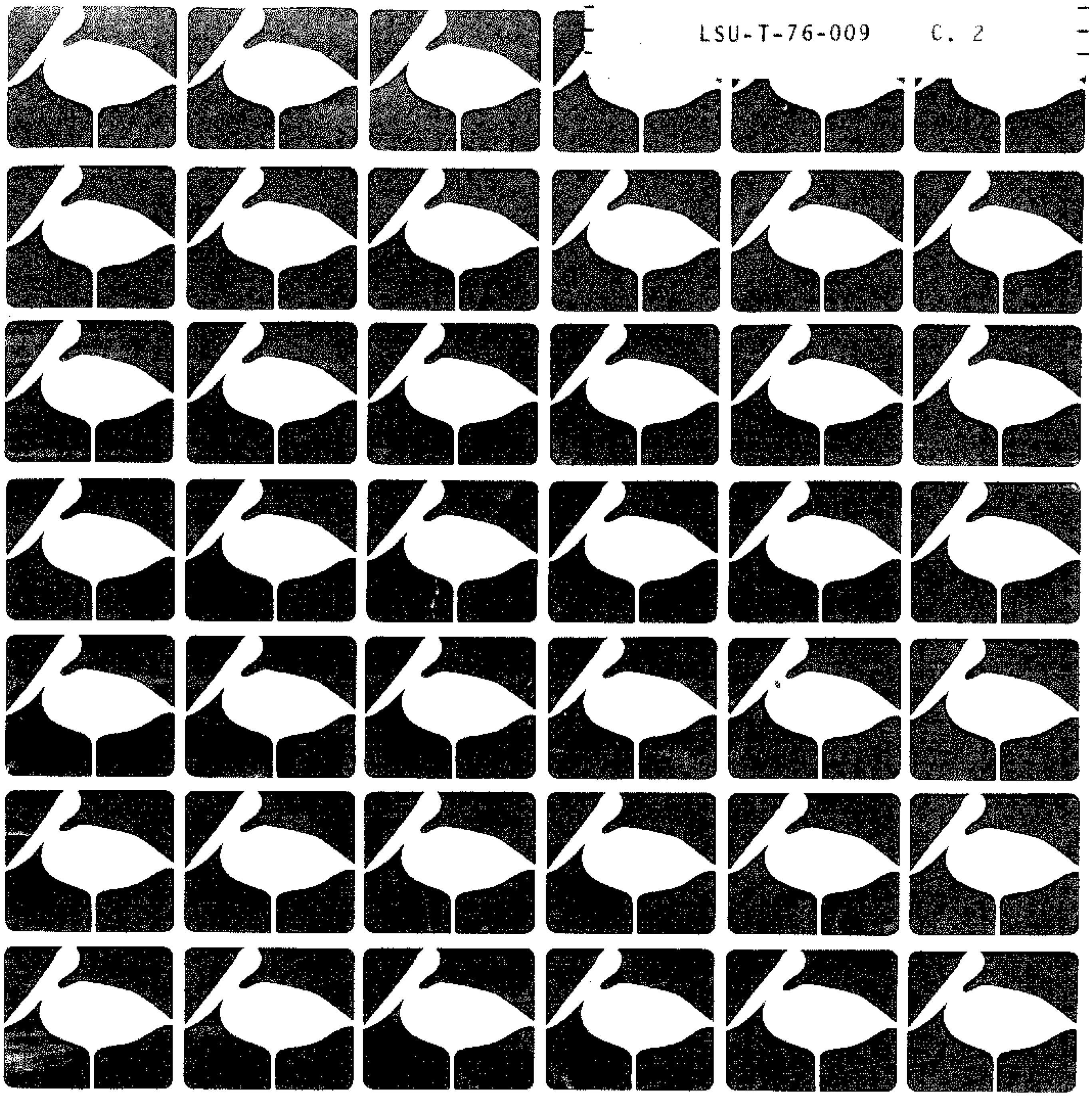

COASTAL ZONE MANAGEMENT SERIES

NUTRIENT TRANSFORMATIONS IN LOUISIANA SALT MARSH SOILS

R. D. DeLAUNE W.H. PATRICK JR. J.M. BRANNON

SEA GRANT PUBLICATION NO. LSU-T-76-009
CENTER FOR WETLAND RESOURCES · LOUISIANA STATE UNIVERSITY · BATON ROUGE, LOUISIANA 70803

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R. D. DeLaune is Research Associate and W. H. Patrick Jr. is Professor respectively, Agronomy Department, Louisiana State University, Baton Rouge, La. 70803

J. M. Brannon was formerly a graduate assistant in the LSU Marine Sciences Department, now Marine Geochemist, U.S. Army Engineers Waterways Experiment Station, Vicksburg, Miss. 39180

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Introduction

Louisiana's Barataria Bay salt marsh can be considered a chemical system in the broadest sense. Chemical and microbiological oxidation-reduction (redox) processes occurring in marsh soils influence plant rhizosphere conditions and the availability of plant nutrients. The lack or deficiency of oxygen results in the predominance of reduction processes that create an anaerobic plant root zone. Reduced forms of iron, manganese, nitrogen, and sulfur predominate. Organic matter decomposition is not as rapid nor as complete as under aerated conditions, and organic acids and other toxic substances are present. Marsh plants have specialized gas transport systems that enable them to obtain atmospheric oxygen internally. In addition to the ability to obtain oxygen, the adaptability of plant species to such an environment is determined by their ability to tolerate or neutralize toxic conditions brought on by anaerobic conditions as well as by additional restraints such as salinity and temperature.

Marsh soils of Barataria Bay are more or less permanently saturated or submerged. The upper layer of soil, which is important to plant growth, is either a peat or muck. This organic matter provides a source of electrons for biological reduction. Oxygen movement through the overlying floodwater is much slower than the rate at which oxygen can be consumed in the underlying soil or sediment. Generally the oxygen in the overlying tidal water remains relatively high because of the rather low density of oxygen-consuming organisms, photosynthetic oxygen production by algae, and the movement of water by wind and convection currents. The marsh soil or sediment is in an extremely reduced condition, with no measurable oxygen at a depth of more than a few millimeters.

A striking feature of the salt marsh is the productivity of the marsh grass *Spartina alterniflora*. *Spartina* covers the marsh in almost pure stands and is the only higher plant of importance in large regions of the marsh. *Spartina* is a large-scale contributor to estuarine productivity and is a tremendous source of substrate and nutrients for microbial transformation processes.

Characteristics of Wetland Soils

Absence of Molecular Oxygen

The soils and sediments of Barataria Bay generally remain either inundated or saturated. The periodic rise and fall of the tide is subject to the effects of changing weather conditions. Prolonged southerly winds will move gulf water into the bay. The depth of flooding is determined by the duration and velocity of the winds. During the winter strong northerly winds have an opposite effect, and water levels as low as two feet below normal are not uncommon. The marsh will not have any overlying tidal water, but the marsh surface will generally remain saturated. Gas exchange between saturated or submerged soils and air is drastically curtailed. Oxygen and other atmospheric gases can enter the soil only by molecular diffusion in the interstitial water. This process is much slower than diffusion in gas-filled pores. Within a few hours of submergence, microorganisms use up the oxygen present in the water or trapped in the soil and render a submerged soil void of molecular oxygen.

Reduction Processes

Redox potential can be used as an indicator of the intensity of oxidation or reduction in sediments. An oxidation-reduction reaction is a chemical reaction in which electrons are transferred from a donor to an acceptor. ·The electron donor loses electrons and increases its oxidation number or is oxidized; the acceptor gains electrons and decreases its oxidation number or is reduced. The source of electrons for biological reduction is organic matter. A redox potential measurement is of much more value in flooded soils and sediments than in well-drained systems because, in well-drained systems, the redox potential range only extends from about +700 mv to +400 mv, whereas in flooded marsh systems where oxygen is depleted, the redox potential range can extend over the entire range from +700 mv to -300 mv, which is a highly reduced system. Reduction of flooded soils proceeds in a sequential manner. Oxygen is the first soil component to be reduced, and it becomes undetectable within a day after submerging a soil. The next oxidant to be attacked is nitrate, but nitrate reduction begins only after the oxygen concentration has dropped. Just as the presence of oxygen retards nitrate reduction, so does the presence of nitrate retard the reduction of other redox components such as manganese, iron, and sulfate.

Manganese follows nitrate in the reduction sequence, with manganic forms being reduced to the more soluble manganous form. Ferric iron is the next mineral system in the thermodynamic sequence to be reduced. Sulfate is then attacked by specialized anaerobic bacteria and reduced to sulfide. After most of the sulfates have been reduced to sulfide, methane begins to be produced, thus resulting in carbon dioxide being converted to methane soon after the sulfate reduction takes place. Figure 1 shows the redox potential where each of the above reactions occur. An energy source is necessary for all of these reduction reactions to occur.

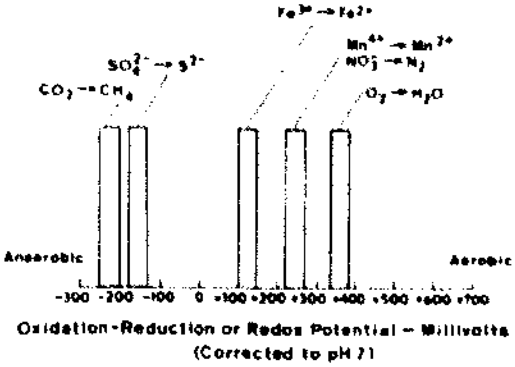

Figure 1. Oxidation-reduction potential at which various reducible inorganic substances in flooded soils and sediments are reduced.

