

BIOGEOCHEMICAL EFFECTS OF SEAWATER RESTORATION TO DIKED SALT MARSHES

J. W. PORTNOY¹ AND A. E. GIBLIN²

¹United States Geological Survey—Biological Resources Division, Cape Cod National Seashore, 99 Marconi Road, Wellfleet, Massachusetts 02667 USA

²Ecosystems Center, Marine Biological Laboratory, Woods Hole, Massachusetts 02543 USA

Abstract. We conducted greenhouse microcosm experiments to examine the biogeochemical effects of restoring seawater to historically diked Cape Cod salt marshes. Peat cores from both seasonally flooded and drained diked marshes were waterlogged with seawater, and porewater chemistry was subsequently monitored for 21 mo. The addition of seawater to highly organic, seasonally flooded peat caused the death of freshwater wetland plants, 6–8 cm of sediment subsidence, and increased N and P mineralization. Also, sulfides and alkalinity increased 10-fold, suggesting accelerated decomposition by sulfate reduction. Addition of seawater to the low-organic-content acidic peat from the drained marsh increased porewater pH, alkalinity, PO₄-P, and Fe(II), which we attribute to the reestablishment of SO₄ and Fe(III) mineral reduction. Increased cation exchange contributed to 6-fold increases in dissolved Fe(II) and Al and 60-fold increases in NH₄-N within 6 mo of salination.

Seawater reintroductions to seasonally flooded diked marshes will cause porewater sulfides to increase, likely reducing the success of revegetation efforts. Sulfide toxicity is of less concern in resalinated drained peats because of the abundance of Fe(II) to precipitate sulfides, and of NH₄-N to offset sulfide inhibition of N uptake. Restoration of either seasonally flooded or drained diked marshes could stimulate potentially large nutrient and Fe(II) releases, which could in turn increase primary production and lower oxygen in receiving waters. These findings suggest that tidal restoration be gradual and carefully monitored.

Key words: acid sulfate soils; Cape Cod; coastal wetland subsidence; diking; eutrophication; salt marsh restoration; salt water intrusion; *Spartina alterniflora*; sulfur cycling.

INTRODUCTION

Efforts to restore tidal flow and associated estuarine habitat values to diked salt marshes are increasing. Observations of disturbed sediment budgets (Thom 1992, Warren and Niering 1993), vegetation change (Roman et al. 1984), water quality problems (Breemen 1982, Soukup and Portnoy 1986, Portnoy 1991), pest insect outbreaks (Ferrigno and Jobbins 1968, Portnoy 1984), and reduced fish and wildlife use (Neely 1958, Portnoy et al. 1987) resulting from diking have encouraged managers to reduce or remove tidal restrictions. Land management interest in restoration is particularly active along the New England coast (Rozsa 1987, Soil Conservation Service 1994) where salt marsh diking and drainage for agriculture and mosquito control have a long history (Nickerson 1978, DeSista and Newling 1979).

There has nevertheless been little study of the potential biogeochemical consequences of renewed seawater flooding despite evidence that the structure and chemistry of wetland sediment profoundly changes after decades of tidal restriction and drainage (Breemen

1982, Bricker-Urso et al. 1989, Portnoy and Giblin, *in press*). Diking blocks seawater flow, causing wetland salinity to decline (Roman et al. 1984). Subsequent sedimentary changes depend on whether peats behind dikes remain waterlogged or are drained.

Diked marshes that remain at least seasonally waterlogged (i.e., "impounded" *sensu* Montague et al. 1987) accrete freshwater wetland peat of higher organic content than salt marsh peat (DeLaune et al. 1990, Nyman et al. 1994, Portnoy and Giblin, *in press*). This occurs because diking restricts the inorganic sediment supply normally imported by flood tides (Thom 1992). Also, decomposition in freshwater peats, dominated by methanogens, is slow (Capone and Kiene 1988). Porewater nutrient concentrations are low (Portnoy and Giblin, *in press*) probably as a result of both reduced decomposition and ion exchange. Seawater restoration in these wetlands should increase nutrient release to porewater and surface waters by two mechanisms. First, seawater will provide abundant SO₄²⁻, increasing decomposition by dissimilatory sulfate reduction, which is energetically superior to methanogenesis (Capone and Kiene 1988). Second, greatly increased ionic strength will increase ion exchange. Although increased nutrient availability should enhance macro-

Manuscript received 2 November 1995; revised 20 September 1996; accepted 16 October 1996.

phyte growth, dissolved sulfides that inhibit plant growth (Koch et al. 1990) may accumulate due to the scarcity of reactive iron for their precipitation in these low-mineral-content sediments (DeLaune et al. 1987, Portnoy and Giblin, *in press*). Sulfide accumulation is of special concern where post-diking subsidence (Roman et al. 1984) results in more prolonged flooding and sustained anaerobiosis than in natural marshes.

