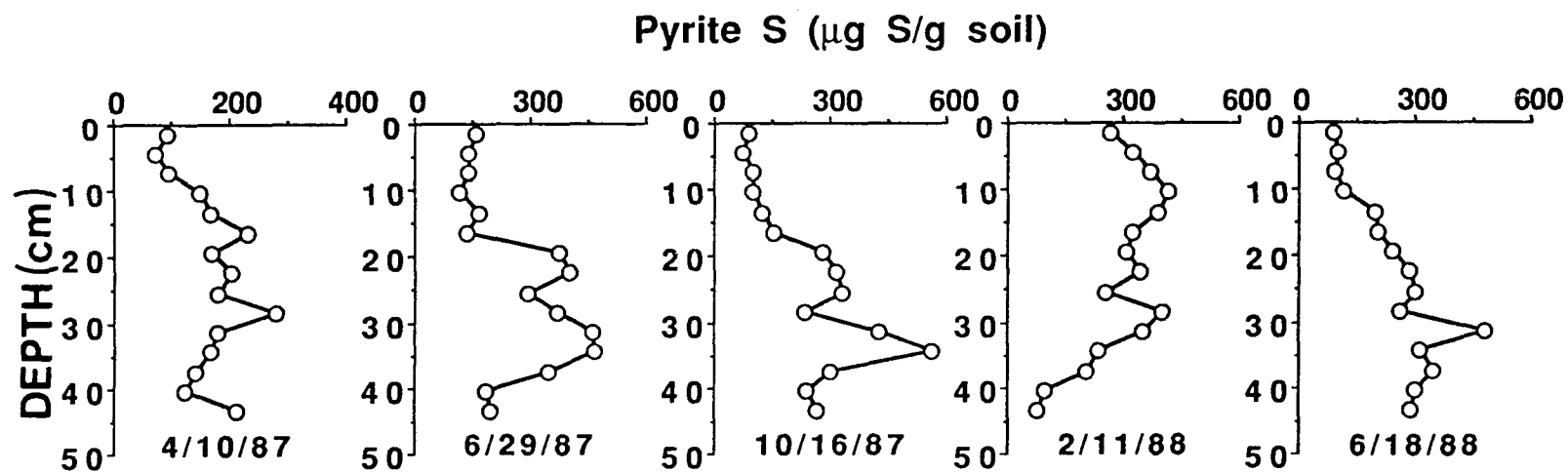


Figure 4.4. Profile distribution of pyrite S ( $\text{FeS}_2$ ) in salt marsh soils collected from Barataria Basin, LA during April 1987 through June 1988. Data points are plotted at the midpoint of each section (3-cm interval).

fluctuations in pyrite S content. Hearing et al. (1989) also concluded that pyrite S is not responsible for the variation in total S in Chesapeake Bay tidal marsh soils. With the exception of the February 1988 core, significant correlation between pyrite S and total S was found in April, June, and October of 1987, and June 1988 ( $r = 0.79^*$ ,  $0.98^{***}$ ,  $0.93^{**}$ , and  $0.86^*$ , respectively). This observation probably resulted from the significant increase in pyrite S concentrations with depth corresponding to coincidental increases of total S in most of the year, rather than the contributions of pyrite S fraction to the total S.

In the upper 20 cm, the pyrite S concentrations ranged from  $72.8 \mu\text{g S g}^{-1}$  in April 1987 to  $388 \mu\text{g S g}^{-1}$  in February 1988. In the deeper profile ( $>20$  cm), where soils became more anaerobic, the pyrite S concentrations ranged from  $75.4 \mu\text{g S g}^{-1}$  in winter 1988 to  $560 \mu\text{g S g}^{-1}$  in fall 1987. On an annual average, the concentration of this S fraction was lower in the surface section ( $<20$  cm) than that at depth ( $>20$  cm) ( $P < 0.003$ ). Also, a significant correlation between pyrite S concentration and depth was found both in the upper 20-cm depth ( $r = 0.97^{***}$ ) and below 20-cm depth ( $r = 0.95^{***}$ ). The least variation in pyrite S concentration was found in April 1987, whereas the greatest variation was found in February 1988. A mean low concentration of  $135 \mu\text{g S g}^{-1}$  observed at  $<20$ -cm depth in April 1987 was in agreement with that of  $135 \mu\text{g S g}^{-1}$  in June 1988. These low concentrations probably reflect the oxidation and dissolution of pyrite during the spring season (see equation 1 and 2). The oxidation of pyrite in the marsh surface in early spring is also reported at this site by Feijtel et al. (1988). In addition, Luther and Church (1988) found that low pyrite concentrations in the Great marsh of Delaware as a result of pyrite oxidation.

Although mean concentrations of pyrite S did not show a significant difference among the five sampling periods, the mean concentration was greatest in winter 1988. This suggests that the formation of pyrite is favored over the oxidation of pyrite in winter than in other seasons, presumably a result of plant inactivity. Luther and Church (1988) found that plant activity can apparently induce more oxidation in the surface section ( $<20$

cm) of the Great marsh of Delaware in spring and summer than in fall and winter. During the growing seasons at the Great Sippewissett marsh, Giblin and Howarth (1984) also reported that the salt marsh grasses can oxidize the sediments and a large percentage of sedimentary pyrite S is converted to an oxidized iron mineral (see equation 2). In addition, they observed a net increase in pyrite S concentration over the fall and winter seasons as the grass is anaerobically decomposed. In the present study, shallow pyrite S maximum of  $415 \mu\text{g S g}^{-1}$  occurred in February 1988 at 10-cm depth but disappeared by June 1988. The loss mechanism is presumably oxidation of pyrite as discussed previously. In this Louisiana salt marsh, a rapid rate of pyrite formation is evidenced by the abundant presence of single crystals or lenses of minute octahedral crystals (Feijtel et al. 1988). Such rapid rates of pyrite formation and oxidation in the shallow depths have also been reported in a New England salt marsh (Howarth 1979; Howarth and Teal 1979), Great Sippewissett marsh (Giblin and Howarth 1984), and the Great marsh of Delaware (Lord and Church 1983; Luther and Church 1988).

Below 20-cm depth pyrite S maxima were detected in all five sampling periods. This observation is in agreement with one observed in this Louisiana salt marsh by Feijtel et al. (1988) and in the Great marsh of Delaware by Cutter and Velinsky (1988), which is indicative of slower pyritization. Lord and Church (1983) found the presence of framboidal pyrite as an evidence of slow pyrite formation in the deeper marsh sediments (>15 cm). In the present study, significant correlations between the pyrite S concentration and depth were found in the late spring ( $r = 0.90^{**}$ ), early summer ( $r = 0.82^*$ ), and fall ( $r = 0.88^{**}$ ) of 1987. The increase of pyrite S concentrations with depth is fairly similar to that observed by Cutter and Velinsky (1988) in the Great marsh of Delaware, but the concentrations of pyrite S from our study are approximately 10-fold less. The relationship of increasing pyrite S concentrations with depth in most of the year supports evidence of slow pyrite formation in the deeper profile from the reaction of iron monosulfide with elemental S (equation 3 and 4) as postulated by Goldhaber and Kaplan

(1974) and Howarth (1979). However, pyrite S concentration in the month of February 1988 tended to decrease with depth (>30 cm) and became less than that in the upper 20-cm depth. During the less productive winter season, even though sulfate reduction is the predominant biogeochemical process, the rate of sulfate reduction is dramatically decreased as a result of winter temperatures (Luther and Church 1988). Therefore, Fe (II) is gradually precipitated during this season to form pyrite (Cutter and Velinsky 1988).

Like marine sediments, the pyritization process in marsh systems appears to be dependent on the other S fractions. In a certain growing season, this process is somewhat dependent on AVS, pore water S, and elemental S and/or organic S (as discussed later). The data present in this study partially support the conclusion on pyrite formation observed in Louisiana salt marsh (Feijtel et al. 1988) and elsewhere (Lord and Church 1983; Cutter and Velinsky 1988). They generally stated that pyrite formation is the result of two processes: (i) fast reaction of Fe (II) with polysulfides in the surface zone, and (ii) slow reaction of iron sulfide with elemental S intermediate in the deeper profile (>15-20 cm).

#### ORGANIC S

In the present study organic S accounted for 64 to 84 % of total S. Between 53 and 89 % of the organic S was C-bonded S which was the dominant S form (Fig. 4.9). King (1988) estimated that organic S makes up to 50 % of total S in stands of *S. alterniflora* in South Carolina salt marsh. Several studies have reported that most of S (84-97 % of total S) in salt marsh and marine sediments is present in the form of inorganic S, mainly as pyrite S (Kaplan et al. 1963; Berner 1964; Howarth and Teal 1979; Cutter and Velinsky 1988). The lack of agreement between our study and other workers may be due to a limited availability of iron to form pyrite in Louisiana salt marshes as reported by Feijtel et al. (1988). They further concluded that a large part of the S pools in Louisiana salt marshes occurs in a nonpyritic forms. Several studies have

also reported that organic S is the major fraction of the S pools. Wieder et al. (1987) claimed that 83 to 85 % of total S in Big Run Bog peat is present as organic S. Organic S also contributes 90 to 93 % of total S in peat from British valley mire (Brown 1985). In marine mangrove peat in the Florida Everglades, which is ecologically related to salt marshes, about 30 to 60 % (Casagrande and Ng 1979; Casagrande et al. 1979) and 76 % (Altschuler et al. 1983) of total S are present as organic S. Haering et al. (1989) have also reported high organic S levels in Chesapeake Bay tidal marsh soils. Casagrande et al. (1979) and Altschuler et al. (1983) concluded that both ester-sulfate S and C-bonded S are more abundant than is pyrite S.

#### ESTER-SULFATE S

Ester-sulfate S observed in this study ranged from 11 to 47 % of organic S and accounted for 10 to 31 % of total S (Table 4.1), and was the second largest constituent of total S (Fig. 4.9). Analyses of a wide range of agricultural soils summarized by Tabatabai (1984) have shown that about 25 to 75 % (average 50 %) of organic S is present in this form. A relatively low proportion of ester-sulfate S (11 to 28 % of organic S) was also reported for Big Run Bog peat (Wieder et al. 1987) and generally accounts for 30 to 70 % of the organic S in soils (Freney 1986). However, a higher amount of this S fraction, comprising 30 to 60 % of total S, was reported in grassland soils (Bettany et al. 1973).

Freney (1986) stated that the environment in which a soil is formed seems to have a large effect on the proportion of the total S present in ester-sulfate S form. This S form tends to decrease with decreasing temperature and increasing soil moisture. This supposition may be applicable to the present study, in which ester-sulfate S concentration was relatively low in winter 1988. Although no direct evidence on the effect of temperature has been reported, its indirect effect is likely. Luther et al. (1986b) found that a dynamic S cycle in which S is transformed from inorganic to organic species during warmer, more

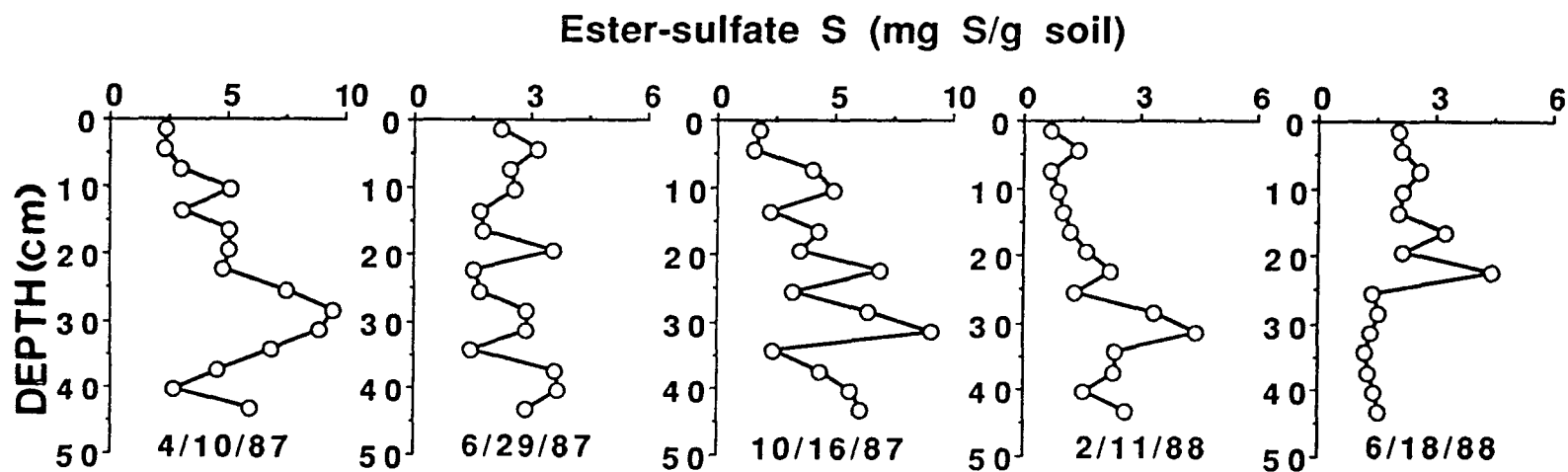


Figure 4.5. Profile distribution of ester-sulfate S in salt marsh soils collected from Barataria Basin, LA during April 1987 through June 1988. Data points are plotted at the midpoints of each section (3-cm interval).

productive seasons, and from organic to inorganic forms during cooler, less productive seasons, does occur in the salt marsh. As a result of increasing temperatures, the microbial activity and decomposition rate of organic matter tends to increase and produce more organic acids and humic materials as end products (Gambrell and Patrick 1978). The ester-sulfate S is considered to be associated mainly with side chain components of fulvic and humic materials (Bettany et al. 1973), which is a major component of organic matter in marine and non-marine sediments (Nissenbaum and Kaplan 1972). Casagrande et al. (1980) reported that 80 % of the S associated with the fulvic acid fraction and 35 % of that with the humic acid fraction in peat are in the form of ester-sulfate S.