Oxidized Sediment-Water Interface

In flooded soils and shallow water bodies oxygen in the overlying floodwater reaches the soil surface through diffusion and convection currents. Because of greater demand for oxygen at the soil surface, as compared to renewal through diffusion, two distinctly different layers are developed (Fig. 2): (1) an oxidized or aerobic surface layer where oxygen is present, and (2) an underlying reduced or anaerobic layer in which no oxygen is present. If biological activity is high enough, sometimes this surface oxidized layer is missing, and the floodwater itself may be reduced. Pearsall and Mortimer (1939) measured various redox components in the water above a lake bottom, in the aerobic surface mud layer, and in the underlying oxygen-free mud and found that the surface layer of mud contained the oxidized forms of iron, manganese, inorganic nitrogen, and sulfur, while the underlying mud contained reduced forms of these elements. Patrick and DeLaune (1972) characterized the oxidized (aerobic) and reduced (anaerobic) soil layers by measuring the redox potential and the distribution of reduced components such as Fe^{2+}, Mn^{2+}, and $S^{=}$. They found that the apparent thickness of the aerobic layer was different when evaluated by the distribution of the various components in the profile, with the sulfide representing the thickest oxidized zone, the manganese profile representing the thinnest oxidized zone, and the iron profile showing an intermediate thickness.

Seasonal changes in redox potential occur in the upper 5 cm of the soil profile for both streamside and inland areas of Barataria Bay (Fig. 2). Soil redox potential drops during the summer when the temperature is higher and when prevailing southerly winds keep the soil inundated. Redox potential values for the surface 5 cm are higher during the winter months when northerly winds tend to keep tidal water away from the marsh. It is important to note that the

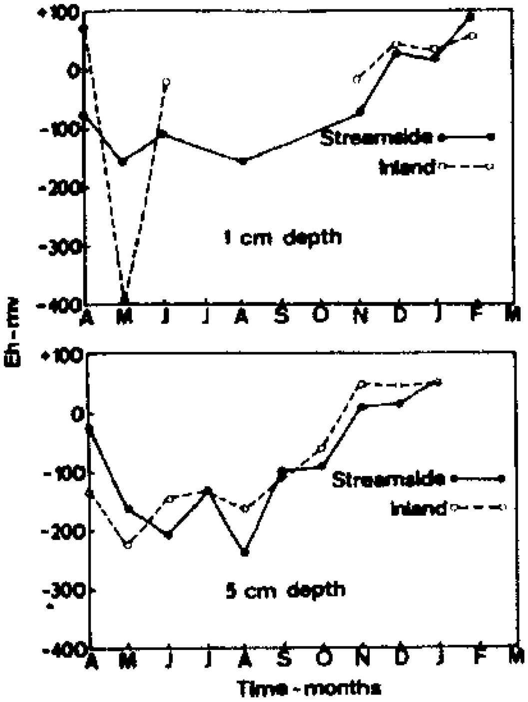

Figure 2. Seasonal variation of redox potential at the 1- and 5-cm depth in the streamside and inland areas.

soils are not oxidizing, even when redox potentials as high as +100 are reached in January and February. There is no significant seasonal redox change at depth of 10 and 30 cm (Fig. 3). The period in which there is no surface water on the marsh is not long enough to cause change at these depths.

Soil Morphology

The marsh soils of Barataria Bay can generally be classified as peats, mucks, or clays, with all occurring in various proportions. The dark brown and black colors of the peats, mucks, and organic clays, and the gray colors associated with reduced conditions are the dominant morphological characteristics (Lytel 1968). The soil materials are silts, silty clays, and clays of recent alluvial origin, plus marine silts and clays overlaid by peats and mucks (Lytle and Driskell 1954).

The depth of the organic layer is determined by the amount of subsidence and the vegetative history of the area. The Barataria Bay area is subsiding at the rate of approximately one foot per century (W. G. McIntire, personal communication). The area is maintaining its

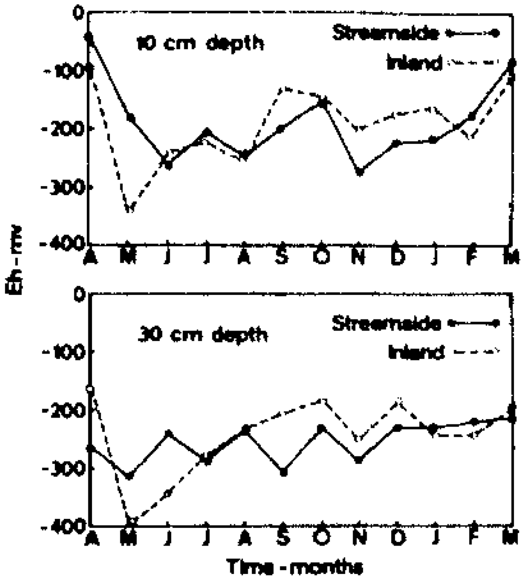

Figure 3. Seasonal variation of redox potential at the 10- and 30-cm depth in the streamside and inland areas.

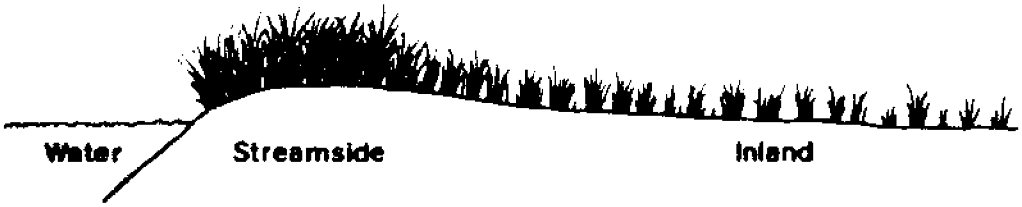

Figure 4. Schematic of the Barataria Bay salt marsh showing streamside and inland areas of the marsh.

surface elevation by building up an organic layer. The organic layer can range from a depth of a few inches to several feet. Spartina alterniflora is the dominant plant species involved in the organic accumulation. As the organic layer builds up, some sediment is entrapped with the organic material that accumulates. Streamside locations have higher elevations as a result of greater sediment capture (Fig. 4). There is also a marked difference in productivity. There is a close relationship between the dry weight of the aboveground plant material and the density of the soil sediment (Fig. 5). Soils with greater densities containing larger amounts of mineral material are more productive. There is an inverse relationship between soil organic carbon and productivity (Fig. 6). Upland mineral soils have oven dry densities in the order of 1.2 g/cc to 1.4 g/cc. The salt marsh of Barataria Bay has soil densities ranging from approximately .18 g/cc to .30 g/cc. The higher density soils are associated with streamside areas; however, lower density soils containing more organic matter are associated with inland areas where there is less productivity.

The nutrient content of Barataria Bay's organic soils may be quite high on a total dry mass basis, but rather low on a volume basis, especially peat soils with low density of the order of .15 to .20 g/cc. Data expressed on a volume basis is more meaningful in explaining plant distribution because plant distribution and productivity must relate to soil in its natural state (Clarke and Hannon 1967).

One streamside area of Barataria Bay marsh contained 19.0 percent organic matter to a depth of one foot, compared to 32.7 percent organic matter in an inland location. The inland area contained 190 mg/g total carbon compared to 110 mg/g in the streamside area. The large difference in total carbon between the streamside and inland areas on a weight basis disappeared when considered on a volume basis. Streamside areas contained 31 mg/cc total carbon compared to 27 mg/cc total carbon in the inland areas on a volume basis.

pH and Conductance

The changes in pH of salt marsh soils of Barataria Bay are governed by the same mechanisms that operate in flooded soils. The overall effect of submergence upon a soil is to increase the pH of acid soils and to depress the pH of sodic and calcareous soils. Submergence makes the pH values of acid soils--with the exception of those low in iron--and alkaline soils converge to pH 7.0 (Ponnamperuma 1972). The pH of submerged soils is buffered around neutrality by the action of substances produced as a result of reduction reactions. The more likely compounds that buffer pH in waterlogged soils are iron and manganese compounds in the form of hydroxides and carbonates, and carbonic acid (Patrick and Mikkelsen 1971). Organic matter can

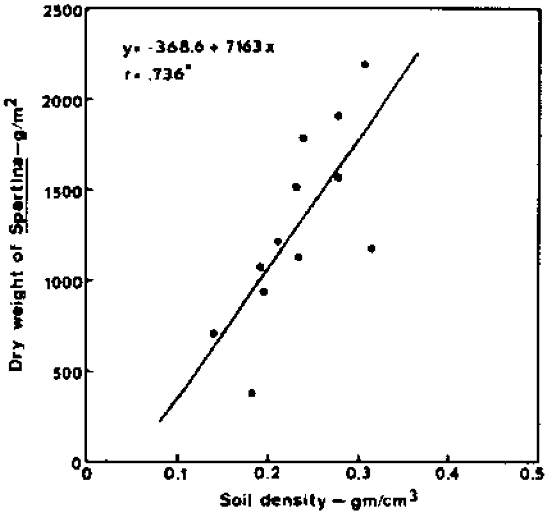

Figure 5. Relationship of soil density to growth of *Spartina alterniflora*. Density values represent soil density to depth of 53 cm. Dry weight of *Spartina* determined by harvesting in September the aboveground plant material contained in meter square plot.