In contrast, the sediments of diked salt marshes that have been drained exhibit a very distinct chemistry that should respond differently to seawater restoration. Drainage, typically accomplished by ditching and stream channelization, lowers the wetland water table, allows sediment aeration, and increases organic matter decomposition (Roman et al. 1984). These changes lead to compaction and subsidence (Roman et al. 1995) sometimes amounting to nearly 1 m (Portnoy and Giblin, *in press*). Meanwhile, abundant mineral pyrite (FeS_2) stored in previously reducing salt marsh sediments is exposed to air and oxidized by O_2 , and secondarily by Fe(III) , producing acid sulfate soils (Breemen 1982, Dent 1986). Consequently, sulfate and acidity are leached into porewaters depressing pH and adversely affecting estuarine fauna (Soukup and Portnoy 1986). The reintroduction of seawater into diked and drained salt marshes should buffer acid sulfate soils and acidified surface waters through the import of bicarbonate and the reestablishment of reducing sedimentary conditions (Breemen 1976); however, the likely rate and possible mechanisms for alkalinity generation and pH recovery have not been studied.

Despite the loss of organic solids in drained marshes, nutrients are still abundant, with N stored as adsorbed NH_4 , and P coprecipitated with Fe and Al minerals (Portnoy and Giblin, *in press*). These minerals are stable in acid sulfate soils (Dent 1986), while the low pH suppresses the nitrification of NH_4 to soluble NO_3 (Focht and Verstraete 1977). The large increase in ionic strength, exchangeable cations, and pH accompanying the return of seawater could result in NH_4 and PO_4 mobilization. Unlike what may occur in diked-waterlogged marshes, enhanced sulfate reduction following seawater reintroduction in drained peats should not result in the accumulation of toxic sulfides because of the abundance of reactive iron for their precipitation (Dent 1986). Thus, mobilized nutrients could stimulate growth of both wetland macrophytes and water column producers without accompanying sulfide inhibition.

As part of a multidisciplinary program of tidal wetland restoration (Portnoy et al. 1987), we investigated the biogeochemical effects of restored seawater flooding on peats of both seasonally waterlogged and drained diked marshes on Cape Cod, Massachusetts. Our hypothesized geochemical changes, i.e., nutrient mobilization, sulfide accumulation, and pH recovery, have a strong potential to affect estuarine biota. Thus, our objective was to examine salination effects on sediment chemistry with special regard for both the re-

colonization of salt marsh vegetation and the restoration of estuarine water quality. The study employed microcosm systems in which soils from historically diked wetlands were subjected to seawater flooding for 21 mo.

METHODS

Microcosm collection sites

We established microcosm experiments in a greenhouse environment to study salination effects on diked, seasonally flooded (=DF) and diked, drained (=DD) marsh peat. Microcosm cores representing the waterlogged condition were from an impounded portion of the North Sunken Meadow salt marsh in Eastham (Massachusetts). Diked and drained salt marsh sediment was obtained at Herring River, Wellfleet (Massachusetts, Portnoy et al. 1987). Dates of diking, wetland elevations, peat depths, modern hydrology, and sediment chemistry are summarized (Table 1, also see Portnoy and Giblin, *in press*).

At DF, diking and impoundment has resulted in the accumulation over the original salt marsh of ≈ 27 cm of freshwater wetland peat. Peat chemistry and $\delta^{13}\text{C}$ below 20 cm are similar to local unaltered marshes (Table 1). Modern vegetation of the coring site is a mix of fresh and halophytic grasses including *Scirpus americanus*, *Spartina patens*, and less dominant *Distichlis spicata*. Maximum flooding depths are controlled by a weir, which also impedes freshwater drainage and causes the normally waterlogged conditions. Apparently as a result of regular flooding, there has been little subsidence: the modern wetland surface is only 15 cm below that of unrestricted salt marsh on the seaward side of the dike.

At DD, constant drainage of the top 20 cm of sediment is achieved by a network of channelized and straightened creeks and large culverts in place since the 1930s. As a result of drainage, wetland plants have been replaced by upland terrestrial species, predominantly *Holcus lanatus*, *Spiraea latifolia* and *S. tomentosa*, and *Solidago rugosa* and *S. tenuifolia*. Aeration has increased organic decomposition so that the soil surface has subsided and is now ≈ 90 cm below extant *Spartina* marsh seaward of the dike. Aeration has also oxidized pyrite, producing acid sulfate soils and pH 3–4 porewaters. Fe and S both remain high at depths below 25 cm (Table 1). From 1 to 5% of sediment N is present as adsorbed NH_4^+ . Within the top 50 cm, 30–60% of total P is inorganic, probably as Al and Fe precipitates given the pH and Eh range (Stumm and Morgan 1981). The $\delta^{13}\text{C}$ values and persistent rhizomes indicate that salt marsh peat (albeit decomposed) extends from 10 to at least 60 cm below the sediment surface.