As shown in Fig. 4.8, higher concentration of ester-sulfate S found in the deeper profile (>20 cm) than in the upper section (<20 cm) ( $P < 0.005$ ) may partly result from more organic acids and humic materials produced by anaerobic degradation of organic matter than by aerobic degradation in the upper zone (<20 cm) (Gambrell and Patrick 1978). Nissenbaum and Kaplan (1972) postulated that S in marine humic acids is largely introduced (*in situ*) during diagenesis in sediments rather than through the mineralization of parent organic material. They suggested that the introduction of S from external sources (possibly through reaction of  $H_2S$ , polysulfides, or  $S^0$  with organic compounds) may explain the high S content of marine humic acids. Regarding enzyme activity, microorganisms and plants can produce sulfatase (sulfohydrolase) enzymes that hydrolyze ester-sulfate S (Oshrain and Wiebe 1979). Arylsulfatase is one of the most importance of these enzymes because of its abundance in soils (Freney 1986). Oshrain and Wiebe (1979) observed arylsulfatase activity in salt marsh soil in stands of *S. alterniflora* and found that the arylsulfatase activity declines with depth.

#### CARBON-BONDED S

C-bonded S clearly constituted a larger portion than ester-sulfate S in all periods of sampling (Fig. 4.9). The C-bonded S accounted for 53 to 89 % of organic S or equiva-

lent to 34 to 75 % of total S (Table 4.1). These high percentages coupled with the significant correlation between C-bonded S and total S in all cores illustrate the importance of C-bonded S as a major component of total S in the present study. Freney (1986) noted that about 90 % of S compounds existing in plants and microorganisms is S containing amino acids, such as cysteine (-C-S-H), cystine (-C-S-S-C-), and methionine (-C-S-C-). These compounds, found in marsh plants (source materials for the marsh) and microorganisms (degraders of the marsh substrates), can be expected to be the major source of C-bonded S in this study and elsewhere (Casagrande et al. 1979). In temperate forest soils, C-bonded S averages about 63 to 70 % of organic S compounds (Bettany et al. 1973). This S fraction also accounts for 40 to 70 % of total S in grassland soils and consists mainly of the S amino acids, protein S, and sulfonic acids (sulfonates) (Maynard et al. 1984).

Significant increases in concentrations of C-bonded S with depth were observed in the months of June ( $r = 0.83^*$ ) and October ( $r = 0.94^{**}$ ) of 1987, and February ( $r = 0.90^{**}$ ) and June ( $r = 0.78^*$ ) of 1988 (Fig. 4.6). There was no significant increase in C-bonded S concentration with depth in April 1987. On an annual average, higher concentration of C-bonded S in the upper 20 cm than below 20 cm ( $P < 0.005$ ) was in agreement with the increasing organic matter or decreasing soil bulk density with depth ( $r = -0.92^{**}$ ). King (1988) found that a trend of increasing organic S content with depth coincides with the increase in organic matter with depth in a South Carolina salt marsh in stands of tall *S. alterniflora*. A similar observation has also been reported in Chesapeake Bay tidal marsh soils (Haering et al. 1989). Lower concentrations of C-bonded S in the upper 20 cm than in the deeper profile may be partly due to microbial mineralization as a result of C oxidation to provide energy (Maynard et al. 1984). Bettany et al. (1973) stated that the mineralization of organic S is a predominant process, which occurs in most aerated grassland surfaces. Wieder et al. (1987) also observed that C substrate availability is generally low in aerobic forest soils when compared to that in anaerobic peat. In



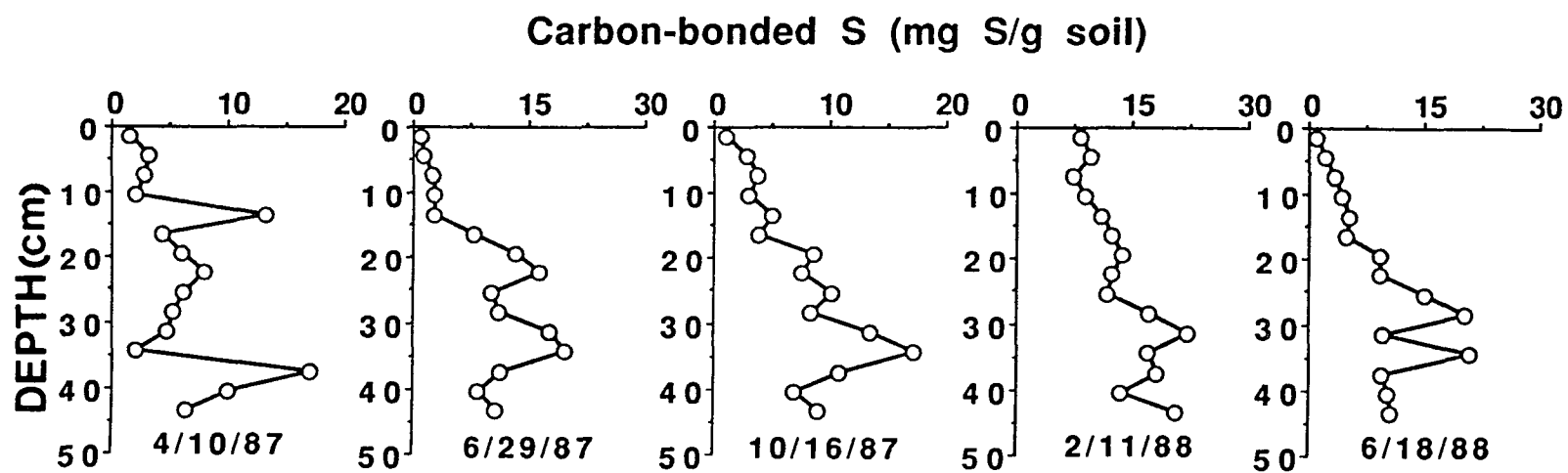


Figure 4.6. Profile distribution of C-bonded S in salt marsh soils collected from Barataria Basin, LA during April 1987 through June 1988. Data points are plotted at the midpoint of each section (3-cm interval).

the present study, a significant negative relationship ( $r = -0.80^*$ ) between C-bonded S and elemental S found in June 1987 implies that the contribution by elemental S to the organic S fraction is likely, but may be a less significant in Louisiana salt marshes. Casagrande and Ng (1979) have demonstrated that some of the organic S can actually originate from elemental S. Luther et al. (1986b) also indicated that a sulfide oxidation process producing elemental S in the salt marsh of Delaware may result in the formation of organic S compounds. Although, on the average, seasonal variability did not exhibit a distinct effect on C-bonded S content, the concentrations of this S fraction were higher in winter than other sampling periods. This finding may result from a decline in the amount and activity of microorganisms, and the absence of growing plants during low temperatures, and thus a low rate of mineralization and plant uptake (Freney 1986).

#### TOTAL S

Total S concentration ranged from  $14.1 \text{ mg S g}^{-1}$  in June 1987 to  $18.1 \text{ mg S g}^{-1}$  in February 1987 (Table 4.1). On an annual average, the concentration of total S was found higher in the deeper profile ( $>20 \text{ cm}$ ) than that in the surface section ( $<20 \text{ cm}$ ) ( $P < 0.001$ ) (Fig. 4.8). In addition, significant relationships between total S and depth were found in all five sampling periods ( $r = 0.81^*$ ,  $0.84^*$ ,  $0.86^*$ ,  $0.84^*$ , and  $0.88^{**}$ , respectively). The temporal changes in total S contents in this study were not primarily due to variability in pyrite S (as discussed previously), rather due to the variability in organic S similar as shown by other studies (Casagrande et al. 1979; Altschuler et al. 1983; Nriagu and Soon 1985; Wieder et al. 1987; Haering et al. 1989). Apparently, the total S showed a significant correlation with C-bonded S in every season ( $r = 0.84^*$ ,  $0.98^{***}$ ,  $0.95^{***}$ ,  $0.89^{**}$ , and  $0.95^{***}$ , respectively). This finding suggests that organic S present as C-bonded S is responsible for much of the variation in total S. Quantitatively, the concentrations of total S were comparable to those found in the Great marsh of Delaware (Cutter and Velinsky 1988) and in a Chesapeake Bay tidal marsh of Maryland (Haering et al.

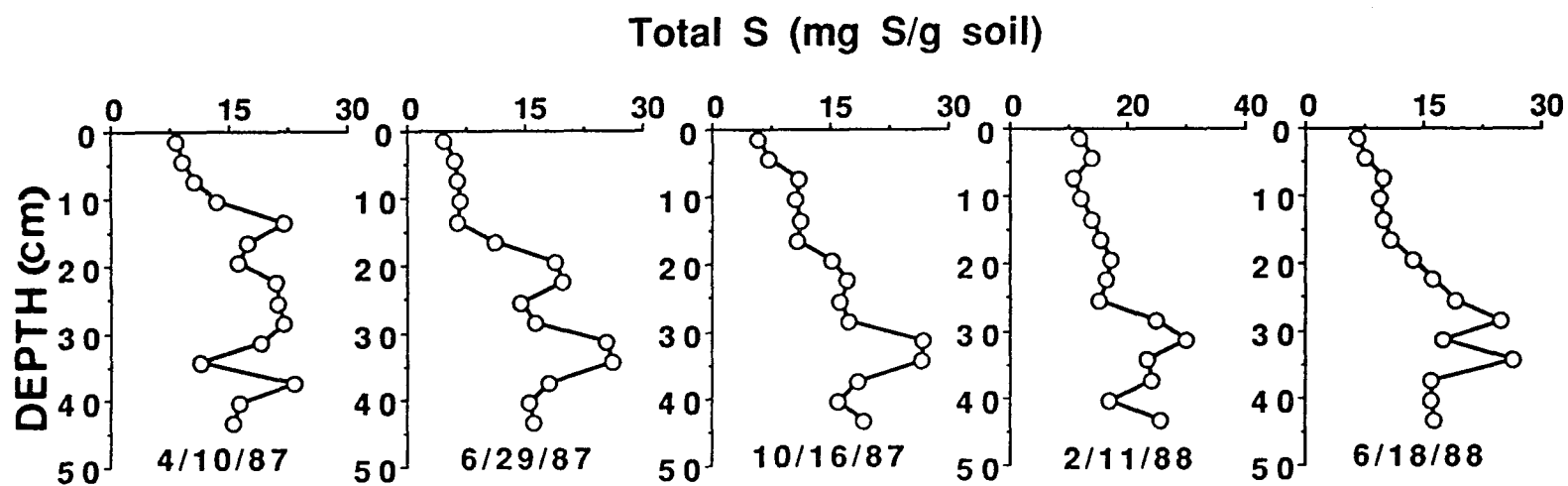


Figure 4.7. Profile distribution of total S in salt marsh soils collected from Barataria Basin, LA during April 1987 through June 1988. Data points are plotted at the midpoint of each section (3-cm interval).

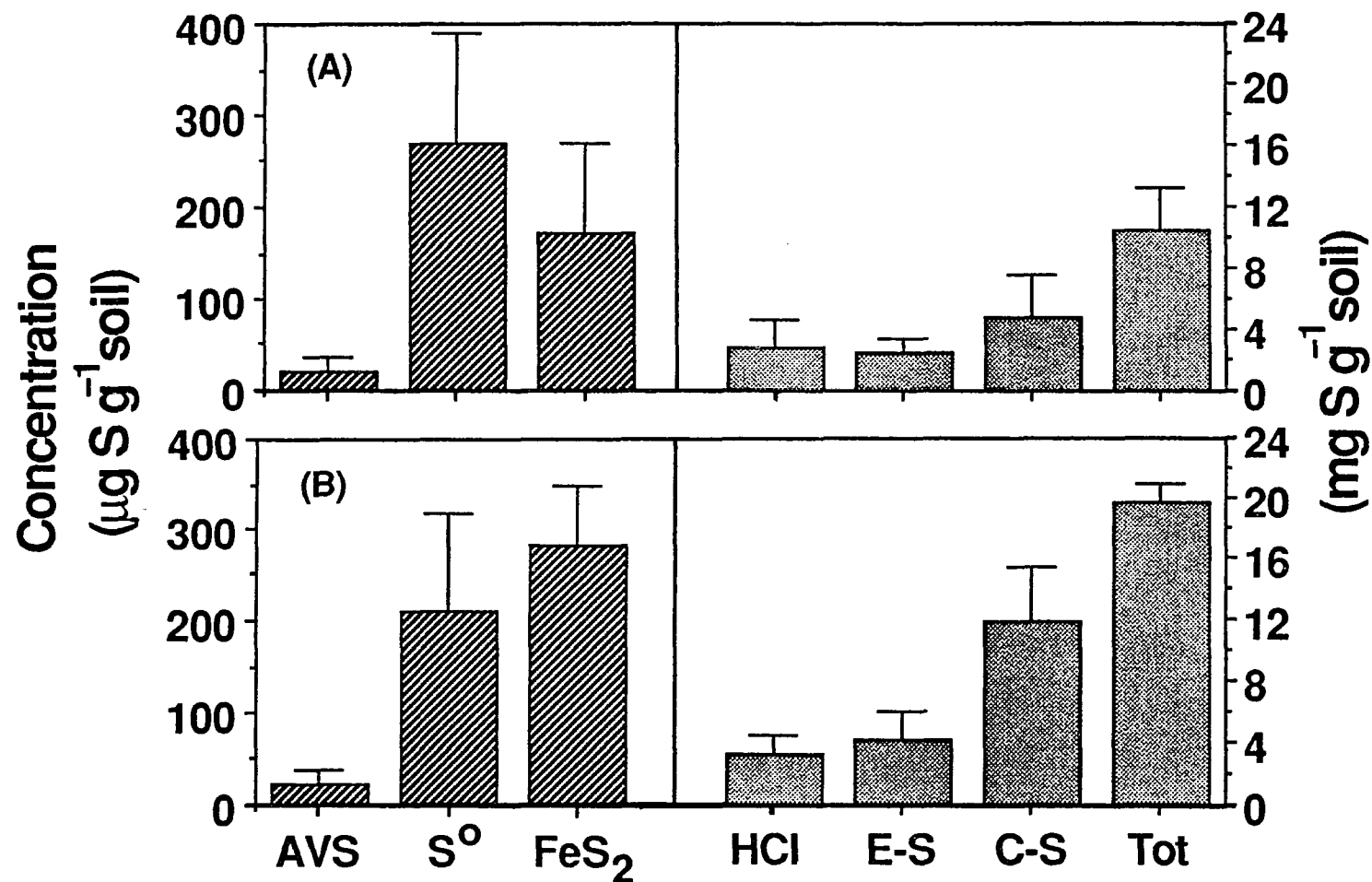


Figure 4.8. Mean concentrations of S fractions averaged over season present as acid-volatile sulfides (AVS), HCl-soluble S (HCl), elemental S ( $\text{S}^0$ ), pyrite S ( $\text{FeS}_2$ ), ester-sulfate S (E-S), C-bonded S (C-S), and total S (Tot) in the oxidized (A) and reduced (B) zones of soils collected from a salt marsh in Barataria Basin, LA during April 1987 through June 1988.