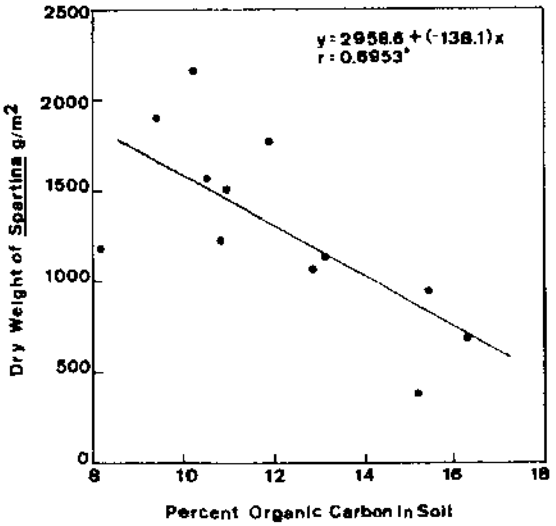

Figure 6. Relationship of soil organic carbon to growth of *Spartina alterniflora*. Organic carbon represents carbon from 0 to 53 cm depth. Dry weight of *Spartina* determined by harvesting in September the aboveground plant material contained in meter square plots.

influence pH changes by intensifying reduction and through the concentration of carbon dioxide and organic acids (Motomura 1962).

Ruttner (1963) postulated that marsh soils may have a low pH limit because of humic acids. Gardner (1973) found peak pH values near 6.65 in samples obtained from marsh areas remote from both marginal sources of fresh groundwater and main tidal creeks. The dilution of samples of highly reduced water with fresh water causes a rise in pH and Eh in these interstitial waters. Freidman and Gavish (1970) noted pH values ranging from 6 to 6.6 in a Connecticut tidal marsh. The range of pH for surface soils in the Australian salt marsh was from 4.1 to 7.6. The surface soil in the more landward zones tended to be more acidic, whereas the subsurface soil remained relatively constant throughout. There was no apparent change associated with season or locality (Clarke and Hannon 1967). Coultas (1970) reported a pH value of 7.1 for the salt marsh of northern Florida located some distance from the open gulf. Values for pH obtained in southern Barataria Bay sediments were between 7.0 and 7.8 (Ho 1971).

Seasonal pH values of Barataria Bay marsh soil are generally between 6 and 7, except for the streamside locations where several values were reported as low as pH 5 during the winter months (Fig. 7). There is a lack of pH change in the inland area because it remains underwater for a much greater time than the streamside areas. During the winter months a lower pH at the slightly higher elevated streamside locations occurs when tides less frequently cover the marsh because of prevailing northerly winds.

Differences in the specific conductance of a flooded marsh soil or sediment throw considerable light on chemical changes occurring in the system. The specific conductance of a soil increases when it is submerged. This increase is caused by the mobilization of Ca^{++} and Mg^{++} in neutral and alkaline soils and in acid soils by the increase in concentrations of Fe^{++} and Mn^{++} and the displacement of mainly Ca^{++} and Mg^{++} by cation-exchange reactions (Ponnamperuma 1965). The changes in conductance reflect the balance between reactions that produce ions and those that inactivate them or replace them with slower moving ions (Ponnamperuma 1972). Ponnamperuma et al. (1966) studied the relationship between specific conductance and ionic strength in flooded soils. They found that in spite of wide variations in the ionic composition of the solutions of reduced soils, the ionic strength in moles per liter was numerically equal to 16 times the specific conductance (k) in mhos/cm at 25°C up to ionic strengths of 0.05.

There is a definite seasonal trend in specific conductivity of soil water (Fig. 8). Specific conductivity of soil water increases in spring and summer and decreases through the fall and winter, varying between 17 and 27 ppt in salt. Microbial activity increases in the spring and summer when temperature increases, thus increasing intensity of reduction and concentration of the reduced forms of iron and

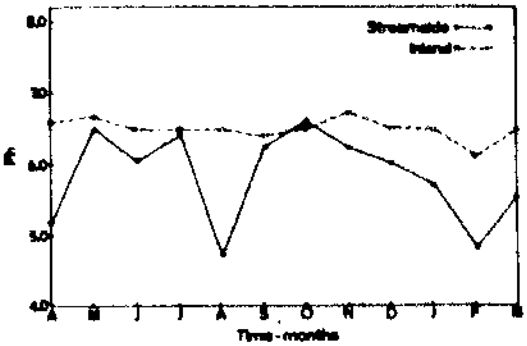

Figure 7. Seasonal variation of pH in the streamside and inland areas. Measurements determined by inserting combination pH electrode 5 cm into the soil.

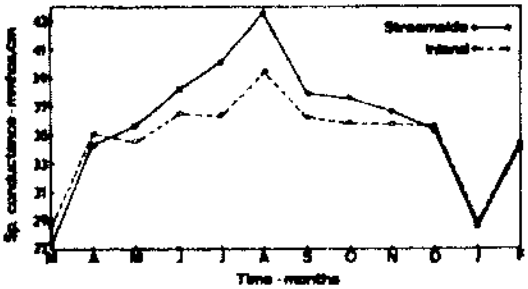

Figure 8. Seasonal variation of specific conductance in the streamside and inland areas.

manganese. Prevailing southerly winds during the spring and summer months tend to blow more saline water from the Gulf of Mexico into the marsh, which also increases specific conductivity of soil water.

Chemical Transformations Occurring in Wetland Soils and Sediment

Carbon

The two main transformations of carbon in the wetlands of Barataria Bay occur through photosynthesis and respiration. Net photosynthesis occurring in *S. alterniflora*, the predominant plant species, fixes as much as 1,500 g C/m^2/year. In the flooded marsh soil, respiration (decomposition of organic matter) is the main transformation process.

Organic matter decomposition

The decomposition of organic matter in submerged soils and sediments is slower, and the end products are different from that in well-drained or aerated soils. In a well-drained soil, decomposition of plant residue is accomplished by a large group of microorganisms. The high energy release associated with the aerobic respiration of these organisms causes rapid decomposition of substrate and synthesis of cell substance. Organic matter in aerated soils disappears largely as carbon dioxide. In submerged soils the decomposition of organic matter is almost entirely the work of facultative anaerobes. Anaerobic bacteria operate at a much lower energy level, with decomposition and assimilation being much slower in submerged soils. The accumulation of organic matter in Barataria Bay marsh soils illustrates this point.

The metabolic degradation of carbohydrates is the same under both aerobic and anaerobic conditions until the formation of pyruvic acid as the final end product. In aerobic soil pyruvic acid enters the Krebs cycle. This is a common pathway not only for the oxidation products of glycolysis, but also for the ultimate oxidation of the fatty acids and the carbon skeleton of many amino acids. The cycle converts all of these carbocylic acids to carbon dioxide and water in the presence of molecular oxygen. In flooded marsh soils, marked by the virtual absence of oxygen, the terminal oxidation is suppressed, resulting in the accumulation of pyruvic and reduced nicotinamideadenine dinucleotide. The pyruvic acid in turn undergoes various transformations not specific to any organism, but presenting a common feature of anaerobic decomposition.

The end products of anaerobic decomposition are chiefly carbon dioxide, methane, hydrogen, organic acids, ammonia, amines, mercaptan, hydrogen sulfide, and resistant residues.

The metabolic channel of protein breakdown is probably the same both under aerobic or anaerobic conditions until the formation of amino acids occurs. Under aerobic conditions, the process of deamination takes place, and the carbocylic acids formed are channeled into the Krebs cycle. The ammonia formed is either held on colloidal particles or is oxidized to nitrate through the action of nitrifiers. Under anaerobic conditions, on the other hand, the products of deamination and of subsequent decarboxylation may accumulate or be transformed into gaseous products. The final end products of the decomposition of protein in flooded soils and sediment are ammonia, carboxylic acids, amines, mercaptan, and hydrogen sulfide.

Methane production

Methane is a typical end product of the anaerobic decomposition of organic matter in sediment soils of Barataria Bay. The gas escapes from the marsh in large amounts, probably accompanied by smaller amounts of carbon dioxide, hydrogen sulfide, and hydrogen. Methane formation is ecologically important because it helps in the disposal of large amounts of organic matter in sediments and flooded soils.

Carbon dioxide is susceptible to anaerobic carbon dioxide respiration by methane bacteria. Carbon dioxide produced by the oxidation of organic matter or present in flooded soils is reduced to methane by anaerobic respiration, although the biochemical reduction mechanism has not been established. Several bacteria are capable of using molecular hydrogen in reducing carbon dioxide to methane:

$$CO_2 + 4\ H_2 \longrightarrow CH_4 + 2\ H_2O$$

Although hydrogen is a common end product of anaerobic metabolism, loss of hydrogen to the atmosphere from flooded soils is small because methane-producing bacteria use molecular hydrogen as a source of energy for growth.

Methane is produced by a small group of obligate anaerobes found in reduced sediments. Methane bacteria are highly substrate specific and can only metabolize a small number of simple organic and inorganic substances. Organic acids rather than sugars constitute the basic substrate for the production of methane. The anaerobic carbon breakdown must therefore be characterized by the formation of organic acids, methane, and carbon dioxide as the major end products.

Anaerobic breakdown of organic materials to form methane proceeds in three steps: (1) hydrolysis of organic material by enzymes, (2) production of organic acids by facultative anaerobic bacteria, and (3) production of methane by nonmethanogenic and methanogenic bacteria in sediments (Lawrence 1971). The conversion of acids to methane is considered the rate-limiting step, and the methanogenic bacteria appear more sensitive to environmental factors such as pH, Eh, and inhibitory substances than the acid producers.