Marsh coring and greenhouse setup

We established triplicate microcosms for both waterlogged and drained sites by collecting 15 cm di-

TABLE 1. Dates of diking and hydrologic and chemical characteristics of North Sunken Meadow (diked, seasonally flooded = DF) and Herring River (diked, drained = DD) study sites.

Variable	DF	DD
Year of diking	1840	1909
Peat depth (m)	1.6	2.5
Surface elevation (m, mean sea level)	1.7	1.0
Flooding depth (cm)		
Winter, summer	+5, -10	-25, -60
Surface flooding duration	Dec-Jun	none
Porewater (45-cm depths)		
pH	6.4	3.9
Alkalinity (mmol/L)	4	0.1
Fe(II) ($\mu\text{mol/L}$)	3-10	30-1000
Fe(III) ($\mu\text{mol/L}$)	0-2	10-800
Sulfides (mmol/L)	0.1-0.6	0
$\text{SO}_4\text{-Cl}$	0.0-0.1	0.2-0.4
$\text{NH}_4\text{-N}$ ($\mu\text{mol/L}$)	10	75
$\text{PO}_4\text{-P}$ ($\mu\text{mol/L}$)	1	2
Sediment solids (5-cm, 45-cm depths)		
pH	5.5, 6.5	3.9, 4.0
Eh (mV)	300, 0	500, 300
Water (%)	88, 90	75, 55
Bulk density (g/cm^3)	0.1, 0.1	0.2, 0.6
Organic matter (% dry mass)	65, 75	45, 12
Total Fe (% dry mass)	1.0, 0.2	1.5, 2.5
Total S (% dry mass)	0.5, 3.2	0.5, 2.0
Total N (% dry mass)	2.0, 2.0	1.5, 0.5
$\text{NH}_4\text{-N}_{\text{KCl-Exch.}}$ (% total N)	0.8, 0.2	1.1, 5.0
Inorganic P (% dry mass)	0.02, 0.005	0.04, 0.03
Organic P (% dry mass)	0.08, 0.03	0.06, 0.04
$\delta^{13}\text{C}$	-18.2, -17.5	-25.3, -17.2

ameter by 45 cm deep cores in polyvinyl chloride cylinders in October 1992. After being driven to the 45-cm depth, the tubes were dug from the marsh. Their bottoms were sealed with polycarbonate disks. Each disk had a hole drilled in the center and a stainless steel fitting installed in the hole to accept teflon tubing, which served as a bottom porewater port. Microcosms were mounted in their permanent greenhouse bench environment within 3 h of collection. The greenhouse provided ambient light and temperature while preventing precipitation that would disturb experimental salinity and water level manipulations.

Greenhouse microcosms were kept waterlogged and flushed monthly with 1 L of fresh water from October 1992 to late January 1993 when pretreatment chemistry was completed. The fresh water was prepared to chemically match that collected and analyzed over the past 2 yr from the Truro National Atmospheric Deposition site (pH 4.5, alkalinity 0.0 mmol/L, SO_4 0.04 mmol/L, Portnoy 1996). Each microcosm received fresh water from a constant water level device (Hussey and Odum 1992) attached to the greenhouse bench and connected by tubing to the microcosm at the level of the sediment surface. Cores were flushed with 10 L of 30 g/kg artificial seawater (Marine Enterprises, Incorporated; pH 8.5, alkalinity 2.0 mmol/L, and SO_4 56 mmol/L) on 19 February 1993. From March through May 1993, all microcosms were flushed monthly with 1 L of seawater. By the end of this period, bottom port salinities approached 50 g/kg and it was apparent that the accu-

mulation of salt could not be controlled by flushing with seawater. Therefore, we replaced all subsequent water loss, including sampled water, with artificial precipitation and increased monthly sample volumes from 150 mL (June 1993-March 1994) to 500 mL (April-October 1994) to remove accumulated salts. As a result, salinities declined steadily reaching 30-42 g/kg by May and 25-38 g/kg by October 1994.

In general, we did not intend the extracted sample volumes to approximate the porewater flushing rates expected in the field after tidal restoration. These flushing rates are not predictable because of the lack of site-specific hydrogeology plus uncertainties regarding the actual topography, hydrography, and hydroperiod of a "restored" system. Treatments of constant waterlogging and minimal flushing may appear extreme but probably reflect future field conditions because of subsidence since diking and concurrent sea-level rise. Further, the observed silty and peaty sediments have low permeability and high field capacities (Mitsch and Gosselink 1993), restricting vertical flow and resisting air entry even when hydraulic conditions are favorable. Despite uncertainties about future field conditions, experimental treatments of salination and waterlogging should at least qualitatively mimic expected radical changes in sediment biogeochemistry.