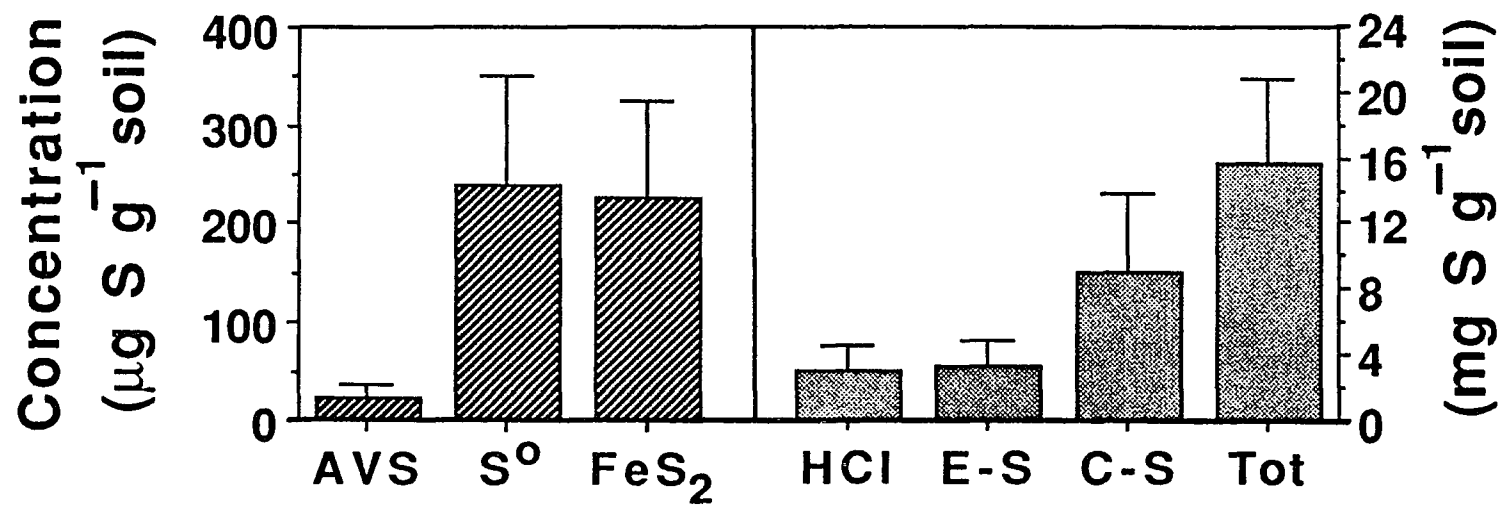


Figure 4.9. Mean concentrations of S fractions averaged over season and depth (0-50 cm, N =15) present as acid-volatile sulfides (AVS), HCl-soluble S (HCl), elemental S (S<sup>0</sup>), pyrite S (FeS<sub>2</sub>), ester-sulfate S (E-S), C-bonded S (C-S), and total S (Tot)

Table 4.1. Concentrations of various S fractions averaged over depth (0-50 cm) and bulk density (mean  $\pm$  SD, N = 15), and pH range of soils taken from a salt marsh in Barataria Basin, LA during April 1987 through June 1988. Data in parentheses are mean values of S fractions as percent of total S.

Sampling Period	Sulfur Fraction						Total S	Soil pH	Bulk Density g cm <sup>-3</sup>
	AVS ----- $\mu\text{g S g}^{-1}$ soil	Elemental S ----- $\mu\text{g S g}^{-1}$ soil	Pyrite S ----- $\mu\text{g S g}^{-1}$ soil	HCl-soluble S ----- $\mu\text{g S g}^{-1}$ soil	Ester-sulfate S ----- $\mu\text{g S g}^{-1}$ soil	C-bonded S ----- $\mu\text{g S g}^{-1}$ soil			
Spring (4/10/87)	5.9c $\pm$ 2.6 (0.04 )	67.0b $\pm$ 35.7 (0.43 )	158a $\pm$ 55 (1.02)	5.51a $\pm$ 1.64 (34.0)	4.84a $\pm$ 2.28 (30.1)	5.75b $\pm$ 3.89 (34.4)	16.4b $\pm$ 4.80	4.5-7.7	0.32a $\pm$ 0.07
Summer (6/29/87)	10.9c $\pm$ 5.6 (0.09)	214ab $\pm$ 99 (2.35)	242a $\pm$ 128 (1.98)	1.84b $\pm$ 1.09 (14.9)	2.50ab $\pm$ 0.78 (23.8)	9.09ab $\pm$ 6.10 (56.9)	14.1c $\pm$ 6.80	6.1-7.0	0.32a $\pm$ 0.07
Fall (10/16/87)	22.2b $\pm$ 4.0 (0.17)	342a $\pm$ 179 (2.49)	216a $\pm$ 138 (1.48)	2.62b $\pm$ 0.45 (20.2)	4.22ab $\pm$ 2.12 (30.8)	7.41b $\pm$ 4.40 (44.8)	15.3bc $\pm$ 5.90	6.1-6.7	0.31a $\pm$ 0.05
Winter (2/11/88)	45.5a $\pm$ 36.8 (0.27)	306a $\pm$ 108 (1.87)	299a $\pm$ 102 (1.83)	1.98b $\pm$ 0.77 (11.6)	1.69b $\pm$ 1.05 (9.54 )	12.9a $\pm$ 4.49 (74.9)	18.1a $\pm$ 5.70	6.5-7.8	0.27a $\pm$ 0.07
Spring (6/18/88)	25.4b $\pm$ 12.6 (0.21)	269a $\pm$ 111 (2.17)	222a $\pm$ 109 (1.65)	3.02b $\pm$ 1.11 (23.9)	2.08b $\pm$ 0.86 (17.0)	8.05ab $\pm$ 5.99 (55.0)	14.6c $\pm$ 5.70	6.3-7.1	0.27a $\pm$ 0.06

Any two mean values having a common letter are not significant difference at the 5 % level of significance based on a Duncan's Multiple Range Test (DMRT)

1989). The highest mean content of total S in the present study was found in winter 1988 ( $18.1 \text{ mg S g}^{-1}$ ), while the lowest concentration was observed in summer 1987. Based on a Duncan's Multiple Range Test, no significant difference in total S concentration was observed during the growing seasons of spring, summer, and fall.

In this study organic S, in the forms of ester-sulfate S and C-bonded S, constituted a majority (64-84 %) of total S. Inorganic S consisted 16 to 36 % of total S, with HCl-soluble S accounting for 74 to 95 % of the inorganic S. Pyrite S and elemental S together made up 4 to 24 % of inorganic S compounds. Pyrite S accumulation occurred more in winter than in other seasons. Transformations of S either from inorganic S to organic S or from organic S to inorganic S occur mostly during the summer growing season. These observations suggest that the cycling of S pools in Louisiana salt marshes is controlled to some extent by plant activity. Further investigations, which assess these findings, will give insight to the dynamics of S in salt marsh systems.

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**CHAPTER FIVE**  
**COMPARISON OF SOIL SULFUR FRACTION**  
**WITHIN LOUISIANA MARSH PROFILES**

### ABSTRACT

The dynamics of sulfur biogeochemistry in estuarine systems involves the presence of various sulfur forms. This study was conducted to quantify the amount and profile distribution of specific sulfur forms in Barataria Basin, Louisiana. Soil samples from freshwater, brackish, and salt marshes were fractionated into acid-volatile sulfides (AVS), HCl-soluble sulfur, elemental sulfur, pyrite sulfur, ester-sulfate sulfur, carbon-bonded sulfur, and total sulfur. Inorganic sulfur was a larger component in salt marsh, constituting 24 % of total sulfur, than in freshwater (22 %) and brackish (13 %) marshes, respectively. HCl-soluble sulfur, which was composed mainly (52-89 %) of dissolved sulfate, was the greatest component of the inorganic sulfur fraction (78-86 %) in all marsh types. Pyrite S was not the major sulfur form in any marsh type sampled. Elemental sulfur was significantly higher in salt marsh than in freshwater and brackish marshes. Organic sulfur, in the forms of ester-sulfate sulfur and carbon-bonded sulfur, was the major constituent (76-87 %) of total sulfur in all marshes. However, a more significant correlation between carbon-bonded sulfur and total sulfur was found in freshwater and salt marshes than in the brackish marsh, where the highest content of carbon-bonded sulfur was present. Ester-sulfate sulfur was significantly correlated with total sulfur only in the salt marsh. Based on the sample volume, each sulfur form, except elemental sulfur, increased seaward along the salinity gradient, corresponding to increased dissolved sulfate and sediment input, and decreased organic matter content. Also, the rates of sulfur accumulation were greater in salt marsh than in freshwater and brackish marshes. Organic sulfur fractions were the most important sulfur form and were responsible for much of the variation in the total sulfur pool in all three marsh types of Louisiana.

Louisiana Gulf Coastal marshland is one of the most wetland-rich regions of the world, representing 40 % of all coastal wetlands in the United States (Mitsch and Gosselink, 1986). Marshes border the entire coastline of Louisiana and extend inland for distances up to 50 miles. Because of the tremendous width of these marshes, environmental conditions vary and waters range from fresh to highly saline with the occurrence of broad transitional zones of brackish and intermediate marshes (Chabreck, 1972). These large areas of economically and ecologically valuable soils are often saturated to the surface with freshwater, brackish, and salt waters, and tend to be rich in organic matter because of high plant production and the slow rate of decomposition (Mitsch and Gosselink, 1986).

For broad descriptive purpose, coastal marshes categorized as freshwater, brackish, and salt marshes reflect the influence of seawater. This suggests that sulfur incorporation in the marsh soils is proportional to the sulfur concentration in sea water. Acid precipitation, however, appears to be an important source of sulfur in freshwater environments (Nriagu and Soon, 1985; Rudd et al., 1986; Wieder et al., 1987). The nature and distribution of inorganic and organic forms of sulfur has received little attention and is very important in studies of marsh development, and the different origin and type of soil material (Lowe and Bustin, 1985).

The dynamics of sulfur include aqueous, sedimentary, and atmosphere phases, as well as a wide range of oxidation states (-2 to +6) and as a result the sulfur cycle is very important in wetland systems (Landers et al., 1983; Luther et al., 1986; Mitsch and Gosselink, 1986). Sulfur is responsible for a number of important biogeochemical processes in tidal wetlands, such as sulfate reduction, pyrite formation, metal cycling, energy transfer, and atmospheric sulfur emission (see Luther et al., 1986). It can be hypothesized that increased sulfate concentrations in marsh pore waters should result in increased sulfur concentration in soil. Sulfur is a key element in metabolism in coastal marine sediments (i.e. salt and brackish marshes, and subtidal sediments) because of its role as

an electron acceptor, carrier, and donor (Troelsen and Jorgensen, 1982; Howarth and Giblin, 1983). The importance of S cycling, however, appears to have less influence on decomposition pathways and energy flow in freshwater wetlands (Mitchell et al., 1984; Lowe and Bustin, 1985; Nriagu and Soon, 1985).

Sulfate reduction rates in salt marsh soil are reported to be higher than in brackish and freshwater marsh soils as a result of a large input of organic substrates, a rapid resupplying rate of sulfate to the soil by infiltrating tidal waters (Howarth and Teal, 1979), and the reoxidation of reduced sulfur (Giblin and Howarth, 1984). Landers et al. (1983) have shown with  $^{35}\text{SO}_4^{2-}$  that small amounts of organic S are formed via sulfate reduction in freshwater sediments. Sulfide diffusing from a reducing soil environment to oxygen-enriched marsh water and soil was shown to be rapidly chemically oxidized to elemental S in Louisiana Gulf Coast brackish and salt marshes (Whitcomb et al., 1989), where the supply of dissolved  $\text{SO}_4\text{-S}$  is higher than in freshwater marshes. Elemental sulfur has been shown to be a dynamic chemical species of shallow marine sediments (Troelsen and Jorgensen, 1982; Thode-Andersen and Jorgensen, 1989).

Pyrite ( $\text{FeS}_2$ ) accumulation appears to be iron-limited in salt marshes (Giblin and Howarth, 1984; Cutter and Velinsky, 1988; Feijtel et al., 1988; Haering et al., 1989; Griffin and Rabenhorst, 1989) and brackish marsh (Feijtel et al., 1988), whereas its formation is sulfur-limited in freshwater environment (Lowe and Bustin, 1985; Nriagu and Soon, 1985; Rudd et al., 1986). In Chesapeake Bay tidal marsh soils, Haering et al. (1989) reported that organic S dominates in inland marsh, whereas pyrite is the major form of S in the streamside soils in which sedimentary iron input is higher. Pyrite has been reported to be the primary form of S accounting for 60 to 80 % of total S in some tidal marsh soils (Kaplan et al., 1963; Howarth and Teal, 1979; Cutter and Velinsky, 1988; Haering et al., 1989). Nonetheless, several studies on marine- and freshwater-mangrove sediments (Casagrande et al., 1977), freshwater peat (Lowe and Bustin, 1985; Wieder et al., 1987), lake sediments (Mitchell et al., 1984; Nriagu and Soon, 1985; Rudd

et al., 1986), and brackish-derived material (Lowe and Bustin, 1985) have concluded that organic sulfur compounds, in the forms of ester-sulfate S and C-bonded S, are much more abundant than pyrite S, and organic S contributed 57 to 97 % of total S in those materials. Since organic matter decomposition is retarded in the saturated marsh environment, the accumulation of soil organic matter results from the surficial deposition of marsh grass detritus and ,more importantly, from roots and rhizomes (Griffin and Rabenhorst, 1989). Regarding the origin of organic S, Lowe and Bustin (1985) have noted that in high  $\text{SO}_4\text{-S}$  level environments the dissimilatory reduction process is likely to be predominant while in freshwater systems, where  $\text{SO}_4\text{-S}$  is normally in short supply, S is largely incorporated into the substrate via plant assimilation. Thus, organic S may be an important S component to consider when interpreting S cycling in coastal marsh profiles.