While organic volatile acids are nontoxic in concentrations up to 6,000 ppm (except possibly proponic acid), some heavy metals at concentrations higher than 1 ppm are considered toxic to methane production. With sulfides present at concentrations of several hundred ppm in the marsh soil of Barataria Bay, higher total concentrations of metals are likely tolerable as the solubility products of heavy metal sulfides are very low and the metals are removed from solution.

There is a relationship between sulfate reduction and methane production. Methane production does not occur until most of the sulfate present in soils is reduced to sulfide. Methane seems to be produced at an Eh as low as or slightly lower than where sulfate reduction occurs. Reduction of sulfate to sulfide thus acts as an Eh buffer, preventing methane from being formed until all of the sulfate is reduced. Because of the presence of sulfate in seawater, methane production is probably not as pronounced in the lower end of the estuary as in the upper end. Sulfate is reduced to sulfide in the range of between -150 and -200 mv. Methane is produced between -200 and -250 mv.

Nitrogen

Nitrogen occurs in marsh soils mainly as organic nitrogen and ammonium nitrogen. Nitrate is very unstable under reducing conditions and undergoes denitrification, and thus does not accumulate. The organic fraction consists of a vast array of simple and complex substances. The greater portion is in the organic form (as high as 6,000 ppm), and only a small amount appears in the inorganic form, mainly as ammonium. Any nitrate formed in the oxidized surface layer or in the oxidized root rhizosphere is rapidly denitrified or taken up by the plant. It is the inorganic fraction that is the immediate source of plant available nitrogen, with the organic form being unavailable unless it is converted to the inorganic form.

Nitrogen mineralization

The mineralization of organic nitrogen in flooded marsh soils stops at the ammonia stage because of the lack of oxygen for nitrification to nitrate (Ponnamperuma 1972). Ammonia therefore accumulates in anaerobic soils unless it is taken up by plants. Nitrogen mineralization is carried out by general purpose heterotrophic bacteria, which utilize nitrogenous organic compounds as their energy source. The immobilization process transforms the inorganic nitrogen into organic compounds. The inorganic nitrogen is assimilated by microorganisms and metabolized into nitrogenous constituents of their cells. In the general case, mineralization is always accompanied by immobilization, and the two processes tend to counteract each other as far as the production of inorganic nitrogen is concerned (Jansson 1963).

The nitrogen mineralization process is endothermic and requires a plentiful supply of organic material as an energy source. This organic matter is readily available in the peats and mucks of the salt marsh of Barataria Bay. The restricted, less efficient group of organisms involved in anaerobic organic matter decomposition has a low nitrogen requirement (Alexander 1961). Waring and Bremner (1964a,b) found that considerably more nitrogen was mineralized under waterlogged conditions than under aerobic conditions for a number of soils. Incubation of organic soils under waterlogged conditions shows that much of the mineralizable nitrogen was derived from the acid-soluble organic nitrogen, coming mostly from the hexosamine-nitrogen, amino acid-nitrogen, and unidentified-nitrogen fractions. Considerable microbial turnover of hydrolyzable-nitrogen to refractory (nonhydrolyzable)-nitrogen occured (Isirimah and Keeney, 1973).

Ammonium in the sediment is capable of being held in either the exchangeable or fixed form. It has been well established that soils have the capacity to fix ammonium (Bremner 1965). Allison et al. (1953) showed that illite and vermiculite can more easily fix ammonium than montmorillonite.

Ammonium, like other cations, is capable of occupying the exchange sites of various silicate minerals. The amount of exchangeable ammonium present will depend on the abundance and type of clay minerals present. Hall et al. (1970) have shown that S. alterniflora contains a relatively high percentage of amino acids. The bacterial degradation of these acids is probably the most important source of nitrogen in the marshes. Maye (1972) found low concentrations of exchangeable ammonium in the marsh sediments of Georgia in July and August. The concentrations were quite varied and showed no distinct relationship with depth. The ammonium concentration was highest in areas of thick S. alterniflora growth, although concentrations in these areas were low until depths of 40 to 60 cm had been reached in the cores. Fixed ammonium was always present in greater concentrations than the exhangeable form, being on the average five times higher in concentration.

A definite seasonal variation existed in extractable (water-soluble + exchangeable) ammonium in both the streamside and inland areas (Fig. 9). Extractable ammonium was low in spring for both locations, with increases beginning in August for the inland area and in September for streamside. These low levels in spring and higher values in fall and winter correspond to the seasonal variation of ammonia in the water of Airplane Lake in Louisiana (Ho 1971). The inland area peaked at 48.5 µg/g in October, while the streamside area reached its maximum a month later in November with 23.4 µg/g. When considered on a volume basis these maxima were virtually identical, 6.5 mg/cc for streamside compared to 7.0 mg/cc for inland. After the peak values, there was a steady decline during the fall and winter until a rise was noted in March.

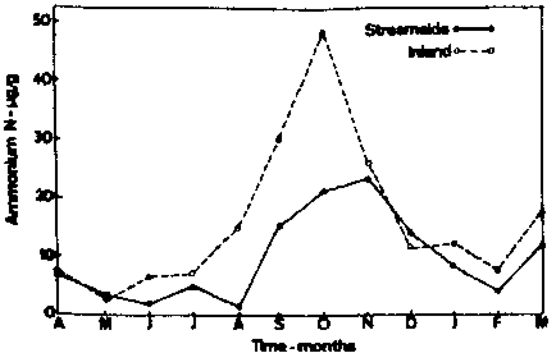

Figure 9. Seasonal variation of extractable ammonium-N in the streamside and inland areas. Ammonium was extracted with 1 N sodium acetate, pH 4.0, steam distilled, and analyzed colorimetrically by nesslerization.

The main factors influencing the levels of extractable ammonium nitrogen in the salt marsh appear to be plant growth and temperature. Levels of ammonium were low in spring when maximum uptake of ammonium by S. alterniflora was occurring, even though there was a constant renewing of soil ammonium by mineralization. Laboratory studies have shown that Barataria Bay marsh soil is capable of supplying approximately 12 µg nitrogen per gram of soil per week (Fig. 10). The low ammonium content of the soil in spring coincided with the period of peak true net production of S. alterniflora in both areas (Kirby 1972). As the true net production decreased and reached a steady value, ammonium concentration in the soil increased. If the ammonium concentration is considered on a dry weight basis, it appears that there was sufficient inorganic nitrogen for good plant growth, but values for extractable ammonium in spring on a volume basis were less than 1 µg/cc for both areas. This would seem to indicate the S. alterniflora was removing ammonium (the only form of inorganic nitrogen in the soil at the Eh values found) from the soil solution at nearly the same rate as mineralization occurred. There may be a plant response to added ammonium in the spring in view of the low values found for extractable ammonium.

Denitrification

Denitrification can be defined as the biochemical reduction of nitrate to gaseous end products such as N_2 or N oxides. Denitrification is brought about by a large number of bacteria and fungi that include heterotrophic and autotrophic species. These facultative organisms transform nitrate to nitrogen and its oxides at only very low oxygen concentratons.

Denitrifying organisms need a source of hydrogen ions and electrons to reduce nitrate and a carbon source and ammonia for all synthesis.

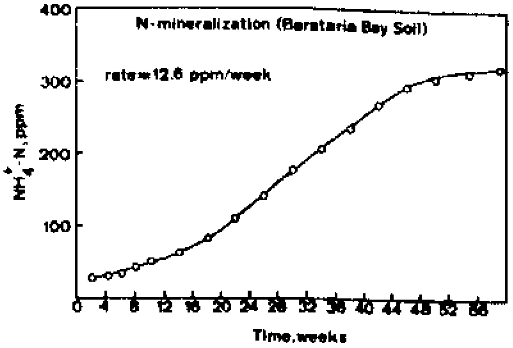

Figure 10. Nitrogen mineralization rate of Barataria Bay soil. Ammonium nitrogen released by mineralization from soil was continuously extracted with a slow flow of oxygen-free (2 percent) NaCl solution.

The high organic marsh soils of Barataria Bay provide all of these ingredients. The limiting factor in denitrification is the production of nitrate in these anaerobic soils.

The surface aerobic layer corresponds to an oxidized zone where microorganisms live aerobically. In the root rhizosphere of *S. alterniflora* the soil in close proximity to the root is distinctly oxidized as a result of oxygen diffusion through the root and into the sediment. In these oxidized microzones of flooded marsh soils ammonia can be oxidized to nitrate. The soluble nitrate thus diffuses into the adjoining anaerobic layer and is denitrified. An estimated twenty kilograms of nitrogen per hectare per year (20 Kg N/ha/yr) is estimated to be lost from the Barataria Bay system through this process.

Nitrogen fixation

Biological nitrogen fixation is the reduction of nitrogen gas to ammonia. Submerged sediments, containing blue-green algae and sometimes nitrogen-fixing photosynthetic bacteria at the surface and nitrogen-fixing bacteria in the bulk of the sediment are a favorable environment for nitrogen fixation.

There is increasing evidence that nitrogen-fixing bacteria make a significant contribution to the total nitrogen budget in aquatic environments. Patriquin and Knowles (1972) indicated that a marine angiosperm, *Thalassia testudinuns*, obtained virtually all of its nitrogen through the activities of nitrogen-fixing bacteria in the rhizosphere. Other marine grasses, including *S. alterniflora*, probably also rely on the activities of these bacteria to varying extents, depending on the availability of combined sources of nitrogen in the environment.