Porewater sampling and analysis

We sampled microcosms monthly for pH, salinity, alkalinity, and dissolved sulfides, SO_4^- , Cl^- , Fe(II),

Fe(III), NH_4^+ , PO_4^- , and NO_3^- from the bottom port at 45-cm depth. In addition, we sampled porewater within root zones (10–20 cm) by inserting a 3-mm inside diameter stainless steel tube with a crimped and slotted point into the sediment and withdrawing sample from the top of the tube with a syringe. This arrangement prevented aeration of anoxic porewater. The larger bottom-port samples were collected by directing flow from the teflon bottom-port tubes into flasks flushed with N_2 gas. Aliquots for sulfide analysis were withdrawn by pipette and immediately discharged into 2% zinc acetate and determined colorimetrically (Cline 1969). We determined pH and titrated alkalinity (Edmond 1970) within 6 h of collection. Aliquots for sulfate and chloride analysis by ion chromatography were filtered (0.45 μm) and degassed with N_2 to remove sulfides. A final aliquot was acidified to pH 2 with trace metal grade HCl and stored at 4°C for the subsequent determination of nutrients, Fe(II), total Fe (TFe), and by difference Fe(III). We measured $\text{NH}_4\text{-N}$, $\text{PO}_4\text{-P}$, and $\text{NO}_3\text{-N}$ by flow injection analysis using automated phenolate, ascorbic acid, and cadmium reduction colorimetric methods, respectively (APHA 1992). Fe(II) iron was determined by the ferrozine method, as was TFe after reduction with hydroxylamine (Stookey 1970). We determined total dissolved Al using 8-hydroxyquinoline (James et al. 1983).

We also monitored porewater chemistry at microcosm collection sites from May 1993 until October 1994, and at an unaltered salt marsh vegetated with short-form *Spartina alterniflora* just seaward of DF during summer 1994. Samples were collected with the above-mentioned stainless steel tube.

Microcosm solid phase analysis

Microcosm sediments were subsampled by piston corer in October 1994 and cut into 5-cm sections. We measured pH and Eh (redox potential) immediately by forcing probes ≈ 5 mm into each sediment section at three locations and recording average values. We measured pH with a KCl-filled combination electrode with calomel junction; we measured Eh with a platinum electrode (Howes et al. 1981). Core sections were then dried to a constant mass at 105°C for determinations of percentage water and bulk density. We measured organic content from the mass loss on ignition at 550°C for 2 h. Total Fe was determined by digesting ≈ 0.1 g of dry sediment in 5 mL of concentrated HNO_3 in a water bath at 70°C for 2 h, followed by the addition of 5 mL of concentrated HCl and further heating for 1 h. Resulting extracts were filtered, diluted, and Fe content was determined by atomic absorption. We determined total and inorganic P per Krom and Berner (1981); acid extracts were diluted and P measured by flow injection analysis using the ascorbic acid reduction method (APHA 1992). Total S was determined by combustion in a Leco (St. Joseph, Michigan) sulfur analyzer, and

C and N by combustion in a Perkin-Elmer (Norwalk, Connecticut) elemental analyzer.

We inferred sediment chemistry changes due to tidal flooding by comparing the salinated microcosm cores (posttreatment, $N = 3$) at the end of the experiment with untreated sediments (pretreatment, $N = 2$), using one-way analysis of variance (ANOVA, $P = 0.05$) with salination as the fixed treatment. The untreated cores were collected along with the microcosm cores in fall 1992. We compared pre- and posttreatment pH, Eh, and bulk density profiles by 5 cm depth interval using a randomized block design ANOVA. Sediment stocks of water, organic matter, Fe, P, S, C, and N were totaled for each 45 cm deep core by summing the products of concentration, bulk density, and volume of all 5-cm depth increments; the pre- and posttreatment totals were compared using a completely randomized design (CRD) ANOVA. Porewater chemistries within microcosm root zones before and after salination were compared to each other and to porewater from a natural salt marsh using a CRD ANOVA ($P = 0.05$), again with salination as the fixed treatment.

Because all of the cores were from the same diked or waterlogged marsh, results are not strictly transferable to other systems. However, additional diked salt marshes cored in Massachusetts and Connecticut (Portnoy 1996) show management-induced changes in sediment chemistry consistent with results from DF and DD. Therefore, we believe that salination effects observed for DF and DD are representative and can be anticipated in similarly altered salt marshes.

RESULTS

Plant survival

Both *Scirpus* and *Spartina patens* in the DF cores had died after 3 mo of salination to 30–40 g/kg. In the DD cores from the drained marsh, *Holcus* was quickly killed after salination. The rapid death of *Scirpus americanus* and *Spartina patens* in DF microcosms, and *Holcus* in DD, was apparently due to salt stress as mortality occurred before porewater sulfide increased (Fig. 1). *Distichlis*, which happened to occur in only one DF microcosm, survived salinities >40 g/kg and spread within DF3 until the end of the experiment. Most studies suggest that *Distichlis* is more salt tolerant than *S. patens*, and perhaps even than *S. alterniflora* (see Taylor 1939, Adams 1963, Parrondo et al. 1978, Kemp and Cunningham 1981).