Because the presence of inorganic and organic S forms shows some variation, the transformation and translocation of these forms in a certain site can play a key role in the S dynamics of tidal marsh soils. To more closely understand biogeochemical S transformations and translocations, the amount of specific forms of S and their distributions as related to origin and type of material should receive more attention (Lowe and Bustin, 1985; Wieder et al., 1987).

The purpose of this study was (i) to quantify the amount and to depict the profile distribution of specific forms of S as related to three certain marsh types of Louisiana and (ii) to characterize representative tidal marsh soils with respect to sulfur fractions, thus allowing us to assess the biogeochemical dynamics of S and its ecological implications for tidal wetlands.



## MATERIALS AND METHODS

### Study Area

Sampling sites were established in freshwater, brackish, and salt marshes located in Barataria Basin, Louisiana (Fig. 5.1). Barataria Basin is a 400 000-ha intertributary Louisiana Gulf Coast estuarine basin with well-defined vegetative units that is bounded on the east by the Mississippi River and on the west by the river's most recently abandoned channel, Bayou Lafourche. Several primary vegetative marsh units that generally correlate with substrate type and salinity can be identified within this highly productive basin: freshwater marsh, brackish-intermediate marsh, and salt marsh (Bahr and Hebrard, 1976). Freshwater marsh (salinity  $<1$  ‰) covers 19 % of the basin and is characterized by *Panicum hemitomon* Schult., *Sagittaria lancifolia* L., and *Eleocharis* spp. Brackish and intermediate marshes (salinity 1-10 ‰) together cover about 20 % of the basin. The brackish marsh is vegetated largely by *Spartina patens* (Ait.) Muhl., *Distichlis spicata* (L.) Greene., and small amounts of *S. alterniflora* Loisel. Salt marsh (salinity  $>10$  ‰) occupies approximately 14 % of the basin. *Spartina alterniflora* Loisel. is the dominant vegetation, representing 63 % of the entire salt marsh system. *Juncus roemerianus* Scheele., *Distichlis spicata* (L.) Greene., and *S. patens* (Ait.) Muhl. are also found in the marsh area (Chabreck, 1972). Freshwater, brackish, and salt marshes accumulate an equivalent of 37, 54, and 21 %, respectively, of the aboveground productivity. The majority of the carbon export in the basin originates in the tidal salt marsh (Feijtel et al., 1985). The freshwater and brackish marshes exhibit a much greater vertical redox fluctuation than in the salt marsh (Feijtel et al., 1988) and thus can affect S transformations. Hatton et al. (1983) found that vertical marsh accretion in this basin is a rapidly continuing process and the inorganic sediment supply seems to increase with increased hydraulic energy toward the Gulf of Mexico.

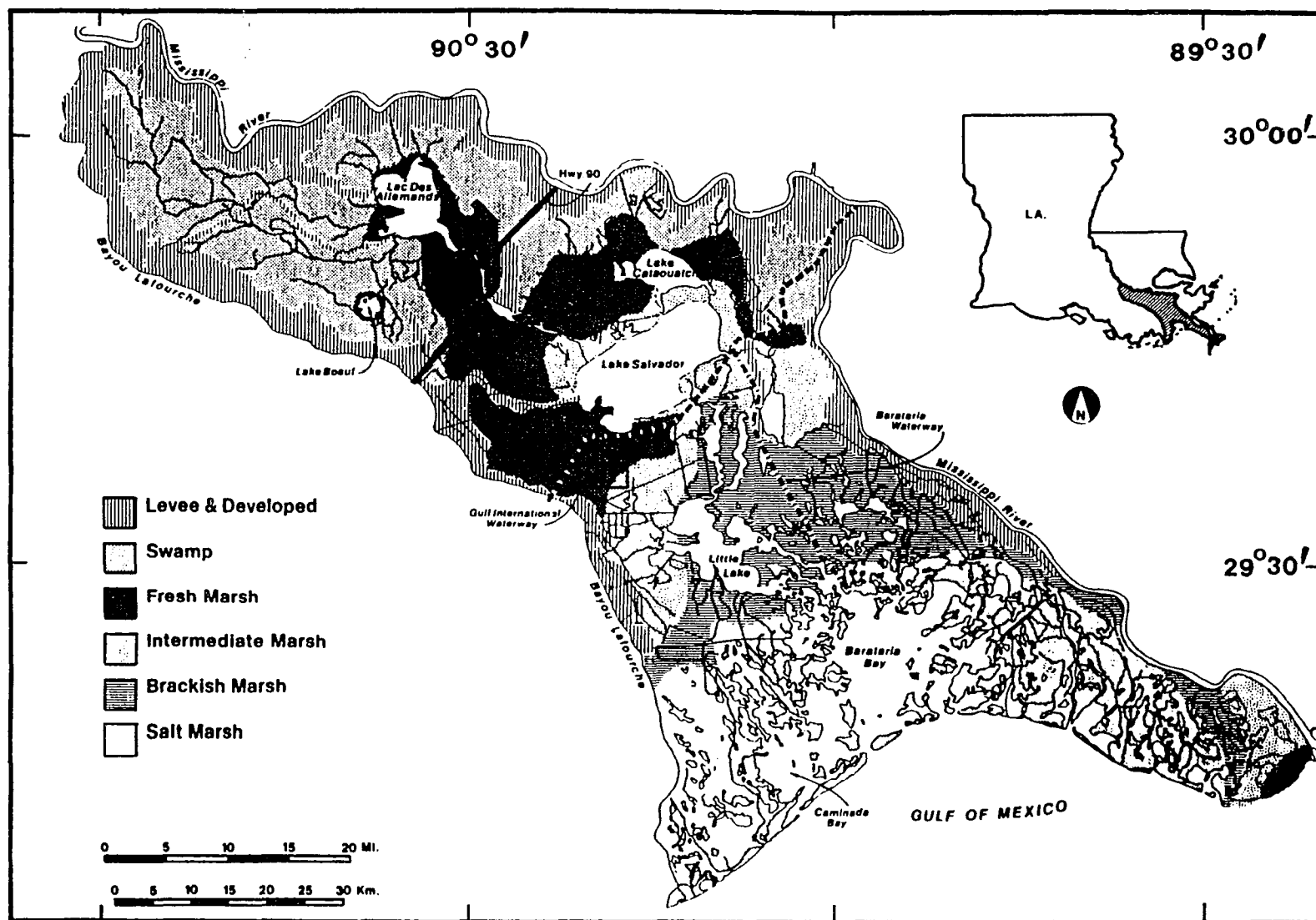


Figure 5.1. Map of Barataria Basin, LA showing study sites

### Sampling and Analysis

Soil sampling was conducted quarterly during April 1987 through August 1988 in freshwater, brackish, and salt marshes. Five soil cores were collected from each marsh at a site between streamside and inland within a radius of 3 m to minimize the effect of spatial heterogeneity. Soil samples were obtained by twisting an aluminum core (15-cm i.d. and 50-cm height) into the marsh substrate. This sampling method allowed little compaction. The cores were extruded and sectioned into 3-cm intervals immediately upon return to the laboratory. Approximately 75 % of each section was rapidly sealed in a plastic bag and then frozen, and was subsequently used for S fractionations. The remaining 25 % was utilized for the determinations of pH, soil bulk density, and soil water content (Table 5.1). Prior to chemical analysis, the soil samples were thawed and thoroughly mixed and any live roots, animal skeletons, and debris were removed.

The procedure used for the sequential extraction of S fractions (Fig. 2.1) is a modification of Nriagu and Soon (1985). The extractions were performed using a modified Johnson-Nishita (J-N) digestion-distillation apparatus (Johnson and Nishita, 1952) (Fig. 2.2). Extractant was introduced to the boiling flask by syringe injection through a serum cap at the upper end of the condenser. This was a more convenient way to add an acid and reduced the risk of  $H_2S$  loss during acid addition (Frenay et al., 1970). Sulfur species containing in each S fraction are shown in Table 2.1. Moist marsh sample equivalent to 5 to 10 g of oven-dried weight (60 °C) was used. Acid-volatile sulfides (AVS), HCl-soluble S, elemental S ( $S^0$ ), pyrite S ( $FeS_2$ ), and ester-sulfate S were extracted by the method described by Nriagu and Soon (1985). For ester-sulfate S, the extractant (HI reducing mixture) was prepared by a method outlined by Landers et al. (1983). The concentration of each S fraction was determined with inductively coupled argon plasma spectrometry (ICP) instead of the gravimetric method utilized by Nriagu and Soon (1985). Carbon-bonded S was estimated by subtracting all of the other S fractions (sum) from total S. Pore water was extracted by centrifuging a 50 to 100 g fresh

Table 5.1. Some properties of three Barataria Basin tidal marsh soils.

Sampling Site	Soil pH	Soil organic matter †	Soil bulk density	Soil water content
		%	g cm <sup>-3</sup>	kg kg <sup>-1</sup>
Freshwater	6.6 ± 0.1	52 ± 6	0.12 ± 0.02	8.34 ± 1.40
Brackish	7.3 ± 0.1	42 ± 3	0.17 ± 0.02	6.82 ± 0.65
Salt	7.0 ± 0.4	20 ± 3	0.29 ± 0.06	3.32 ± 0.92

† Hatton et al. (1983)

aliquot for 20 min at 8 000 x g (7 000 rpm, Sorvall GSA-400 rotor, Dupont Co., Wilmington, DE). The supernatant was filtered through a 0.45- $\mu$ m membrane filter. Dissolved SO<sub>4</sub>-S and Fe in the filtrate were measured with ICP. The residual aliquot was oven dried at 60 °C to constant mass, ground, sieved (150-mesh size), and thoroughly mixed prior to digestion with HNO<sub>3</sub>-HClO<sub>4</sub> (Beaton et al., 1968). The digested content was filtered through a 0.45- $\mu$ m membrane filter. Sulfur in the filtrate was determined with ICP. The sum of pore water S and soil S fractions represented total S. All values are reported on an oven-dried soil weight basis. Because of the high water content of the soil samples, however, mean concentration of each S form was expressed on both an oven-dried weight and a volume basis. Pearson's correlation coefficients and Duncan's Multiple Range Test (DMRT) were calculated with Statistical Analysis System (SAS Institute Inc., 1985).

## RESULTS AND DISCUSSION

### Inorganic S Fraction

#### *Acid-volatile sulfides (AVS-S)*

The AVS-S fraction was not an important S component in any marsh profile (Fig. 5.2), comprising <1 % of total S (Table 5.2). The AVS-S content was significantly higher in brackish marsh than in freshwater and salt marshes (Fig. 5.4), however, its concentration was relatively low. The content of AVS-S in freshwater, brackish, and salt marsh soils averaged 10.8, 29.3, and 22.3 mg S kg<sup>-1</sup> soil, respectively. The AVS-S concentration, based on the sample volume, increased toward the Gulf Coast (Fig. 5.4). This suggests the possibility of higher H<sub>2</sub>S production along the seaward gradient. Comparable AVS-S content has also been reported in some tidal marsh soils (Kaplan et al., 1963; Nedwell and Abram, 1978) and lake sediments (Nriagu and Soon, 1985; Rudd et al., 1986). It appears that the presence of low AVS-S in these environments is due to a low availability of Fe (II) and low H<sub>2</sub>S (produced from bacterial sulfate reduction).

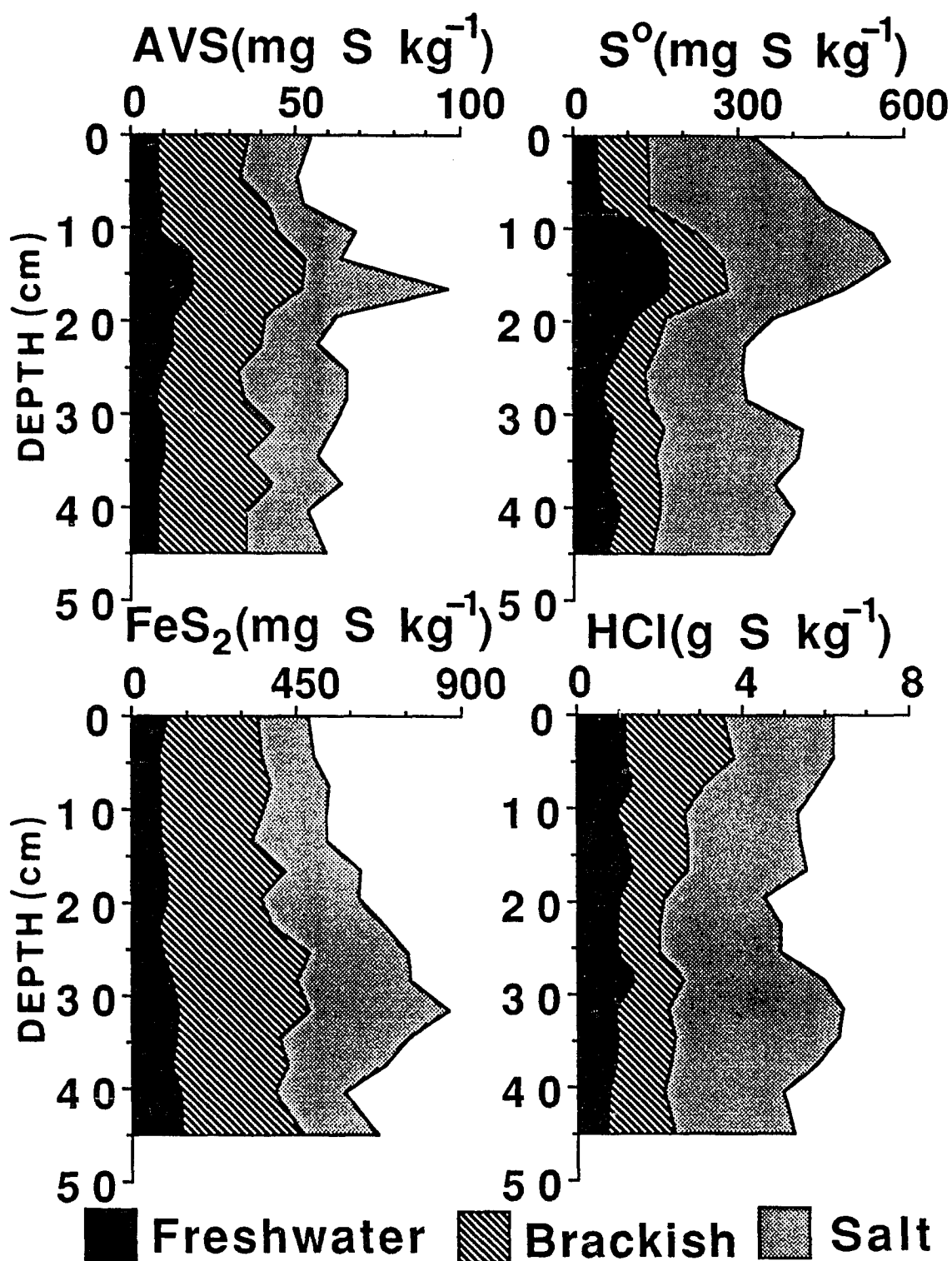


Figure 5.2. Comparison of profile distribution of inorganic sulfur constituents present as acid-volatile sulfides (AVS), elemental S ( $\text{S}^0$ ), pyrite S ( $\text{FeS}_2$ ), and HCl-soluble S (HCl) in soils collected from three marsh types