Blue-green algae of the genera, Nostoc, Anabaena, Ocillatoria, Tolypothrix, Calothrix, Phormidium, Aulosira, and others have been shown to be able to fix nitrogen in flooded environments. Nitrogen fixation by free-living bacteria is perhaps equally important because the environment of flooded marsh soils is suitable for both aerobic and anaerobic nitrogen fixing. Aerobic bacteria presumably can thrive in the oxygenated surface layer and in the oxygenated rhizosphere of Spartina, sustained by soluble substrates diffusing from the roots and from the anaerobic soil matrix.

Nitrogen gas, along with oxygen, is transported from the shoot to the root of Spartina and presumably diffuses out with oxygen into the rhizosphere. This ensures a supply of nitrogen for the aerobic fixers in the rhizosphere and perhaps for the anaerobic fixers just outside the oxygenated rhizosphere.

Measured fixation rates of the soil-plant system at a streamside location in Barataria Bay showed that nitrogen was being fixed in the order of 10 kg N/ha/yr. There is some capture of sediment at the streamside location. The sediment nitrogen is mineralized, thus reducing the demand for nitrogen through fixation at the streamside sites.

Laboratory studies have shown that Barataria Bay soils fixed more nitrogen under highly reducing conditions near pH 7. As these soils are oxidized and pH decreases, the fixation rate declines.

Nitrogen Budget of Streamside Location
in Barataria Bay

Eh	pH	µ/g N/m sediment fixed per day
-250	7.0	1.34
0	6.2	1.08
+410	5.1	0.15
+700	4.4	0.08

Determination of nitrogen budgets is of unquestionable value in understanding the dynamics of the various forms of nitrogen as a nutrient in natural systems. Research on the nitrogen status of the Barataria Bay marsh-estuarine habitat has led to the completion of a workable nitrogen model for a streamside location in a S. alterniflora marsh.

Figure 11 illustrates measured or estimated values for: (a) nitrogen fixation, (b) nitrogen input from sediments, (c) nitrogen added by rainfall, (d) nitrogen loss through detrital export, (e) plant uptake, (f) mineralization of soil organic nitrogen, and (g) denitrification losses.

Figure 11. Nitrogen budget of *Spartina alterniflora* in streamside location, g/m^2.

The marsh soil contains 7,850 kg/ha of nitrogen in the *Spartina* root zone. This nitrogen is mainly organic nitrogen, some of which is capable of being mineralized. Approximately 250 kg/ha/yr of the soil organic nitrogen is mineralized to inorganic nitrogen, which is available to plants. *S. alterniflora*, the dominant plant species, incorporates 130 kg/ha/yr in shoot tissue, and 100 kg/ha/yr is estimated to be incorporated in roots, or a total of 230 kg/ha/yr in the complete plant. The remaining 20 kg/ha/yr is thought to be lost through denitrification.

Detrital export is estimated to remove 40 kg/ha/yr from the system. The two pathways in which nitrogen is lost from the system are detrital export and denitrification, which removes a total of 60 kg/ha/yr.

The main nitrogen inputs into the system are from sediment deposited at streamside areas and from biological nitrogen fixation. Nitrogen fixation was determined in the field seasonally using the acetylene reduction technique (Stewart et al. 1967). Nitrogen was found to be fixed at a rate of approximately 10 kg/ha/yr. Greater fixation rates were observed in the warmer months of spring and summer. Nitrogen coming in with sediment deposited at a streamside area was calculated to be 40 kg/ha/yr. The area in study is subsiding at a rate of 3 mm per year. The marsh at the streamside location is maintaining its elevation by building up a peaty soil layer containing some entrapped sediments. A 3-mm layer of sediment (.56 percent nitrogen), with a bulk density of .24 g/cm^3 being deposited yearly would add 40 kg/ha/yr of nitrogen to the system. An additional 8 to 10 kg/ha/yr would be added through rainfall. Total nitrogen input is estimated to be 60 kg/ha/yr.

Iron

One of the most important chemical changes that takes place when a soil is submerged is the reduction of iron and the accompanying increase in its solubility. The chemical consequences of iron reduction are: (a) the concentration of water-soluble iron increases, (b) pH increases, (c) cations are displaced from exchange sites, (d) the solubility of phosphorus and silica increases, and (e) new minerals are formed (Ponnamperuma 1972). Patrick (1964) noted a large release of ferrous iron when the redox potential of the soil fell below +200 mv. This increase was attributed to the reduction of insoluble ferric compounds that became unstable at this reducing potential. Turner and Patrick (1968) found that no reduction of iron occurred until both oxygen and nitrate had disappeared from flooded soils. The oxides and hydroxides of ferric iron (ferric oxyhydroxides) are the major forms of iron in the sediment that are affected by reduction-solubilization reactions. Strengite ($FePO_4 \cdot 2H_2O$) also partially dissolves under reducing conditions. The greatest release of iron and phosphate occurs in the presence of low redox potential in conjunction with low pH (Patrick et al. 1973). The release of iron increases with increasing organic matter in flooded soils. The organic matter serves as an energy source for the microorganisms that reduce ferric iron to the ferrous form (Redman and Patrick 1965).

Higher temperatures (38°C) resulted in high concentrations of Fe^{++} that soon drop because of increasing pH. Low temperature (20°C) retarded but did not prevent the buildup of Fe^{++} in the soil solution. The Fe^{++} concentrations were most persistent at 20°C. Acid soils high in organic matter and iron can build up concentrations of Fe^{++} as high as 450 ppm in the interstitial waters within two to three weeks after submergence (Cho and Ponnamperuma 1971).

The concentration of exchangeable ferrous iron in the streamside area of Barataria Bay is markedly higher than in the inland area (Fig. 12). This difference is because of the lower content of mineral material in the inland area. The streamside area had a ferrous iron concentration in the range 300 to 500 μg/g, as compared to 50 to 100 μg/g for the more organic inland area.

Seasonal fluctuations of ferrous iron at both locations are probably because of changes in redox potential, which in turn are because of changing water regime. Ferrous iron may also be removed from the soil solution by precipitation of ferric oxides around the oxidized rhizosphere of S. alterniflora during the summer when the plant is actively growing.

Ferrous iron on a dry weight basis is extremely low in the marsh, compared to levels of ferrous iron in mineral soils after submergence (Redman and Patrick 1965). Mineral soils usually reach levels between 1,000 and 2,000 μg/g of extractable ferrous iron after thirty days' submergence. When considered on a volume basis, the differences are even more striking. The streamside area varied between 164.7 μg/cc and 37.5 μg/cc extractable ferrous iron during the year, while the inland area was even lower and varied within 20.6 μg/cc and 3.8 μg/cc extractable ferrous iron. These low levels of ferrous iron in the marsh

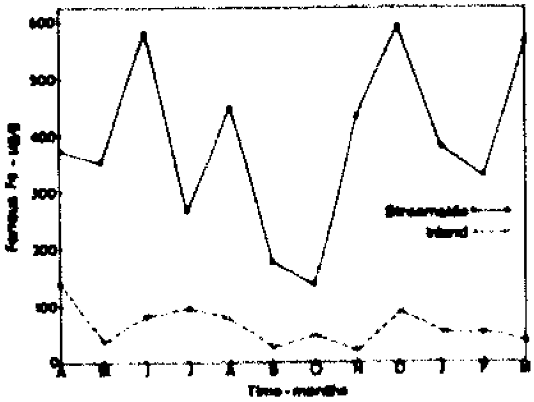

Figure 12. **Seasonal variation of extractable ferrous iron in the streamside and inland areas.** Ferrous iron extracted with 1 N sodium acetate, pH 4.0 and analyzed by atomic adsorption spectrophotometry.

soil, even when the soil is most reducing, have a great effect on the chemistry of the marsh soil. In these reduced marsh soils with sulfate available, a low iron content results in most of the hydrogen sulfide formed from reduction of the sulfide escaping into the atmosphere. Excess sulfide could cause an iron deficiency by precipitating all available ferrous iron as insoluble ferrous sulfides, although Yamane and Sato (1961) found added iron ineffective in preventing the evolution of free hydrogen sulfide from muck soils. Harter and McLean (1965), on the other hand, found iron effective in preventing hydrogen sulfide evolution from a soil with 16 percent organic matter.

Manganese

Little work has been done on manganese in marsh soils. Most work to date has been with flooded mineral soils. Turner and Patrick (1968) found that the conversion of easily reducible manganese to the exchangeable and water-soluble form in a waterlogged soil began at a redox potential of +400 mv and was greatest when the redox potential decreased to around +200 mv. As the content of exchangeable Mn^{++} increased, the content of reducible Mn of an anaerobic silty clay decreased. Soluble and exchangeable manganese increased with decreases in both pH and Eh down to pH 6.0. At pH 5.0 the effect of acidity in bringing manganese into solution was so marked that changes in redox potential had little effect on manganese solubility. Manganese reactions in soils are apparently regulated not only by chemical restraints on the manganese systems in flooded soils, but also by microbial oxidation-reduction processes (Gotoh and Patrick 1972). The influence of temperature on the kinetics of manganese concentrations is similar to that of iron. Low temperatures (20°C) retarded the buildup of Mn^{++}, but the concentration so developed is most persistent at this temperature. Acid soils high in manganese and organic matter build up water-soluble Mn^{++} concentrations as high as 90 ppm within a week or two after submergence, then decline rapidly to a fairly stable level of about 10 ppm (Cho and Ponnamperuma 1971). Little is known about the mineralogy of manganese in submerged soils (Ponnamperuma 1972) since the dominant form in well-drained soil, pyrolusite (MnO_2), is unstable under reducing conditions.