Sediment subsidence and porewater changes

A striking physical change by July 1993 was the 6–8 cm subsidence of the surface of all three DF microcosm cores. We detected no changes in the level of DD sediment during the experiment.

Diked-flooded sediment.—After an initial decline, pH quickly recovered to pretreatment levels and remained stable throughout the remainder of the exper-

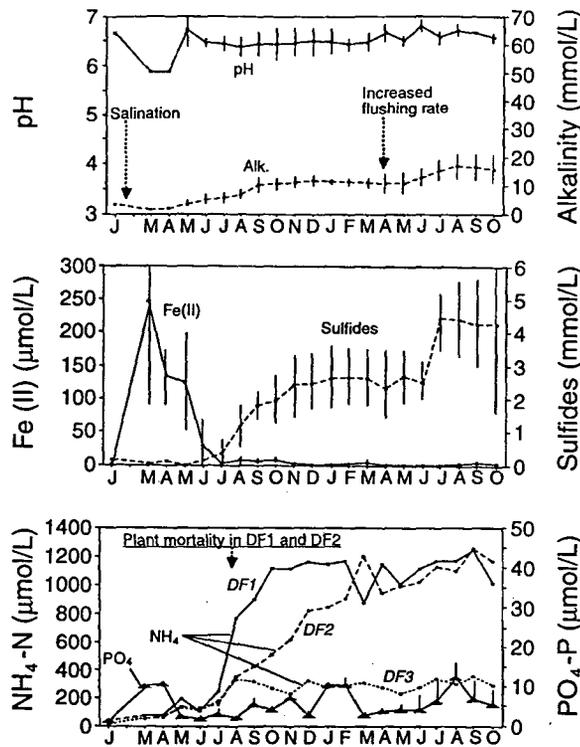


FIG. 1. Trends in porewater chemistry in salinated DF (diked, seasonally flooded) marsh peat. Data are means \pm 1 SE ($N = 3$) except for NH_4 , which is plotted separately for the three replicates, DF1, DF2, and DF3. Samples are from 45 cm deep bottom ports.

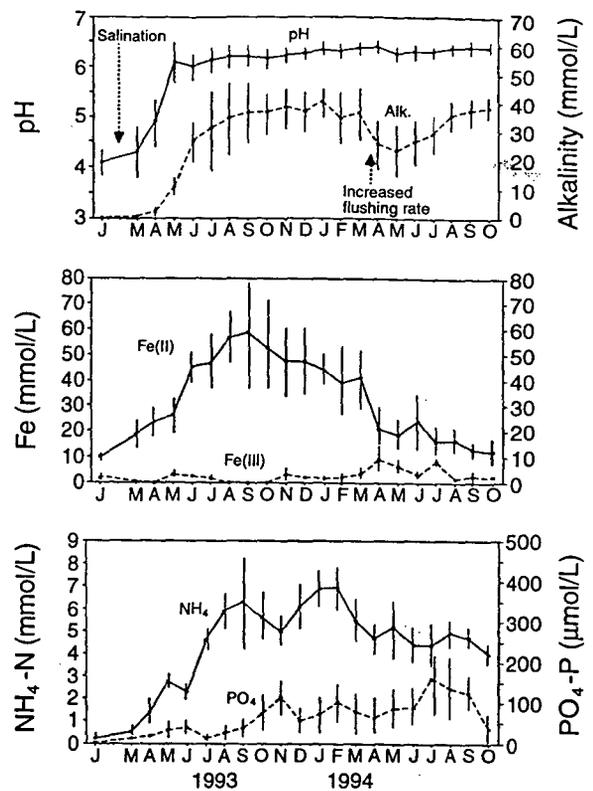


FIG. 2. Trends in porewater chemistry in salinated DD (diked, drained) marsh peat. Data are means \pm 1 SE ($N = 3$) for samples collected from microcosm bottom ports.

iment (Fig. 1). Alkalinity and sulfides increased 10-fold between January salination and August 1993; Fe(II) increased about 50-fold by March but was depleted by July. Despite differences in plant vigor and presumably growth-dependent nitrogen assimilation, NH_4 concentrations consistently increased after salination even in the microcosm with live *Distichlis*. Dissolved inorganic phosphorus (DIP), though temporally more variable, also increased 2 to 10 times field concentrations.

Diked-drained sediment.—After 5 mo of salination, pH had risen steeply from ≈ 4 to 6, while alkalinity increased from nil to nearly 30 mmol/L (Fig. 2). Salination caused major increases in porewater Fe(II), NH_4 , PO_4 , and Al. Fe(II) rose from ≈ 10 to 60 mmol/L, peaking in September 1993. Pretreatment NH_4 concentrations of ≈ 100 $\mu\text{mol/L}$ increased to 4–6 mmol/L in the microcosms by midsummer 1993. KCl extractions from dried and ground DD soil (Fig. 3) indicate that this NH_4 was released from the soil exchange complex. Dissolved inorganic phosphorus also increased, exceeding field concentrations (Portnoy 1996) by 20-fold from fall 1993 until the end of the experiment. Total dissolved Al, derived from clay minerals and likely complexed with PO_4 at low pretreatment pHs (Dent 1986), increased 6-fold after salination of DD cores (Fig. 4).