In the present study, the content of interstitial Fe (II) at all sampling sites was low (Table 5.2). It is obvious that dissolved Fe (II) was utilized in the formation of AVS-S, iron monosulfide (FeS) in particular. The greatest abundance of AVS-S corresponded to the lowest concentration of interstitial Fe in brackish marsh soils, whereas the presence of the lowest abundance of AVS-S was consistent with the greatest content of dissolved Fe in freshwater marsh soils. The soils in freshwater and brackish marshes contained low dissolved SO<sub>4</sub>-S level, while in salt marsh soils a higher dissolved SO<sub>4</sub>-S was detected (Table 5.2). The water content in these marsh soils was 8.34, 6.82, and 3.32 kg kg<sup>-1</sup>, respectively, which could be translated to a dissolved pore water SO<sub>4</sub>-S concentration of 66, 169, and 801 mg S L<sup>-1</sup>, respectively. The low SO<sub>4</sub>-S concentration in freshwater and brackish marsh soils are not surprising because these two marshes are situated in the northern part of the Barataria Basin where the salinity is relatively low (<10 ‰). The high dissolved SO<sub>4</sub>-S in salt marsh soils is apparently due to its location close to the open water body of the Gulf of Mexico and as a result it is susceptible to tidal flushing and high salinity (>10 ‰). Goldhaber and Kaplan (1982) have suggested that dissolved SO<sub>4</sub>-S concentrations <320 mg S L<sup>-1</sup> may limit the rate of sulfate reduction. In freshwater and brackish marshes, the low dissolved SO<sub>4</sub>-S levels undoubtedly affect the rate of sulfate reduction and thus the H<sub>2</sub>S production. Upon bacterial sulfate reduction, H<sub>2</sub>S is the only extracellular S product which may readily precipitate with the Fe (II) present in the pore water to form iron monosulfides (Thode-Andersen and Jorgensen, 1989). As a result, the low H<sub>2</sub>S and dissolved Fe (II) together results in low AVS-S (H<sub>2</sub>S and FeS) content. In salt marsh, where sulfate reduction was favorable with respect to dissolved SO<sub>4</sub>-S levels, the major limitation to the rate of bacterial sulfate reduction may be the availability of readily decomposed organic matter. Goldhaber and Kaplan (1982) have indicated that organic matter in recent sediments rapidly transforms to a more complex form such as humates and kerogens, which are less susceptible to bacterial attack. Although high rates of sulfate reduction have been reported in highly organic-matter-rich

Table 5.2. Distribution of sulfur fractions average over depth (0-50 cm) as percent of total sulfur, pore water sulfur and interstitial iron concentrations (mean  $\pm$  SE, N = 15) in soils collected from the three marsh types of Louisiana.

Sampling Site	AVS S	HCl-soluble S	Elemental S	Pyrite S	Ester-sulfate S	C-bonded S	Total S	Pore water SO <sub>4</sub> -S	Interstitial Fe
	----- % Total S -----						----- g S kg <sup>-1</sup> -----	----- mg Fe kg <sup>-1</sup> -----	
Freshwater	0.19b $\pm$ 0.07	19.0b $\pm$ 5.2	1.59b $\pm$ 0.89	1.76b $\pm$ 0.24	20.7a $\pm$ 3.2	57.0b $\pm$ 5.9	5.7a $\pm$ 0.9	0.55a $\pm$ 0.14	2.09c $\pm$ 0.63
Brackish	0.19b $\pm$ 0.03	9.9a $\pm$ 2.7	0.54a $\pm$ 0.08	2.01c $\pm$ 0.32	23.2b $\pm$ 5.4	64.1c $\pm$ 6.6	15.6b $\pm$ 1.1	1.15a $\pm$ 0.43	0.74a $\pm$ 0.14
Salt	0.15a $\pm$ 0.07	20.7b $\pm$ 5.8	1.73b $\pm$ 0.88	1.56a $\pm$ 0.20	21.1b $\pm$ 4.3	54.7a $\pm$ 9.9	15.7b $\pm$ 4.9	2.66b $\pm$ 0.44	1.13b $\pm$ 0.60

Any two mean values having a common letter are not significant difference at the 5 % level of significance based on a Duncan's Multiple Range Test (DMRT)



nearshore sediments (i.e. Howarth and Teal, 1979; Howarth and Giblin, 1983), organic carbon availability is likely to be limiting sulfate reduction rates in the salt marsh soils we studied. Howarth and Giblin (1983) have observed that lower rates of sulfate reduction in Georgia marshes than in the Massachusetts marshes are the result of a lower rate of organic carbon input. A better understanding of sulfate reduction would certainly improve our understanding of what is really controlling the amounts and rates of sulfate reduction in Louisiana marsh soils.

Depth profiles of AVS-S (Fig. 5.2) shows that AVS-S concentrations in all marshes reached the maxima at 14- to 17-cm depth. The presence of high  $\text{H}_2\text{S}$  and  $\text{FeS}$  in the surface zone (<20 cm) has also been found in some marshes (Kaplan et al., 1963; Nedwell and Abram, 1978), brackish coastal sediment (Thode-Andersen and Jorgensen, 1989), and freshwater-derived materials (Nriagu and Soon, 1985; Rudd et al., 1986). This finding may be a result of upward diffusion of excess  $\text{H}_2\text{S}$  accompanied by downward diffusion of  $\text{SO}_4^{2-}$  and its reduction in the anaerobic microzone (Nedwell and Abram, 1978). The  $\text{H}_2\text{S}$  then may react with dissolved Fe (II) in the pore water to form  $\text{FeS}$ . Beyond the depth of maximal AVS-S content (<14 cm), where redox potential (Eh) is approaching maximum (Feijtel et al., 1988), the  $\text{H}_2\text{S}$  diffusing out of the reducing soil to more oxygen-enriched surface soil will be rapidly chemically oxidized to elemental S ( $\text{S}^0$ ) (Whitcomb et al., 1989), and then removed from the marsh surface by tidal flushing or perhaps by surface runoff due to high rainfall. This mechanism can cause a loss of  $\text{S}^0$  in the upper marsh surface (<10 cm) as shown in Fig. 5.2 (see discussion later). There was a significant inverse relationship between AVS-S and  $\text{S}^0$  in the salt marsh (Table 5.5), whereas no such relationship was observed in freshwater and brackish marshes (Table 5.3 and 5.4). This suggested that S transformation from AVS-S to  $\text{S}^0$  occurred largely in the salt marsh environment, resulting in higher  $\text{S}^0$  concentration as compared to freshwater and brackish marshes, where the low concentration of dissolved  $\text{SO}_4\text{-S}$  seemed to limit the rates of sulfate reduction.

### *HCl-soluble S (HCl)*

HCl-soluble S was present as the largest constituent of inorganic S fraction in freshwater, brackish, and salt marsh soils (Fig. 5.4), accounting for 84, 78, and 86 %, respectively. Concentrations of HCl-soluble S, which was comprised mainly of pore water  $\text{SO}_4\text{-S}$ , were significantly different between the three marsh sites. The HCl-soluble S increased from freshwater marsh to salt marsh corresponding to the increasing concentration of pore water  $\text{SO}_4\text{-S}$  from the upper part of the basin to the Gulf Coast, which was apparently due to dissolved  $\text{SO}_4\text{-S}$  from water input (Table 5.2). The contribution of pore water  $\text{SO}_4\text{-S}$  to HCl-soluble S in freshwater, brackish, and salt marshes was 89, 77, and 52 %, respectively. The presence of pore water  $\text{SO}_4\text{-S}$  undoubtedly reflects the influence of  $\text{SO}_4^{2-}$  in seawater at each marsh locality. A significant relationship based on the sample volume between pore water  $\text{SO}_4\text{-S}$  and HCl-soluble S was found in freshwater marsh ( $r = 0.71^{**}$ ), whereas there was significant correlation based on the oven-dried weight observed in brackish and salt marshes (Table 5.4 and 5.5). Nriagu and Soon (1985) claimed that S-containing amino acids (C-bonded S), which would be hydrolyzed by hot dilute HCl, can possibly be a source of HCl-soluble S. A significant inverse correlation between C-bonded S and HCl-soluble S in freshwater marsh (Table 5.3) suggested that some of C-bonded S was likely incorporated into the HCl-soluble S fraction in freshwater marsh soils where the organic matter content was relatively high (Table 5.1). The other S forms that could possibly contribute to the remaining of the HCl-soluble S fraction would be soluble organic S, thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ), polythionates ( $\text{S}_{3+n}\text{O}_6$ ,  $n = 0\text{-}3$ ), and polysulfides ( $\text{S}_n^{2-}$ ) (Nriagu and Soon, 1985). These S species, which are intermediates in sulfide oxidation, have been found in tidal marsh systems (Luther et al., 1986).

A significant inverse relationship between HCl-soluble S and depth (Table 5.3 and 5.4) indicated that this S form was decreasing with depth in freshwater and brackish marsh soils (Fig. 5.2). This suggested that the variation of dissolved  $\text{SO}_4\text{-S}$  was rela-

Table 5.3. Correlation matrix with correlation coefficient (r) for various sulfur fractions, pH, and bulk density in freshwater marsh soils (oven-dried soil weight basis, N = 75).

Variable	Depth	AVS	HCl soluble-S	Elemental S	Pyrite S	Ester sulfate S	C-bonded S	Porewater S	Total S	Soil pH	Bulk density
Depth	1.00	NS	-0.90**	NS	NS	NS	0.90**	NS	0.85*	NS	NS
AVS		1.00	NS	0.96***	NS	NS	NS	NS	NS	NS	NS
HCl-soluble S			1.00	NS	NS	NS	-0.89**	NS	-0.88**	NS	NS
Elemental S				1.00	NS	NS	NS	NS	NS	NS	NS
Pyrite S					1.00	0.83*	NS	NS	0.78*	NS	0.85**
Ester-sulfate S						1.00	NS	NS	NS	NS	0.76*
C-bonded S							1.00	NS	0.94***	NS	NS
Porewater S								1.00	NS	NS	NS
Total S									1.00	NS	NS
Soil pH										1.00	NS
Bulk density											1.00

\*, \*\*, \*\*\* significant at  $P < 0.05$ ,  $< 0.01$ , and  $< 0.001$ , respectively. NS = not significant

Table 5.4. Correlation matrix with correlation coefficient (r) for various sulfur fractions, pH, and bulk density of brackish marsh soils (oven-dried soil weight basis, N = 75).

Variable	Depth	AVS	HCl soluble-S	Elemental S	Pyrite S	Ester sulfate S	C-bonded S	Porewater S	Total S	Soil pH	Bulk density
Depth	1.00	NS	-0.75*	NS	NS	NS	-0.83*	NS	NS	NS	NS
AVS		1.00	NS	NS	NS	NS	NS	NS	NS	NS	-0.81*
HCl-soluble S			1.00	NS	NS	NS	NS	0.95***	NS	-0.79*	NS
Elemental S				1.00	NS	NS	NS	NS	NS	NS	-0.87**
Pyrite S					1.00	NS	NS	NS	NS	NS	NS
Ester-sulfate S						1.00	NS	NS	NS	NS	-0.76*
C-bonded S							1.00	NS	0.78*	NS	NS
Porewater S								1.00	NS	NS	NS
Total S									1.00	NS	NS
Soil pH										1.00	NS
Bulk density											1.00

\*, \*\*, \*\*\* significant at  $P < 0.05$ ,  $< 0.01$ ,  $< 0.001$ , respectively.

NS = not significant

tively high in the surface zone (<20 cm). Although no significant correlation between HCl-soluble S and depth was found in salt marsh soils, the concentration of HCl-soluble S was higher in the deeper profile than in the top 20 cm ( $P < 0.003$ ) because the deep soil (>20 cm) was usually saturated with seawater. Immobilization of soluble S forms, predominantly  $\text{SO}_4\text{-S}$ , from the water input resulting in S accumulation in soil and sediment (Mitchell et al., 1984) was obviously an important source of HCl-soluble S accumulation in the present study.