Many of the factors that affect iron reduction also influence manganese reduction. Changes in redox potential should affect the levels of manganese in marsh soils much less than iron, for manganese is much easier to reduce than iron, being reduced at a higher redox potential than iron. Plant uptake and precipitation of MnO_2, along with coprecipitation with ferric oxides in the oxidized rhizosphere of S. alterniflora, could decrease manganese concentration in the soil solution.

Extractable manganese levels of organic marsh soils are extremely low compared to those of mineral soils. Levels during the year ranged from a maximum of 5.3 μg/cc in the streamside area to a maximum of .63 μg/cc in the inland area (Fig. 13). Flooded mineral soils range between 62 μg/g and 1,400 μg/g extractable manganese after flooding (Redman and Patrick 1965). These low levels of manganese in conjunction with low iron in the marsh soil indicate that reduction of the marsh soil upon waterlogging is rapid and that Eh will drop quickly to low values near the critical level for sulfate reduction, since manganese and iron systems, if they are present in high enough concentrations, tend to buffer the soil at an intermediate redox potential of +100 to +300 mv. Both systems must be almost completely reduced before intense reduction can set in (Patrick and Mahapatra 1968).

Sulfides

The salt marsh of Barataria Bay is a suitable environment for sulfate-reducing bacteria. It contains an ample supply of sulfate from seawater, and organic matter for an energy source, and it has a restricted aeration that leads to reducing conditions. Sulfate reduction has been shown to occur in saline sediments (Baas-Becking and Wood 1955; Whitfield 1969; Ho et al. 1970). Brummer et al. (1971) studied microbial reduction of SO_4-S from seawater in muds. The SO_4-S was reduced, with

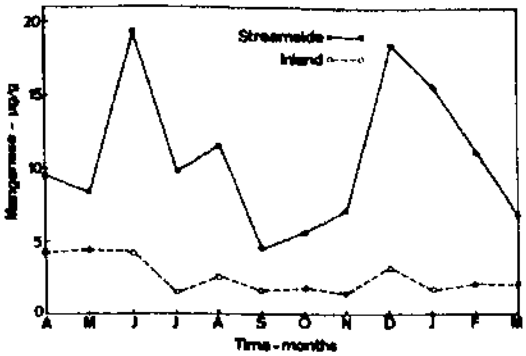

Figure 13. Seasonal variation of extractable manganese in the streamside and inland areas. Manganese extracted with 1 N sodium acetate, pH 4.0 and analyzed by atomic adsorption spectrophotometry.

FeS and elemental sulfur accumulating. The extent of reduction and accumulation depended on the content of organic matter, clay, and iron. Gooch (1968), quoted in Reimold and Daiber (1970), reported that the greatest production of hydrogen sulfide by anaerobic microorganisms in a natural salt marsh in Delaware occurred during the late spring, with the lowest production recorded in late fall. During the early spring when sulfide production was increasing, FeS was formed with the resultant release of phosphorus. In hydrologically dynamic areas near the margins of tidal creeks, fresh seawater influx inhibits maximum development of sulfate reduction (Gardner 1973). Harter and McLean (1965) reported sulfide concentrations in excess of 2,000 ppm without release of hydrogen sulfide from the soil in a clay loam containing 16 percent organic matter after being submerged for forty days.

The production of sulfide is faster in a muck soil than in a sandy soil low in organic matter. Addition of sulfate increased sulfide production in both types of soil (Yamane and Sato 1961). Ogata and Bower (1965) showed that sulfide accumulation increased with time and that the rate of increase was positively related to the organic matter content. Providing sulfate is not limiting, soil organic matter content was shown to be the dominant factor influencing the amount of reduction occurring in poorly drained soils. The sulfide accumulation rate was greater in clay than in sandy soils when both were supplied with equal amounts of organic matter. Connell and Patrick (1969) found added Fe_2O_3 effective in precipitating hydrogen sulfide. The amount of sulfide precipitated from added hydrogen sulfide in two soils was approximately equivalent to the amounts of ferrous iron released by waterlogging. Connell and Patrick (1968) also showed that redox potential was a controlling factor in the reduction of sulfate to sulfide. Sulfate became unstable in the soils studied at potentials around -150 mv. As the redox potential decreased beyond this value, the reduction of sulfate to sulfide was more complete. Little reduction of sulfate to sulfide took place at pH values outside the range 6.5 to 8.5. Yamane and Sato (1961) found that added iron had little effect in preventing the evolution of free hydrogen sulfide from muck soils. They postulated that inactivation of iron as a result of complex formation with soil organic matter resulted in the evolution of free hydrogen sulfide. Allam et al. (1972) showed that hydrogen sulfide accumulates in Louisiana rice soils. The three factors of greatest importance in hydrogen sulfide accumulation were found to be pH, oxidizable carbon, and manganous manganese, with soil pH apparently the predominant factor. Manganese and oxidizable carbon were found to be less important in their study.

Levels of total sulfide (ferrous sulfide, hydrogen sulfide, etc.) range seasonally between 100 and 500 ppm for both streamside and inland areas of Barataria Bay. Levels of total sulfide at both locations are virtually the same when considered on a dry weight basis. On a volume basis, the streamside area is consistently higher. Total sulfides are as low as 100 ppm during the winter months, because of prevailing northerly winds, which move a great deal of the water out of the marsh, thus increasing Eh slightly (Fig. 14). The sharp rise in total sulfide during the spring is because of the increased reduction of sulfate in the water associated with heavier flooding of the marsh and the increase in soil temperature.

The low levels of iron found in these organic soils influence the amount of sulfide accumulation. Large amounts of sulfide would accumulate if there was enough iron to precipitate the sulfide as ferrous sulfide. This is illustrated by the relatively large amounts of free sulfide (hydrogen sulfide) present (Fig. 15), which is sulfide not precipitated by iron or other metals. As much as 50 to 60 percent may be present in this form. The seasonal variation of free sulfides is closely related to the variation in total sulfides for both the streamside and inland areas. The factors that affect seasonal variation in free sulfides are the same factors influencing the seasonal variation of total sulfides.

Random measurement of the amount of hydrogen sulfide diffusing from the marsh soil into the atmosphere indicates greater amounts escaping in fall than in summer. Values range from 45 milligrams per square meter and 51 milligrams per square meter per month for streamside and inland areas, respectively in July to values of 182 milligrams per square meter and 4,200 milligrams per square meter per month in November. The hydrogen sulfide appears to escape preferentially from the soil in certain areas through "channelized" escape routes. Large amounts of sulfide are lost from the marsh each year by this process. This loss of sulfide to the atmosphere is beneficial to S. alterniflora. If all the sulfides produced accumulated in the marsh soil, all anaerobic iron would be removed from the soil solution or toxic levels of free sulfides would be reached, both with disasterous results to the productivity of the salt marsh grasses.

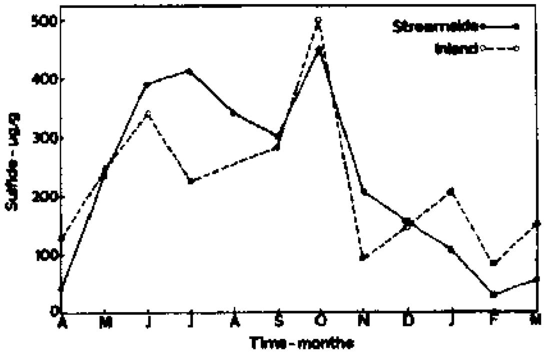

Figure 14. Seasonal variation of total sulfides in the streamside and inland areas. Total sulfide determined by acidifying soil sample and trapping released sulfides in zinc acetate.

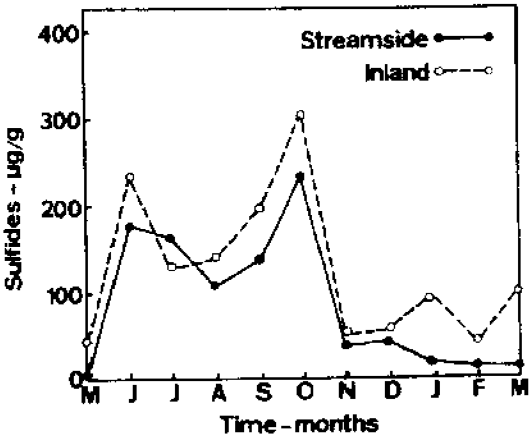

Figure 15. Seasonal variation of free sulfides in the streamside and inland areas. Free sulfide determined by bubbling oxygen-free argon through soil and trapping displaced hydrogen sulfide in zinc acetate.

In summary, there is a large turnover in the sulfur cycle in marsh soils. Sulfate from the overlying seawater diffuses down into the anaerobic soil and is reduced to sulfide. The soil is limited in the amount of sulfate it can retain because of low levels of iron, thus hydrogen sulfide that is formed diffuses out of the soil into the atmosphere.

Phosphorus

Phosphate is not directly involved in oxidation-reduction reactions in flooded systems. It is, however, affected indirectly by oxidation-reduction processes occurring in sediments. Phosphate solubility is related largely to the state of the iron system. Phosphate is released along with the reduction of ferric iron to the more soluble ferrous form, largely because phosphate occurs as an insoluble ferric compound, and also because phosphate is occluded with iron oxide on silt and clay particles. The reduction of iron will strip away the precipitated layer of hydrated iron that has phosphate occluded or coprecipitated in it. For this reason, phosphate is generally more available to plants under reducing conditions.