Solid phase changes

After 21 mo of salination, bulk density of DF sediments had significantly increased and Eh decreased (Table 2). Changes in inorganic element stocks were significant only for Fe, which decreased (Table 3). This Fe loss was not accounted for in sampled water, perhaps

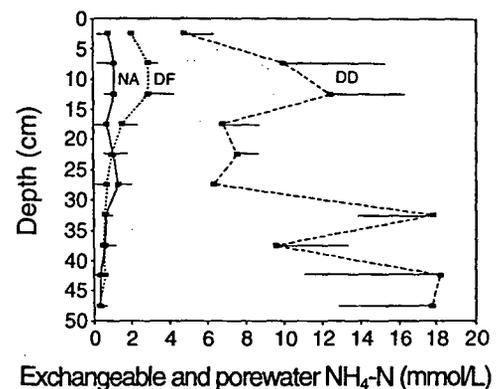


FIG. 3. KCl exchangeable $\text{NH}_4\text{-N}$ in sediment from natural (NA), diked-flooded (DF), and diked-drained (DD) sites. Data are presented as porewater concentrations (mean \pm 1 SE; $N = 2$), computed from the mass of $\text{NH}_4\text{-N}$ extracted divided by the interstitial volume.

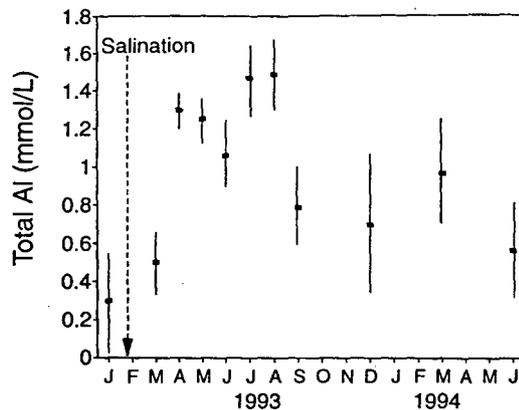


FIG. 4. Trends in total dissolved aluminum in salinated DD (diked, drained) sediments. Mean \pm 1 SE; $N = 3$.

because we did not measure all of the Fe complexed with organic ligands (Luther et al. 1996).

Salination of DD soils caused pH to increase and Eh to decrease significantly (Table 2). Significant losses of C and N were detected in the sediment inventory; organic matter, P, Fe, and S did not change (Table 3).

DISCUSSION

Salination of diked-flooded marsh

Sediment subsidence and significantly increased bulk density (Table 2) in DF cores are likely the result of the death and decomposition of plant roots and rhizomes under salt stress; however, the provision of abundant seawater SO_4 may have played a role in accelerating decomposition of DFs constantly waterlogged and highly organic peats. This is because heterotrophs derive more energy from SO_4 reduction than from methanogenesis (Capone and Kiene 1988). Chemical changes in DF cores, particularly 10-fold increased alkalinity and sulfides (Fig. 1) and significantly decreased Eh (Table 2), support greatly increased organic decomposition by sulfate reduction. Also Fe(II), initially mobilized by cation exchange and reduction of Fe(III) minerals near the seasonally aerobic surface, was exhausted by precipitation with sulfides during summer 1993. Porewater SO_4 :Cl ratios declined below those of aerobic seawater within 3 mo of salination due to the abundance of labile organic matter for dissimilatory sulfate reduction. Observed increases in NH_4 and PO_4 are also expected with accelerated organic decomposition, with disproportionately high NH_4 explained by cation exchange. KCl extractions indicated that salination could result in porewater NH_4 concentrations similar to those at DF1 and DF2 (1 mmol/L) by cation exchange alone (Fig. 3).

Effects on organisms of both diking and seawater restoration are evident by comparing root zone porewaters both before and after salination with those of an adjacent natural salt marsh (Table 4). After seawater flooding, the porewater chemistry of DF did not differ

TABLE 2. Profiles of pH, Eh (mV), and bulk density (BD, g/cm^3) in diked marsh peat before ($N = 2$) and after ($N = 3$) 21 mo of seawater flooding in greenhouse microcosms. Data are presented as means, with one standard error on the next row down.