#### *Elemental S ( $\text{S}^0$ )*

The presence of  $\text{S}^0$  in all marshes was <2 % of total S (Table 5.2) and was comparable to other studies for salt marsh soils (Kaplan et al., 1963; Berner, 1970), brackish and freshwater-derived material (Lowe and Bustin, 1985). Concentration of  $\text{S}^0$  was not significantly different between freshwater and brackish marshes either on an oven-dried weight or a volume basis, but its concentration was significantly higher in salt marsh (Fig. 5.4). The  $\text{S}^0$  concentration showed a significant inverse correlation with AVS-S in the salt marsh (Table 5.5) and its concentration was 2.7- to 3.3-fold higher than in freshwater and brackish marshes. These results are similar to a study in shallow coastal sediments (Troelsen and Jorgensen, 1982). The AVS-S concentration in the salt marsh was relatively low and was significantly lower than that in the brackish marsh, although the concentration of dissolved  $\text{SO}_4\text{-S}$  did not limit the rate of sulfate reduction in salt marsh as was discussed previously. It may be that the sulfide (AVS-S) formed is rapidly transformed (6-8 h) to  $\text{S}^0$  by oxidation with dissolved oxygen in the interstitial water of marsh soils (Whitcomb et al., 1989). In addition, the presence of high concentrations of ferric oxyhydroxides in this salt marsh (Feijtel et al., 1988) is likely to produce higher  $\text{S}^0$  concentration than in brackish marsh (even in the reduced profile) by incomplete oxidation of sulfide with Fe (II) (Troelsen and Jorgensen, 1982). Thode-Andersen

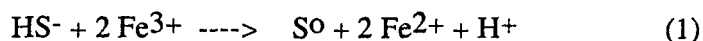
Table 5.5. Correlation matrix with correlation coefficient (r) for various sulfur fractions, pH, and bulk density of salt marsh soils (oven-dried soil weight basis, N = 75).

Variable	Depth	AVS	HCl soluble-S	Elemental S	Pyrite S	Ester sulfate S	C-bonded S	Porewater S	Total S	Soil pH	Bulk density
Depth	1.00	NS	NS	NS	0.84*	NS	0.97***	0.88**	0.94***	0.93**	-0.92**
AVS		1.00	NS	-0.87**	NS	NS	NS	NS	NS	NS	NS
HCl-soluble S			1.00	NS	NS	0.83*	NS	0.88**	0.79*	NS	-0.92**
Elemental S				1.00	NS	NS	NS	NS	NS	NS	NS
Pyrite S					1.00	0.92**	0.94**	0.81*	0.97***	0.84*	-0.82*
Ester-sulfate S						1.00	0.78*	0.81*	0.88**	NS	-0.78*
C-bonded S							1.00	0.85*	0.98***	0.94**	-0.87**
Porewater S								1.00	0.90**	0.78*	-0.96***
Total S									1.00	0.90**	-0.91**
Soil pH										1.00	-0.79*
Bulk density											1.00

\*, \*\*, \*\*\* significant at  $P < 0.05$ ,  $< 0.01$ ,  $< 0.001$ , respectively.

NS = not significant

and Jorgensen (1989) suggested that ferric oxyhydroxides present in marine sediments can react with  $\text{H}_2\text{S}$  to form mostly  $\text{S}^0$  and polysulfide:



These mechanisms may be responsible for higher  $\text{S}^0$  concentration in the salt marsh soils than in freshwater and brackish marsh soils.

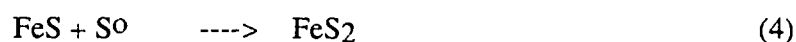
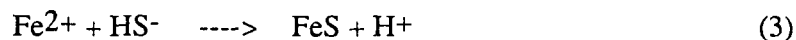
The profile distribution of  $\text{S}^0$  (Fig. 5.2) showed that the  $\text{S}^0$  concentration at all sites attained maximum at 13- to 17-cm from the marsh surface. The presence of a  $\text{S}^0$  maximum was very comparable to the formation of an AVS-S maximum in every marsh (Fig. 5.3). Nriagu and Soon (1985) suggested, from stable isotope measurements, that the  $\text{S}^0$  is derived from the oxidation of AVS-S in the aerobic surficial sediments. The presence of  $\text{S}^0$  maximum in the oxidized surface zone, or above the redoxcline (<20 cm), has also been reported in some recent coastal sediments (Troelsen and Jorgensen, 1982; Cutter and Velinsky, 1988; Thode-Andersen and Jorgensen, 1989). The  $\text{S}^0$  formed from chemical oxidation of sulfide that occurs near the marsh surface can be transported from the marsh to adjacent streams (Whitcomb et al., 1989), probably by tidal flushing or surface runoff. This finding perhaps can explain a loss of  $\text{S}^0$  near the marsh surface (<5 cm) in the present study. The  $\text{S}^0$  maximum occurred in all three marsh sites just above 20-cm depth, which Feijtel et al. (1988) reported to be the redoxcline for these marsh soils, and was possibly produced to some extent by oxidation in the plant root zone. Luther and Church (1988) indicated that the presence of  $\text{S}^0$  in the upper zone (0-15 cm) of a Delaware marsh is also a result of oxidation in the plant root zone. Elemental S does not accumulate because it is alternatively susceptible to oxidation and reduction, and thus can function as a dynamic intermediate in the S transformations within anoxic sediments (Troelsen and Jorgensen, 1982).

### *Pyrite S (FeS<sub>2</sub>-S)*

In the present study, although pyrite S was present as the second largest portion (7-16 %) of the inorganic S, its contribution to the total S was <3 % (Table 5.2). Similar findings have been reported for coastal marine sediments (Berner, 1970), and brackish and freshwater-derived materials (Lowe and Bustin, 1985; Nriagu and Soon, 1985). Our data showed that concentration of pyrite S was relatively low in all three marshes throughout the profiles (Fig. 5.2), averaging 98, 305, and 240 mg S kg<sup>-1</sup>, respectively. In general, the formation of pyrite S involves one of the following pathways, depending on the presence of HS<sup>-</sup> or H<sub>2</sub>S and FeS (AVS-S), and S<sup>0</sup>. The first pathway, in which single pyrite crystals are found, involves direct precipitation of Fe (II) and polysulfides (S<sub>n</sub><sup>2-</sup>) (Rickard, 1975):



The second mechanism, in which framboidal pyrite is formed requires the initial formation of mackinawite (FeS<sub>0.9</sub>), which subsequently combines with S<sup>0</sup> to form pyrite slowly (Berner, 1970; Goldhaber and Kaplan, 1974):



Due to these reactions, it was obvious that low concentrations of dissolved Fe (II) (Table 5.2), AVS-S, and S<sup>0</sup> in the present study could limit the pyritization process and thus result in a relatively low concentration of pyrite S. Feijtel et al.(1988) also found evidence that the pyrite formation in these freshwater, brackish, and salt marsh soils occurs as equation (2) in the upper 20 cm and follows equation (3) and (4) at greater depth (>20 cm). A similar pyritization following the two pathways has been documented in a Delaware marsh (Cutter and Velinsky, 1988).

Although there was a significant correlation between pyrite S and depth observed only in the salt marsh (Table 5.5), the concentration of pyrite S in freshwater and brackish marshes still appeared to increase with depth (Fig. 5.2). The increasing pyrite S



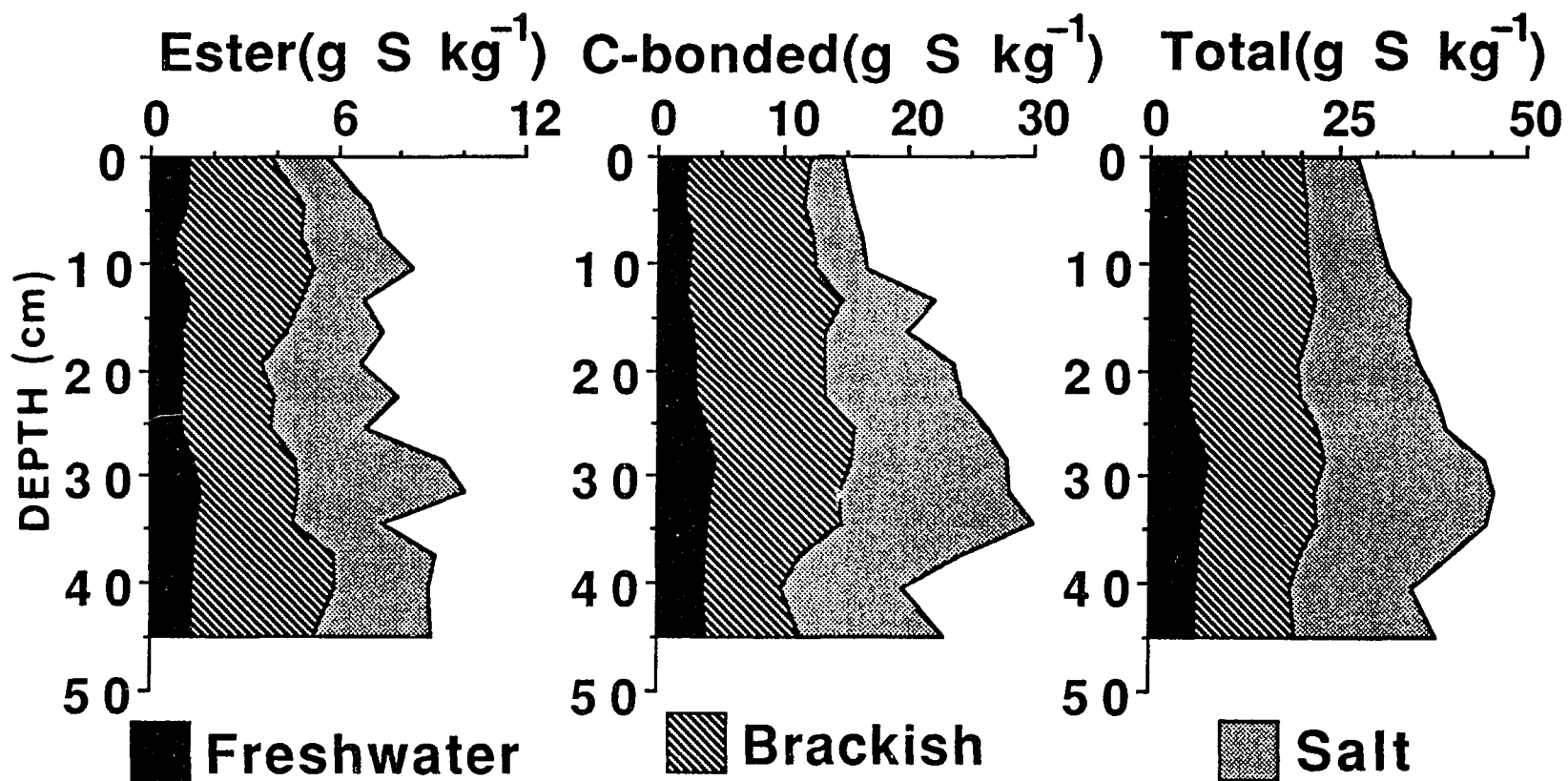


Figure 5.3. Comparison of depth profile of organic sulfur constituents present as ester-sulfate sulfur (E-S)) and carbon-bonded sulfur (C-S), and total sulfur (Tot) in soils collected from three marsh types of Louisiana .

concentration with depth has widely been observed in some tidal marshes (Nedwell and Abram, 1978; Cutter and Velinsky, 1988; Haering et al., 1989). Low pyrite S concentration in the surface zone (20 cm) was likely due to oxygen transport through plant roots (Howarth and Teal, 1979; Giblin and Howarth, 1984) and perhaps by  $O_2$  advection due to falling water levels over the marsh surface, releasing dissolved Fe (II) and  $SO_4$ -S to the pore waters (Giblin and Howarth, 1984; Feijtel et al., 1988; Luther and Church, 1988). This is supported by a higher dissolved Fe (II) and  $SO_4$ -S found in the oxidized surface (<20cm) than in the reducing profile (>20 cm) at all sites (data not shown).

Haering et al. (1989) have noted that pyrite S accumulation may be favored in estuarine marshes as a consequence of the greater sediment input, providing greater Fe input. In freshwater marsh, where the pyrite accumulation was lowest (Table 5.6), organic material produced in situ was the only source for marsh accretion as the marshes sediment supply from the Mississippi River was cut off many year ago. Therefore, high organic matter or low bulk density (Table 5.1), and low sediment (Fe) input would be expected. The concentration of pyrite S in the salt marsh was significantly higher than in freshwater and brackish marshes on volume basis, but it was significant lower than in the brackish marsh on oven-dried weight basis (Fig. 5.4). This result is in good agreement with a previous study in this Barataria Basin marshes (Feijtel et al., 1988). Feijtel et al. (1988) found that the accumulation rates of Fe in the salt marsh is significantly higher than in freshwater marsh, but not significantly higher than in the brackish marsh. They further reported that pyrite S accumulates in the salt marsh at a rate of  $12.5 \text{ g Fe m}^{-2} \text{ yr}^{-1}$  or 23 % of the total Fe flux, while in the brackish marsh pyrite S accumulates at a rate of  $14.0 \text{ g Fe m}^{-2} \text{ yr}^{-1}$  or 34 % of the total Fe flux. The pyrite S concentration in the brackish marsh was not correlated with any S form, soil pH, pore water  $SO_4$ -S, or bulk density (Table 5.4), suggesting a more steady-state pyrite formation than in freshwater and salt marshes, where pyrite S was significantly correlated with other S forms, soil pH,