Maye (1972) obtained values for the various inorganic forms of soil phosphorus in a Georgia salt marsh. The concentration of the aluminum phosphate fraction was 2.80 μmoles/gm, with little variation between cores. The iron phosphate fraction varied from 1.48 to 3.40 μmoles/gm. The calcium phosphate fraction was highest, ranging from 5.17 to 7.69 μmoles/gm with very high calcium phosphate fractions found in cores near the sea. A distinct relationship was found between salinity and the concentration of the various phosphate fractions. Aluminum phosphate and iron phosphate dominated areas with fresher water and slightly acid to neutral pH (6-7). As salinity and pH increased, calcium phosphate became the most important species. The aluminum phosphate and iron phosphate fractions increased with increasing cation exchange capacity (CEC) while calcium phosphate decreased with increasing CEC and was more abundant in the more sandy sediments.

The reductant soluble iron phosphate plus occluded aluminum and iron phosphate fractions of Chang and Jackson (1957) do not contribute to the fertility of well-drained mineral soils but are important in flooded marsh soils because of the instability of hydrated iron oxide under reducing soil conditions. The existence of a marked increase in the availability of native and added phosphate in flooded soils, compared to well-drained soils, has been well established (Shapiro 1958a,b; Davide 1965). These increases in phosphate have usually been attributed to the reduction of ferric phosphate to the more soluble ferrous form and the hydrolysis of phosphate compounds (Patrick and Mahapatra 1968). Patrick et al. (1973) found that strengite releases phosphorus under reducing conditions. Patrick (1964) reported that a decrease in redox potential below +200 resulted in a marked increase in extractable phosphorus. This corresponds to the potential at which ferrous iron began to be released. The amounts of both iron and phosphorus increased with a decrease in redox potential below +200 mv. Mahapatra (1966) studied the distribution of inorganic phosphate fractions before and after waterlogging for one month. The greatest change observed was the conversion of phosphate to ferrous phosphate from the reductant soluble fraction. Reduction of the hydrated ferric oxide present on silt and clay particles releases the occluded phosphates that were previously separated from the soil solution by the ferric oxide layer.

The mechanisms of phosphate release in flooded soils were summarized by Patrick and Mahapatra (1968) as: (1) reduction of insoluble ferric phosphate to more soluble ferrous phosphate, (2) the reduction of the hydrated ferric oxide coating on clay and silt particles resulting in the release of occluded phosphate, (3) phosphate displacement from ferric and aluminum phosphates by organic anions, (4) hydrolysis of ferric and aluminum phosphates, and (5) anion (phosphate) exchange between clay and organic anions. Baas-Becking and Mackay (1956) showed that ferric phosphate reacts with free hydrogen sulfide to form ferrous sulfides and phosphoric acid. Reduction in pH to about 5.4 due to the presence of phosphoric acid was observed, along with complete depletion of oxygen and blackening of the water by colloidal hydrotroilite.

Organic phosphorus can serve as a plant nutrient only after its mineralization into the inorganic orthophosphate form. The solubility and availability of soil phosphorus is increased in waterlogged soils by the processes of reduction and chelation. These processes are enhanced by organic matter (Shapiro 1958b). Organic matter may also cause a reduction in the amount of inorganic phosphorus due to the process of assimilation by bacteria decomposing the organic matter.

Extracted phosphorus (phosphorus adsorbed on the soil exchange complex) of Barataria marsh soils ranged between 20 and 35 μg/g phosphorus on a dry weight basis (Fig. 16). However, on a volume basis, only 10.6 grams per cubic meter and 4.8 grams per cubic meter extractable phosphorus was found in streamside and inland areas, respectively, when their peak values were reached. On a volume basis, extractable phosphorus in the streamside area was twice as high as in the inland area during most of the year.

The inland area exhibited the same basic seasonal trends as the streamside area. Extracted phosphorus was low in April and May, increased sharply in June, and decreased to a low point in August. Following an August low, a highly significant increase was noted in October, which persisted until December. A highly significant decrease was noted from December to February.

The spring increase in extractable phosphorus can be attributed to a number of factors stemming from spring tides covering the marsh:

1) The reduction of ferric phosphate to the more soluble ferrous phosphate.

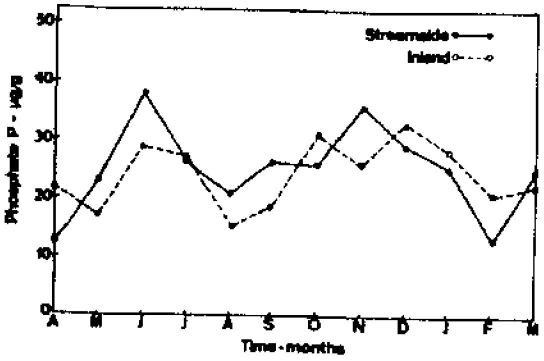

Figure 16. Seasonal variation of extractable phosphorus in the streamside and inland areas. Phosphorus extracted with 1 N sodium acetate, pH 4.0 and phosphate in the extract analyzed colorimetrically using the chloromolybidic acid method.

2) Release of occluded phosphate from ferric oxide precipitation.

3) Displacement of phosphate from ferric and aluminum phosphate by organic anions.

The extractable phosphorus decrease after the spring increase may be attributed to the following factors:

1) Plant uptake. Broome et al. (1973) found a response to phosphate in some areas of the North Carolina marsh. Reimold (1972) found that *S. alterniflora* can act as a natural pump, translocating significant quantities of phosphorus from the salt marsh sediment to the leaves and, with tidal inundation, into the estuarine water.

2) Phosphate may be precipitated as the more insoluble ferric phosphate around the oxidized rhizosphere of the *S. alterniflora* plant.

Potassium

The coastal marshlands of Louisiana seem to have an ample supply of potassium. Amounts of extractable K^+ ranging from 500 to 1,000 ppm were reported by Brupbacher et al. (1973). On upland soils this level of potassium is much higher than is required for good plant growth. Soil of poorly drained areas releases much more indigenous potassium when the soil is air dried before flooding. This is especially true of organic soils, the release being three times greater than that of mineral soils (Takahashi 1965). Potassium may be immobilized by fixation when soils containing illite clays dry (Ponnamperuma 1965). The potassium utilized by a crop is that adsorbed on the exchange complex and the small amount present in the soil solution. Potassium is displaced from the exchange complex into the soil solution by the reducing conditions caused by flooding. The potassium ions are replaced by ferrous, manganous, and aluminum ions on the exchange complex (Patrick and Mikkelsen 1971).

The graph (Fig. 17) shows that no significant seasonal variation existed in the levels of extractable potassium in the sediments of the streamside and inland areas of Barataria Bay. The amounts present are sufficient for plant growth and averaged 1820 μg/g extractable potassium in the streamside area and 2,140 μg/g extractable potassium in the inland area. Considered on a volume basis, streamside had a higher content, 510 μg/cc extractable potassium compared to 310 μg/cc extractable potassium for the inland area.

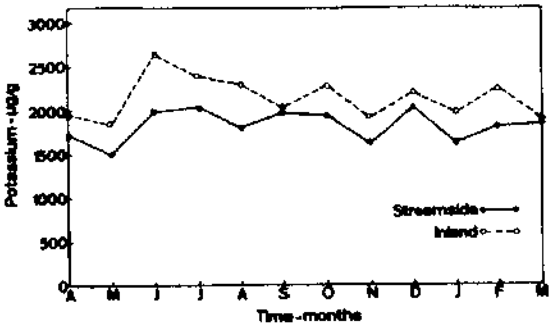

Figure 17. Seasonal variation of extractable potassium in the streamside and inland areas. Potassium extracted with 1 N sodium acetate, pH 4.5 and analyzed by atomic adsorption spectrophotometry.

Soil—Plant Relations

The salt marsh of Barataria Bay has been shown to be one of the most productive marsh environments in the United States (Day et al. 1972). Kirby (1972) showed an annual net production of approximately 30,000 kilograms per hectare dry weight for a pure stand of *S. alterniflora*. In addition to a favorable climate and a long growing season, a large supply of plant nutrients must be available from the sediment in order to maintain production at this level. Analyses have shown that the sediments contain large amounts of the major plant nutrients (Brupbacher et al. 1973). Nonetheless, with the high requirement for plant nutrients necessary to maintain a high level of production, deficiencies may develop during the growing season.

Little and incomplete information is available on the nutrient adequacy of marsh sediments for *Spartina*. Broome et al. (1973) found that Spartina responded to nitrogen but not to phosphorus in a North Carolina marsh area of silt loam texture. A response was obtained to both nitrogen and phosphorus in a sandy marsh. Nitrogen has also been suggested as the major limiting nutrient for phytoplankton growth in coastal marine waters (Ryther and Dunstan 1971; Goldman et al. 1973).

Supplemental nitrogen increased the yield of S. alterniflora by 15 percent in Barataria Bay. The use of an ^{15}N-labelled nitrogen compound showed that the percentage of plant nitrogen derived from the added inorganic nitrogen ranged from 41 percent in early summer to 31 percent in September. Twenty-nine percent of the 200 kg/ha of added nitrogen was recovered in the aboveground portion of the plants in September. The total concentration of nitrogen in the plant was increased by one-fourth to one-half by the added nitrogen. Although the concentration of phosphorus in the plant was increased about 20 percent by the addition of inorganic phosphate, no yield increase resulted. This study indicates that the salt marsh is deficient in nitrogen but not in phosphorus for growth of S. alterniflora.