Depth (cm)	Pretreatment			Posttreatment		
	pH	Eh	BD	pH	Eh	BD
Diked-flooded						
0-5	5.4	326	0.14	6.1	156	0.16
	0.6	81	0.02	0.4	186	0.01
5-10	5.6	341	0.60	6.3	62	0.49
	0.2	51	0.15	0.5	267	0.12
10-15	5.7	283	0.95	6.7	-87	1.00
	0.5	24	0.51	0.4	39	0.23
15-20	6.0	141	0.33	6.7	-117	0.25
	0.5	226	0.27	0.1	32	0.03
20-25	6.0	2	0.14	6.6	-98	0.19
	0.2	62	0.00	0.3	10	0.01
25-30	5.7	-15	0.13	6.4	-98	0.17
	0.5	14	0.03	0.1	25	0.01
30-35	6.3	-11	0.11	6.5	-82	0.15
	0.3	49	0.00	0.1	6	0.01
35-40	6.2	-23	0.10	6.4	-82	0.16
	0.1	53	0.01	0.1	29	0.02
40-45	6.2	-23	0.10			
	0.4	99	0.02			
Diked-drained						
0-5	4.1	528	0.26	8.1	-142	0.23
	0.2	28	0.03	0.3	316	0.09
5-10	4.0	563	0.50	7.0	-82	0.41
	0.3	52	0.01	0.1	25	0.03
10-15	3.7	591	0.58	6.6	20	0.55
	0.0	76	0.02	0.1	58	0.05
15-20	3.7	621	0.65	6.4	75	0.66
	0.3	98	0.09	0.1	52	0.03
20-25	3.5	586	0.65	6.5	65	0.70
	0.1	1	0.01	0.1	38	0.11
25-30	3.7	510	0.59	6.5	48	0.74
	0.3	46	0.05	0.1	10	0.13
30-35	3.9	490	0.55	6.5	67	0.79
	0.1	26	0.06	0.1	23	0.16
35-40	3.9	382	0.58	6.4	85	0.82
	0.1	210	0.03	0.1	17	0.07
40-45	4.0	366	0.61			
			0.0	18	0.02	

Notes: Subsidence during seawater flooding and compaction during coring caused the decreased posttreatment sediment depths of diked-flooded and diked-drained cores, respectively.

significantly from the natural marsh except for elevated NH_4 , likely mobilized by cation exchange. It should be noted that seemingly similar sulfide concentrations before and after treatment in the DD cores of our laboratory experiment do not reflect field conditions in which concentrations vary with tide height and periodic air entry (Howes et al. 1986, DeLaune 1993). Sulfide in constantly waterlogged DF cores remained high (>3 mmol/L).

Salination of diked-drained marsh

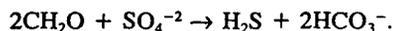
The large increases in alkalinity, and consequently pH (Fig. 2), in DD cores were likely a result of both Fe(III) and SO_4 reduction concurrent with declining Eh. Eh decreases and pH increases were most pronounced in surface soils (Table 2), which are richest in organic

TABLE 3. Original sediment stocks, net change in solid phase inventories, and masses of inorganic elements added with seawater and removed with sampled porewater in microcosms. Data are presented as means, with one standard error on the next row down; all units are grams.

Treatment	Organic matter	Fe	P	S	C	N
DF (diked, seasonally flooded)						
Original stocks	694	6.2	0.76	22.7	377	20.8
	87	0.2	0.01	2.3	48	1.7
Net change	+8	<u>-1.5</u>	-0.05	+2.9	-40	-2.6
	31	0.2	0.06	1.3	14	0.04
Removed with porewater	ND	0.06	T	14.9	ND	0.18
		0.03		0.7		0.10
Added with seawater	ND	T	0.001	13.0	ND	T
DD (diked, drained)						
Original stocks	737	121	2.97	48.9	290	25.7
	76	11	0.19	17.7	16	1.0
Net change	-71	-23	+0.36	-24.3	-48.9	-5.7
	15	6	0.34	3.8	11.2	1.6
Removed with porewater	ND	49.5	0.02	17.0	ND	1.47
		14.0	0.01	0.9		0.2
Added with seawater	ND	T	0.001	13.0	ND	T

Notes: $N = 3$. Underlined net changes are significant ($P < 0.05$). T = trace (< 0.001 g); ND = not determined. Note that dissolved organic species were not determined.

matter consisting of the roots and litter from modern terrestrial vegetation. Seawater flooding promotes reducing conditions by excluding air, supplying abundant SO_4 for organic carbon catabolism, and generating both sulfides and bicarbonate alkalinity (Berner 1971):



The sulfides readily reduce abundant ferric oxyhydroxides to form mackinawite and release base (Fenchel and Blackburn 1979):



Salination caused Fe(II) to increase to a concentration (60 mmol/L) over 10 times that observed when

freshwater was used to artificially flood acid sulfate soils (Breemen 1976). This difference is consistent with sediment extractions in which 2 mol/L KCl extracts are compared with distilled water as the diluent: cation exchange releases about three times the Fe dissolved by water alone (Portnoy and Giblin, *in press*). Seawater can mobilize more Fe(II) because (1) its high ionic strength promotes the exchange of Fe(II) sorbed onto clay particles; and (2) enhanced sulfate reduction lowers Eh and promotes Fe(III) reduction and dissolution. Fe(II) increased in bottom port samples until September 1993 (Fig. 2), indicating that its rate of mobilization exceeded that required for sulfide precipitation. Unlike what occurred in DF cores, free sulfide

TABLE 4. Porewater chemistry within the root zone (10–20 cm depth) of DF (diked, seasonally flooded) and DD (diked, drained) sediments before (Jan 1993) and after (Aug 1994) salination compared with that of a natural salt marsh just seaward of DF in August 1994. Data are presented as means, with one standard error on the next row down.