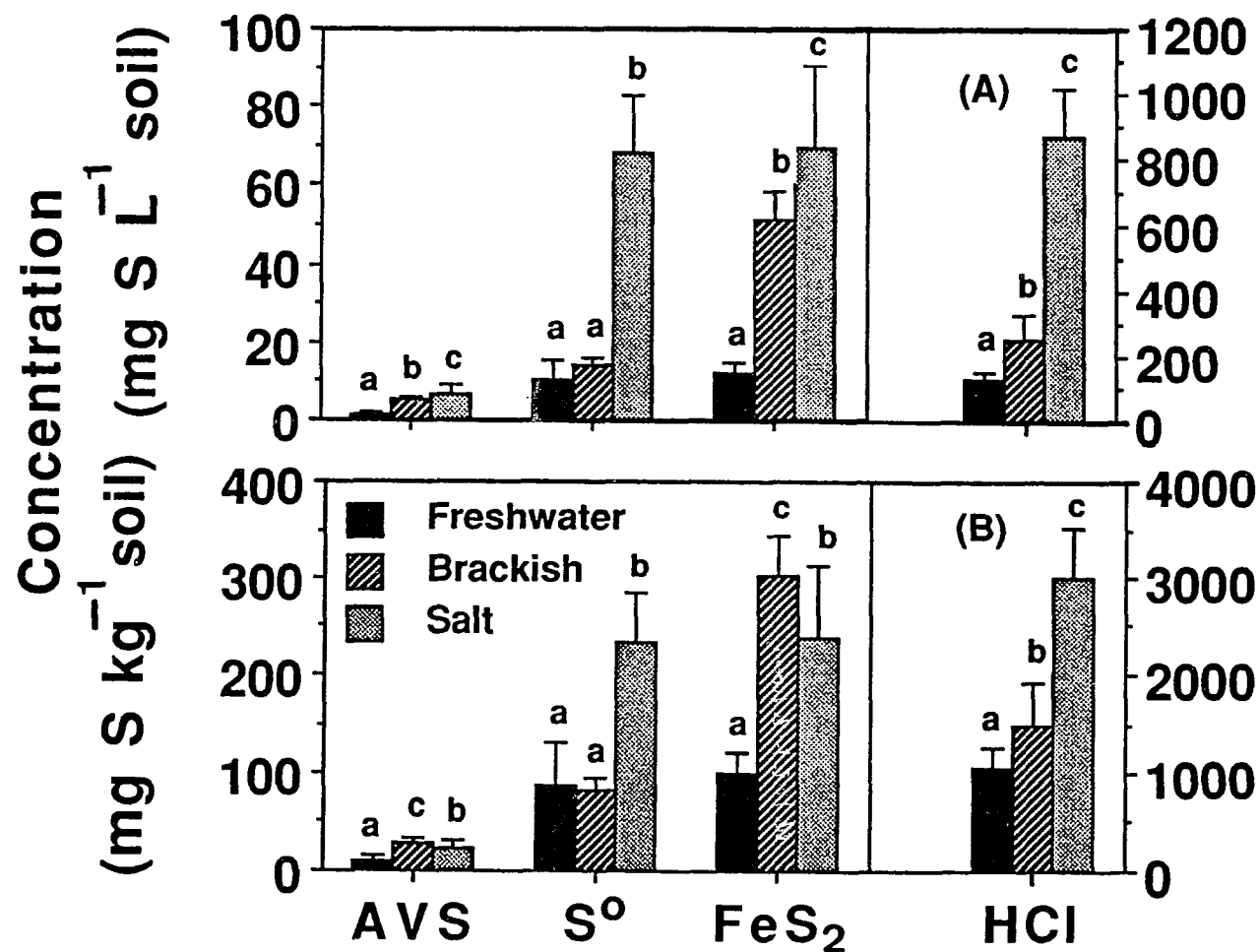


Figure 5.4. Comparison of concentrations (mean  $\pm$  SE,  $N = 15$ ) of acid-volatile sulfides (AVS), elemental sulfur ( $S^0$ ), pyrite sulfur ( $FeS_2$ ), and HCl-soluble sulfur (HCl) in soils taken from three different marsh types; (A) volume basis, (B) oven-dried weight basis. For each sample bar with the same letter is not significantly different at the 5% level of significance based on a Duncan's Multiple Range Test.

and soil bulk density (Table 5.3 and 5.5). In conclusion, it may be noted that a small portion of the accretionary S flux in Louisiana marshes occurs in the form of pyrite S.

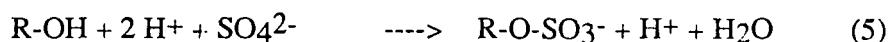
### Organic S Fraction

#### *Ester-sulfate S (E-S)*

Ester-sulfate S was the second largest constituent (26-28 %) of organic S as well as of total S (Table 5.2). The mean concentration in freshwater marsh soils ( $1.2 \text{ g S kg}^{-1}$  soil) was similar to that in the subsurface freshwater peat from Big Run Bog (Wieder et al., 1987), where ester-sulfate S constituted about 24 % of the total S. As a percent of total S, ester-sulfate S was also in accord with previous studies in lake sediment (Mitchell et al., 1984), and freshwater marsh and swamp (Casagrande and Siefert, 1977; Casagrande et al., 1977). In brackish and salt marsh soils, although the mean values ( $3.5$  and  $3.2 \text{ g S kg}^{-1}$  soil, respectively) was higher than those in marine-brackish peat (Casagrande and Siefert, 1977; Casagrande et al., 1977), the percent contribution to the total S was comparable. The concentration of ester-sulfate S in the present study was significantly different among freshwater, brackish, and salt marshes. The mean concentration of ester-sulfate S was significantly higher in the brackish marsh than in freshwater and salt marshes. In contrast, the mean value on volume basis was significantly greater in salt marsh (Fig. 5.5), corresponding to the greater abundance of dissolved  $\text{SO}_4\text{-S}$  in salt marsh environment.

The ester-sulfate S concentration in freshwater and salt marshes increased slightly with depth (Fig. 5.3). In a waterlogged swamp-marsh environments, where organic matter is not readily degraded, humic and fulvic acids tend to accumulate and the active side chain components of these materials can react with various S forms to produce ester-sulfate linkages (Casagrande and Siefert, 1977), leading to the accumulation of this S form in the reduced zone ( $>20 \text{ cm}$ ). The concentration of ester-sulfate S was closely parallel to pore water  $\text{SO}_4\text{-S}$ , C-bonded S, total S, and organic matter content

(referred from soil bulk density) in the salt marsh profile (Table 5.5). This suggested that the presence of ester-sulfate S content in marine environments may be more susceptible to variation due to higher S content in this environment than in the freshwater marsh, depending upon the availability of soil organic matter, dissolved  $\text{SO}_4\text{-S}$ , and C-bonded S. In the brackish marsh, the concentration of ester-sulfate S in the surface section (<20 cm) was 1.5- to 3.4-fold higher than that in freshwater and salt marshes, respectively, and its concentration was very comparable to that below 20 cm (Fig. 5.3). High organic matter accumulation due to higher aboveground and belowground production in brackish marsh than in freshwater and salt marshes (Feijtel et al., 1985) may be responsible for this observation. The importance of organic matter to ester-sulfate S in brackish marsh soils was indicated by a significant inverse relationship between soil bulk density and ester-sulfate S (Table 5.4). Lowe and Bustin (1985) have suggested that the incorporation of  $\text{SO}_4\text{-S}$  into the peat substrate can occur largely via plant assimilation. Rudd et al. (1986) found that ester-sulfate S formation does not involve sulfate reduction (dissimilatory respiration), but rather the reaction of  $\text{SO}_4\text{-S}$  with organic matter:



#### *Carbon-bonded S (C-S)*

C-bonded S was a major contributor to the total S in all marsh soils (Table 5.2). In the present study, concentrations of C-bonded S was 2.8 times higher than that of ester-sulfate S. This is in good agreement with several previous studies for freshwater peat (Lowe and Bustin, 1985; Wieder et al., 1987), lake sediments (Mitchell et al., 1984), brackish-derived materials (Lowe and Bustin, 1985), and marine-mangrove peat (Casagrande et al., 1977), in which C-bonded S is typically 2- to 3-fold more abundant than ester-sulfate S. It is likely that the C-bonded S is generally of a more resistant nature than the ester-sulfate S because C-bonded S is incorporated into the strongly aro-

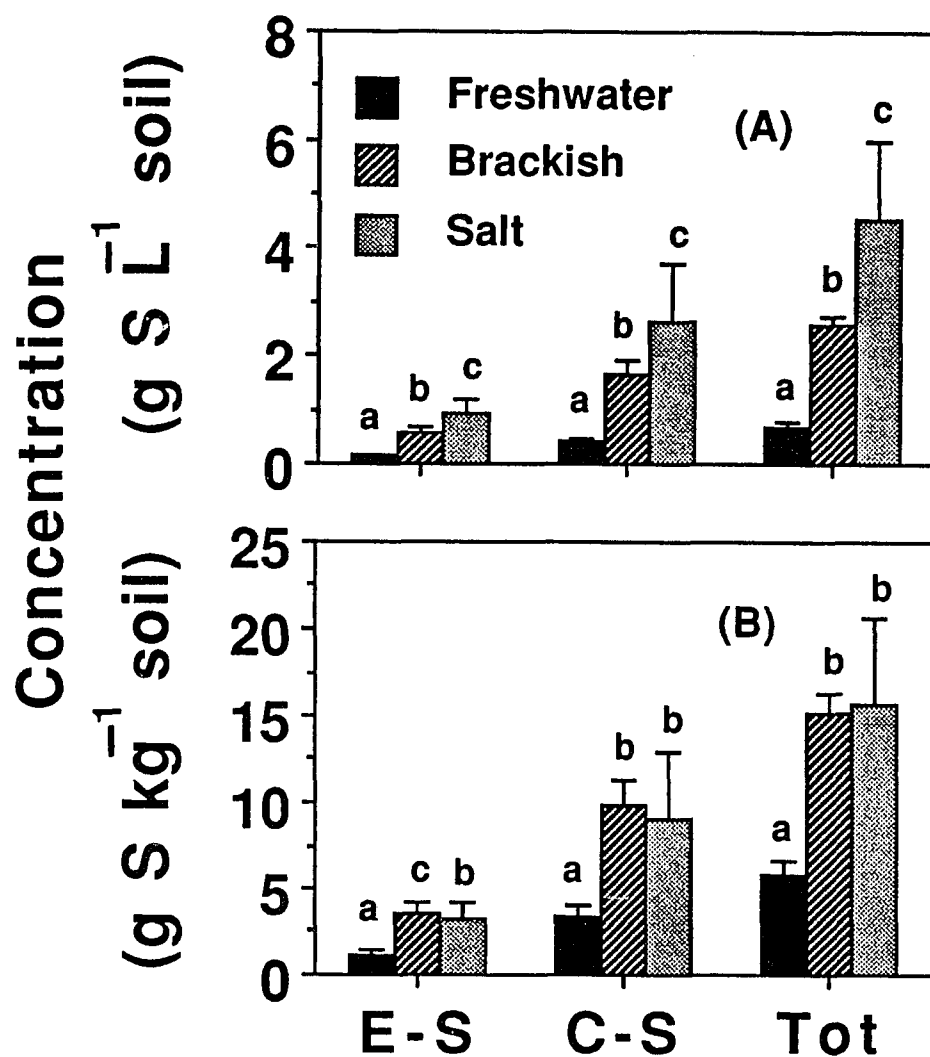


Figure 5.5. Comparison of concentrations (mean  $\pm$  SE, N = 15) of ester-sulfate sulfur (E-S) and carbon-bonded sulfur (C-S), and total sulfur (Tot) in soils taken from three marsh types; (A) volume basis, (B) oven-dried weight basis. For each sample bar with the same letter is not significantly different at the 5% level of significance based on a Duncan's Multiple Range Test.

matic core of humic acids, whereas a significant portion of ester-sulfate S is associated with active side chain compounds of fulvic and humic materials (Bettany et al., 1973).

In freshwater and salt marshes, where C-bonded S increased with depth, the C-bonded S concentration more closely paralleled to the total S concentration than in the brackish marsh, where C-bonded S decreased with depth (Table 5.3, 5.4 and 5.5). This suggested that the sedimentation of organic S is a more significant input of S in the freshwater and salt marsh soils than in the brackish marsh soils. Rudd et al. (1986) also reported on the origin of organic S from sedimentation in some lake sediments, where organic S increases with depth. The concentration of C-bonded S in freshwater marsh was significantly lower than that in brackish and salt marshes. Meanwhile, there was no significant difference in C-bonded S concentration on oven-dried weight basis between brackish and salt marshes (Fig. 5.5). Since the brackish and salt marsh soils contained a higher content of inorganic S than in the freshwater marsh soils, the transformation of the inorganic S into organic S through plants and microorganisms, which is subsequently incorporated into the marsh substrate, may result in a build up of C-bonded S in the brackish and salt marsh soils. Lowe and Bustin (1985) have also noted that the accumulation of C-bonded S through assimilatory reduction can be limited to some degree by the initial  $\text{SO}_4\text{-S}$  level in the environment, which is much lower in freshwater than marine-related systems. On volume basis, the mean concentration of C-bonded S in the salt marsh was significantly higher than in brackish marsh (Fig. 5.5). This indicated that in salt marsh, where sulfate reduction was more prevalent, the organic S in the soils can originate mostly from sulfate reduction, rather than from the sedimentation of organic S in particles. Rudd et al. (1986) proposed the reaction of  $\text{H}_2\text{S}$  produced from sulfate reduction with organic matter, i.e. reaction with hydroxyl groups, to produce C-bonded S:



### **Total S (Tot)**

Total S concentration was significantly higher in brackish and salt marshes than in freshwater marsh (Fig. 5.5). A significant relationship between the total S content and depth was found in freshwater and salt marsh soils (Table 5.3 and 5.5). There was no significant trend with depth observed in brackish marsh soils (Table 5.4). Apparently, the total S present in all three marshes was composed largely of organic S, in the forms of ester-sulfate S and C-bonded S. The organic S fraction composed 76 to 87 % of the total S. This is similar to several studies for freshwater, brackish, and coastal marshes (Casagrande et al., 1977; Lowe and Bustin, 1985; Wieder et al., 1987; Haering et al., 1989), and lake sediments (Mitchell et al., 1984; Nriagu and Soon, 1985; Rudd et al., 1986). Nonetheless, this contrasts considerably with other studies in recent marine sediments (Kaplan et al., 1963; Howarth and Teal, 1979; Cutter and Velinsky, 1988). These workers have concluded that S in the form of pyrite is more abundant than organic S. It is likely that the availability of Fe limits the amount of pyrite and, consequently, inorganic S forms may react with organic matter to produce organic S (Casagrande et al., 1977; Nriagu and Soon, 1985; Rudd et al., 1986) or may be transformed to organic S by plant uptake (Lowe and Bustin, 1985), resulting in a high organic S content. Griffin and Rabenhorst (1989) found that the amount of reactive Fe is limiting pyrite formation in Maryland tidal marsh soils. This seems to be applicable to our study where low dissolved Fe is observed in all marsh sites (Table 5.2). They also reported that when the pyrite S content is low, the dominant S species is organic S.