The yields of plant material harvested in September are shown in Table 1. Added nitrogen caused a statistically significant yield increase of 2,500 kg/ha or 15 percent over the untreated check. Productivity was high in this area with the yield of standing crop in line with values reported earlier by Kirby (1972).

Table 1. Aboveground yield of Spartina alterniflora in September, 1973 in a streamside location in Barataria Bay, Louisiana, as affected by applications of nitrogen and phosphorus.

Treatment	Dry weight yield (kg/ha)
Nitrogen	19,160a*
Phosphorus	16,560b
Check (no nitrogen or phosphorus)	16,660b

*Values followed by a common letter do not differ significantly at the 5 percent level of probability.

Not only is productivity increased by added nitrogen, but the content of nitrogen in the plant material is also increased, as is shown in Figure 18. At the first sampling in June the nitrogen content was 1.4 percent in the treated plots compared to 0.9 percent in the untreated plots. The difference in nitorgen content narrowed somewhat as the season progressed with the content decreasing for both treatments, but nitrogen was still considerably higher when nitrogen had been added. Assuming that the higher content of nitrogen represented an increased protein content, the nutritional value of the Spartina was considerably enhanced by adding supplemental nitrogen. For example, using the factor 6.25 x N = protein, the nitrogen-treated plots produced an average of 1,160 kg/ha protein aboveground compared to 770 kg/ha for the untreated plot, or an increase of 50 percent in the amount of protein produced as a result of nitrogen fertilization. These results indicate that both the quantity and quality of the grass was improved by added nitrogen.

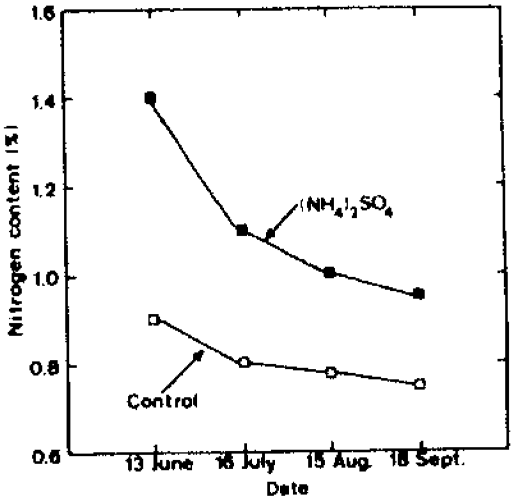

Figure 18. Nitrogen content of *Spartina alterniflora* as affected by addition of ammonium sulfate (200 kg/ha N). Ammonium sulfate was placed 5-10 cm below the soil surface on May 15.

The use of ^{15}N-depleted nitrogen makes it possible to distinguish between the plant nitrogen derived from the fertilizer and that derived from the soil. As shown in Table 2, the amount of nitrogen derived from fertilizer was about 41 percent during June and July and decreased to 31 percent by September. The supply of fertilizer nitrogen was apparently diminished toward the end of the growing season. Data in Table 3 show that of the 185 kg/ha nitrogen in the aboveground portion of the plant on September 18, only 58 kg/ha came from the added inorganic nitrogen. This represented a low recovery of 29 percent.

Table 2. The source of nitrogen contained in the aboveground portion of the plant at various times after addition of nitrogen fertilizer to an actively growing stand of *Spartina alterniflora* on May 15.

Source of plant nitrogen	Percent			
	June 13	July 16	August 15	Sept 18
Ammonium Sulfate	41.4 ± 1.8	41.2 ± 1.9	34.7 ± 3.1	34.4 ± 3.1
Soil	58.6 ± 1.8	58.8 ± 1.9	65.3 ± 3.1	68.6 ± 3.1

Table 3. Recovery of added nitrogen in aboveground portion of *Spartina alterniflora* at harvest on September 18.

Amount of nitrogen applied (kg/ha)	200
Amount of nitrogen in aboveground portion of plant (kg/ha)	185.5 ± 8.6
Plant nitrogen derived from fertilizer (kg/ha)	58.4 ± 2.7
Recovery of applied nitrogen in aboveground portion of plant (%)	29.2 ± 1.3

In order to determine if there were any residue of added fertilizer nitrogen available to the plants the following spring, plant samples representing new growth were taken in April 1974 from the treated plots and analyzed for ^{15}N. The analysis showed that none of the fertilizer added the previous spring was available to the new crop. It is surprising that no residual fertilizer nitrogen was present the following spring since only 29 percent of the added nitrogen was removed in the plant material the previous fall (Table 3). An appreciable fraction of the added nitrogen was either lost from the system or incorporated into organic matter and not released by April, or both.

The uptake of 127 kg/ha nitrogen in the aboveground plant material from native sources illustrates the high capacity of the marsh soil for supplying nitrogen to Spartina. Since a significant portion of the earlier season growth of Spartina had already died and had been degraded before the September sampling (Day et al. 1972), and since appreciable nitrogen was also required for the plant roots, the sediment had very likely supplied a much larger amount of nitrogen to the plants. As shown previously in Figure 10, the marsh soil is capable of supplying approximately 12 g nitrogen per g of oven-dry weight of soil per week. Using density values of the sediment for a 50 cm depth of sediment, this would amount to a weekly nitrogen release from the sediment of 17 kg/ha. This amount of nitrogen should have been adequate to supply all of the plant's requirement, but as the yield data showed, additional nitrogen was needed for maximum yield. The instability of nitrogen in reduced soils probably results in an appreciable fraction of the inorganic nitrogen being lost from the soil before it could be utilized by the plant.

The addition of supplemental phosphate had no effect on productivity, as the yield values in Table 1 show. The phosphorus-supplying capacity of the sediment was apparently high enough to provide an adequate amount for plant growth throughout the growing season. Added phosphorus did increase the percentage of phosphorus in the plants at all sample dates, as is shown in Figure 19. Analyses of available phosphorus in the marsh soils of Barataria Bay (Brupbacher et al. 1973) indicate an adequate supply of phosphate. The sediments making up the marsh soils on which Spartina is grown are relatively unweathered and have not been depleted of phosphorus.

The distribution of nitrogen and phosphorus in the soil-plant system at a productive streamside location is shown in Table 4. Viewing the entire plant-sediment system down to a depth of 53 cm, the distribution of nitrogen will be in the order of 11 grams per square meter in the aboveground Spartina plant, 160 grams per square meter in the roots, and 640 grams per square meter in the sediment. There is a terrific root mass in S. alterniflora, which is why more nitrogen is found in the roots than aboveground plant material. The majority of the nitrogen is located in the sediment, which is one of the major sources of nitrogen for plants. Most of the sediment nitrogen is in organic form.

Looking at phosphorus we find 1 gram per square meter in the aboveground plant, 9 grams per square meter in the roots, and 35 grams per square meter in the sediment.

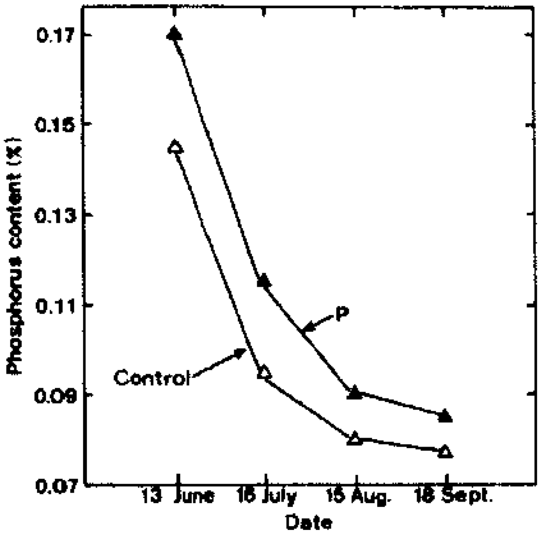

Figure 19. Phosphorus content of *Spartina alterniflora* (dry weight basis) as affected by addition of sodium phosphate (200 kg/ha P). Phosphorus placed 8-10 cm below soil surface on May 15.

Table 4. Nitrogen and phosphorus distribution in the soil-plant system.

	Content in above-ground plant material g/m2	Content in roots to depth of 54 cm g/m2	Content of soil to depth of 53 cm g/m2	Total Content of system g/m2
N	11	160	614	785
P	1	9	35	45

Summary

Barataria Bay salt marsh exhibits high productivity. Many chemical and microbiological processes occurring in the marsh directly affect productivity. The soils are more or less permanently saturated or submerged. Seasonal changes in redox potential occur only in the upper 5 cm of the soil profile. Reduced forms of iron, manganese, nitrogen, and sulfur predominate.

The nutrient content of Barataria Bay's organic soils are quite high on a total dry mass basis but can be rather low on a volume basis, especially for low density soils containing large amounts of organic material. Soils along the streamside with greater density containing a larger amount of mineral material are more productive.

Nitrogen exists mainly as organic nitrogen and ammonium nitrogen. Nitrate is very unstable under reducing conditions and undergoes denitrification. Levels of nitrogen are low in the spring when maximum uptake of ammonium by Spartina is occurring.

Supplemented nitrogen increased the yield of Spartina by 15 percent. Not only is productivity increased by added nitrogen, but the content of nitrogen in the plant is also increased. The addition of supplemented phosphorus had no effect on productivity. The phosphorus supplying capacity of the soil is high enough to provide an adequate amount for plant growth.

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