### **Sulfur Accumulation**

The accumulation of all S forms followed a seaward increase (Table 5.6). It appeared that the accumulation of S in freshwater, brackish, and salt marshes was a function of marsh sedimentation. In the Barataria Basin, the rate of sedimentation of



Table 5.6. Rates of S accumulation in the Barataria Basin tidal marsh soils (mean  $\pm$  SE, N = 15).

Sulfur accumulation rate												
Sampling site	Sedimentation rate †	AVS S		HCl souble S		Elemental S		Pyrite S		Ester sulfate S	C-bonded S	Total S
	mm yr <sup>-1</sup>	mg S m <sup>-2</sup> yr <sup>-1</sup>				g S m <sup>-2</sup> yr <sup>-1</sup>						
Freshwater	8.5	11.1a ± 2.6		1077a ± 228		86a ± 31		104a ± 41		1.27a ± 0.46	3.5a ± 1.3	6.1a ± 1.9
Brackish	9.5	45.6b ± 6.7		2309b ± 654		126b ± 19		479b ± 96		5.37b ± 0.83	15.3b ± 3.4	23.7b ± 3.4
Salt	10.5	68.3c ± 29.4		9030c ± 1043		726c ± 236		713c ± 185		9.57c ± 2.44	25.9c ± 8.8	46.0c ± 10.3

† Feijtel et al. (1988)

Any two mean values having a common letter are not significant difference at the 5 % level of significance based on a Duncan's Multiple Range Test (DMRT)

inorganic and organic sediments is a rapidly continuing processes and increases with increased hydraulic energy toward the Gulf Coast (Hatton et al., 1983). The accumulation rate of inorganic S associated with Fe (AVS-S and  $\text{FeS}_2$ ), for example, was greatest in the salt marsh, where the sedimentation rate of mineral input was also greatest. Feijtel et al. (1988) found that the salt marsh accumulates  $53.6 \text{ g Fe m}^{-2} \text{ yr}^{-1}$ , whereas brackish marsh accretes about  $40.9 \text{ g Fe m}^{-2} \text{ yr}^{-1}$ . The accumulation rate of Fe in these two marshes is significantly higher than that in the freshwater marsh. The rate of organic S accumulation in the present study also increased along the seaward gradient (Table 5.6). This seemed to correspond with the accretionary organic sediment, which increased from the freshwater marsh in the upper part of the basin to the salt marsh (Hatton et al., 1983). Because of the high sedimentation of these marshes reported by Feijtel et al. (1988) (Table 5.6), the accumulation of S seemed to be dependent largely on the sedimentation rate of both inorganic and organic sediments, rather than the chemical reduction processes such as sulfate reduction. The actual level of sediment S deposition may depend on a complex of biotic, abiotic, and other environmental factors (Mitchell et al., 1984).

A significant fraction of marsh energy flow would be entrapped in these accreted reduced S forms. During dissimilatory sulfate reduction, only a fraction of the energy of marsh soil organic matter is lost. Most of the free energy is conserved in reduced S compounds. It is estimate that 75 % is transferred and stored as  $\text{H}_2\text{S}$  (Howarth and Teal, 1979). Pyrite S and elemental S also retain appreciable energy. In Louisiana rapidly accreted coastal marsh, a significant portion of marsh energy flow may enter this sedimentation pool.

## CONCLUSION

In Louisiana tidal marshes, total S was relatively low in the freshwater marsh. The total S was higher and very similar in both brackish and salt marshes. Organic S, in the forms of ester-sulfate S and C-bonded S, was the predominant S form at all sites contributing 76 to 87 % of the total S. The content of C-bonded S was 2.8 fold higher than ester-sulfate S because the majority of C-bonded S incorporated into plants and microorganisms is associated with protein and was more resistant to decomposition than ester-sulfate S.

The contribution of the inorganic S to the total S was greater in salt marsh (24 %) than in brackish (13 %) and freshwater (22 %) marshes. This is because the salt marsh received more sediment input and is situated more closely to the Gulf Coast than brackish and freshwater marshes. The HCl-soluble S, of which 52 to 89 % came from dissolved  $\text{SO}_4\text{-S}$ , was the major component of inorganic S fraction at all sites. Pyrite S, comprising <3 % of the total S, was significantly higher in brackish marsh than in freshwater and salt marshes. The formation of pyrite S appeared to be dependent on the AVS-S,  $\text{S}^0$ , and the availability of Fe. The AVS-S and  $\text{S}^0$  together composed <2 % of the total S. The concentration of AVS-S was significantly different in all three marsh types, similar to that of pyrite S. It is surprising that the  $\text{S}^0$  concentration present in brackish marsh was significantly lower than in salt marsh both on the weight and volume bases that it was not significantly different from the freshwater marsh. The export of  $\text{S}^0$  from the marsh by tidal flushing or subsurface runoff to adjacent streams may possibly be responsible for low  $\text{S}^0$  in brackish marsh and an energy loss. Transformation from AVS-S to  $\text{S}^0$ , was suggested by a significant inverse relationship between AVS-S and  $\text{S}^0$  which occurred largely in salt marsh. Regarding the influence of inorganic sediment input (weight basis) to the marshes, the mean concentration of every S form, except  $\text{S}^0$  and HCl-soluble S, appeared to be predominate in the brackish marsh than in freshwater and salt marshes. On volume basis, all S forms, except  $\text{S}^0$ , showed an increasing trend along the seaward gradient.

The accumulation rate of S followed the increased inorganic and organic sedimentation along the hydraulic energy gradient from freshwater to salt marshes. Accretion of reduced S species apparently plays a significant role in marsh energy flow. This reflects the influence of the rapid vertical sedimentation on nutrient accumulation in the Louisiana tidal marsh soils . However, to understand more closely the dynamics of S cycling and the energy flow in these three different marshes, it is very important to determine the rates of sulfate reduction and a certain amount of energy stored in each reduced S form.

#### ACKNOWLEDGEMENTS

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## SUMMARY AND CONCLUSIONS

Content and profile distribution of specific sulfur forms as influenced by seasonal changes were examined in three different marsh types of Louisiana. Soil samples collected quarterly from those marshes were fractionated into various inorganic and organic S forms. Inorganic S was present as acid-volatile sulfides (AVS), HCl-soluble S (containing  $\text{SO}_4\text{-S} > 50\%$ ), elemental S, and pyrite S. The two major organic S forms were ester-sulfate S and carbon-bonded S.

In the freshwater marsh, acid-volatile sulfides (AVS) were higher in the oxidized zone ( $<20$  cm) than in the reduced zone ( $>20$  cm), resulting from upward diffusion of  $\text{H}_2\text{S}$  coupled with downward diffusion of sulfate and the reduction there. The AVS content was lowest in winter, when sulfate reduction was suppressed, and greatest in summer when microbial activity was intense. The HCl-soluble S was the major inorganic S form and was greater in the upper 20 cm than below 20 cm. Elemental S ( $\text{S}^0$ ) reached a maximum in the upper 20 cm and the content was 2-fold greater than that below 20 cm. This was primarily due to the transformation of  $\text{H}_2\text{S}$  to  $\text{S}^0$  as a result of oxidation processes. The influence of oxidation was dominant in summer when the marsh plant was mostly active. Pyrite content demonstrated great variation in the surface section than at depth as a result of its rapid formation and oxidation. The content of pyrite was maximal below 20 cm, apparently via a process of slow pyritization from the reaction of FeS and  $\text{S}^0$ . Transformation of ester-sulfate to C-bonded S seemed to occur during early summer. The ester-sulfate S content near the root zone (15-20 cm) was 2-fold less during spring and summer growing seasons than in fall and winter, probably because of mineralization of this S form in response to plant growth. Like ester-sulfate S, the presence of C-bonded S was greater in the reduced zone ( $>20$  cm) than in the oxidized layer ( $<20$  cm) as a result of the accumulation of organic acids and the slow rate of organic matter degradation. The ratio of C-bonded S to ester-sulfate S ranged from 2.4 to 3.0. The concentration of

C-bonded S was greatest in spring which may result from the incorporation of dead plant material in winter providing the major flux of organic S in the forthcoming spring.

In the brackish marsh, depth profiles of AVS concentrations varied from one season to another which perhaps resulted from inconsistent seasonal patterns of the vertical redox profile and of dissolved iron (II). The observed low concentration of this S form near the root zone (<20 cm) during fall, spring, and summer was a result of plant root mediated oxidation or plant uptake. The presence of HCl-soluble S varied significantly with pore water S and its content was lowest in spring and highest in summer. The minimal content of this S form occurred just below the root zone (20-30 cm), and may be caused by the greater rates of sulfate reduction here than in the surface layer, probably accompanied by uptake of sulfate by plant roots. Below this depth (20-30 cm), HCl-soluble S increased probably due to high exchange rate of pore water sulfate. Elemental S was restricted to the seasonally oxic portion of this marsh soil where its concentration attained maximum at 12 and 17 cm below the marsh surface and showed the greatest abundance in mid summer and early fall when oxygen seemed to be largely introduced through plant roots during photosynthesis. The effect of soil oxidation by plant root on the pyrite content was observed in summer as well. Like in freshwater marsh soil, pyrite content illustrated more seasonal variation in the surface section (<20 cm) than at depth (>20 cm). The slow pyritization, evidenced by a deeper pyrite maxima (>20 cm), was observed in every season studied. The formation of ester-sulfate S was greatest in summer and corresponded to the decrease in C-bonded S. This suggested that the available supply of C-bonded S could suppress the mineralization of ester-sulfate S. The ratio between C-bonded S and ester-sulfate S was similar to that of the freshwater marsh.

Like freshwater and brackish marshes, AVS content in the salt marsh was low during spring and summer. The variation of AVS at depth (>20 cm) appeared to depend largely on sulfate reduction. Because this salt marsh was usually saturated with seawater at depth, more than 80 % of HCl-soluble S was contributed from pore water S.

Elemental S reached maximum concentration in the upper 20 cm, with the greatest abundance in fall and lowest content in spring. The dominant process of plant root oxidation in spring also resulted in low concentrations of pyrite in the upper part of the profile (<20 cm). The presence of pyrite maxima at depth was similar to freshwater and brackish marshes. Higher content of ester-sulfate S was observed in spring and fall than in winter, suggesting a greater transformation of inorganic S to organic S by plant uptake. Like ester-sulfate S, the C-bonded S content was maximal at depth (>20 cm). The seasonal variability did not exhibit a pronounced effect on C-bonded S content in this salt marsh.

Regardless of the seasonal influence, the profile distributions of S forms were almost similar among the three marshes. The AVS and  $\text{SO}^0$  attained maxima in the oxidized zone (< 20 cm), whereas pyrite content indicated maxima in the reduced zone (>20 cm). The HCl-soluble S content, of which >50 % was attributed to dissolved sulfate, was higher in the upper 20 cm of freshwater and brackish marsh profiles and higher below 20 cm in the salt marsh profile. Organic S, in forms of ester-sulfate S and C-bonded S, was the major contributor to the S pool in all marsh types and displayed an increase with depth. The rates of S accumulation apparently followed the seaward gradient similar to the sulfur content (volume basis). This study provides information on the nature and distribution of S involving the S cycle as it relates to the nature and development of certain coastal marshes of Louisiana.

The significance of these investigation of S cycling in Louisiana Gulf Coast marsh can be summarized below:

- 1) Organic S compounds are much more abundant in Louisiana coastal marsh soils as compared to previous reported studies for Atlantic Coast marshes. Pyrite S has been reported to be the predominant S forms in other U.S. Coastal salt marshes (Howarth, 1984). Pyrite S represented only 2 % of the total S in Louisiana Barataria Basin marshes.

2) Acid-volatile sulfide (AVS) and HCl-soluble S was greater in a salt marsh nearer the coast. These S forms represent the fraction which at elevated levels would be toxic to marsh vegetation. The rapid subsidence and accompanying salt water intrusion occurring in coastal Louisiana will likely result in increases in these fractions. Such increases in AVS and HCl-soluble S could be detrimental to marsh vegetation especially in brackish and freshwater marshes.

3) Accumulation of reduced S forms as a result of vertical marsh accretion serves as an energy sink. During sulfate reduction 75 % of the free energy of the organic matter in marsh soils which is decomposed is transferred and stored as sulfide. The original source of the energy is sunlight which is used by marsh vegetation to fix atmospheric carbon into plant material or organic matter.

## VITA

Nawarat Krairapanond was born on January 23, 1960, in Bangkok, Thailand. In 1982, I graduated from Kasetsart University in Bangkok, Thailand with a Bachelor of Science degree in Agriculture. After graduation, I worked on Soil Salinity Project at the Department of Land Development. I received my Master of Science degree in Soil Science from Kasetsart University in 1984. I attended Louisiana State University in August 1986. I studied sulfur chemistry of Louisiana tidal marsh soils under the direction of Dr. William H. Patrick, Jr. Presently, I am a candidate for the doctorate of Marine Sciences.

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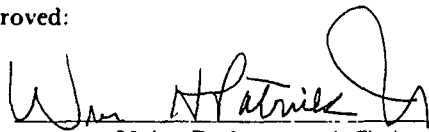
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Nawarat Krairapanond

Major Field: Marine Sciences


Title of Dissertation: Sulfur Chemistry of Louisiana Tidal Marsh Soils

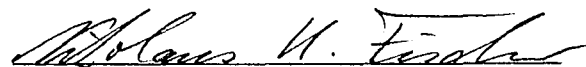
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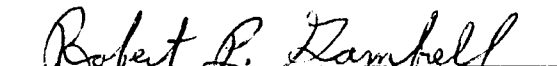
  
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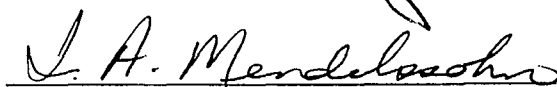












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