	DF		DD		Natural marsh
	Before	After	Before	After	
Salinity (g/kg)	0.7 ^a	33.7 ^b	0.7 ^a	31.6 ^b	31.3 ^b
	0.6	1.5	0.6	2.5	2.1
pH	6.3 ^a	6.7 ^a	4.6 ^b	6.8 ^a	6.7 ^a
	0.3	0.1	0.6	0.1	0.1
Alkalinity (mmol/L)	2.7 ^a	27.7 ^b	0.3 ^a	31.0 ^b	22.3 ^b
	0.7	9.9	0.3	1.0	4.9
Sulfides (mmol/L)	0.0 ^a	5.0 ^b	0.0 ^a	0.4 ^a	5.3 ^b
	0.0	2.5	0.0	0.3	0.4
Fe(II) ($\mu\text{mol/L}$)	25 ^a	1.3 ^a	389 ^b	119 ^c	0.6 ^a
	10	0.1	31	97	1.0
TFe ($\mu\text{mol/L}$)	44 ^a	1.3 ^a	469 ^b	199 ^c	1.0 ^a
	1	0.1	31	127	0.7
$\text{NH}_4\text{-N}$ ($\mu\text{mol/L}$)	2.2 ^a	1127 ^b	165 ^a	4900 ^c	322 ^a
	0.3	46	25	656	94
$\text{PO}_4\text{-P}$ ($\mu\text{mol/L}$)	0.9 ^a	12.3 ^a	20 ^a	135 ^b	6.3 ^a
	0.4	3.8	1	95	0.6

Notes: $N = 3$. For each variable, means with different superscript letters are significantly different ($P < 0.05$).

was never detected in DD bottom port samples, expected with the persistence of >10 mmol/L Fe(II), but did occur at 5-cm depth by August and 20 cm by November 1993. These shallow sediments had lowest Fe and highest organic content (Portnoy and Giblin, *in press*) so that Fe(II) depletion by sulfide precipitation was expected first here.

We attribute the 40- to 60-fold $\text{NH}_4\text{-N}$ increase in DD porewater to cation exchange (Fig. 3). Though most organic matter has decomposed, the retention of N in acid sulfate soils at DD is not surprising. Consistently low pH since diking has probably inhibited both nitrification (Focht and Verstraete 1977) and volatilization losses of NH_4 released by aerobic mineralization. Much of this NH_4 was likely protected from leaching by adsorption to negatively charged soil particles. Thus, an immediate effect of salination was desorption of abundant NH_4 . Ammonium removed in sampled porewater accounts for $\approx 26\%$ of the N loss from sediment stocks (Table 3).

Inorganic P is present in acid sulfate soils as Fe and Al phosphates formed at low pH (Dent 1986). The observed 20-fold P increase is expected with declining Eh (Satawathanant et al. 1991) and the reduction of Fe(III) minerals by newly generated sulfides. Because Al does not undergo redox reactions, its initial dissolution and 6-fold increase in DD sediments (Fig. 4) was due to cation exchange of the sorbed metal, originally leached from aluminosilicate clays under oxidized, acidic conditions. In contrast, dissolved Al remained at levels of only 5–7 $\mu\text{mol/L}$ in DF porewater after salination (Portnoy 1996).

In contrast with DF sediments, salination of DD soils produced root-zone porewaters that differed significantly from the natural marsh (Table 4), with much higher Fe(II), TFe, NH_4 , and PO_4 , and much lower sulfide. In general, high-nutrient, low-sulfide conditions should favor macrophyte growth.

Implications for restoration programs

Sediment subsidence is of particular concern in DF-type marshes following tidal restoration because it will lead to prolonged flooding and may exacerbate sulfide toxicity. Our experiments show that DF sediments accumulate dissolved sulfides when waterlogged with SO_4 -rich seawater, primarily because of the lack of reactive Fe for sulfide precipitation in low-inorganic-content freshwater wetland peat. Reduced plant production is expected from sulfide toxicity (Mendelssohn and McKee 1988), which deactivates enzymes involved in N uptake (Koch et al. 1990), although this effect can be offset by high N availability (Howes et al. 1986) particularly as observed within shallow root zones (Table 4). The DF peat surface in our study is already ≈ 15 cm below unrestricted *Spartina* marsh on the seaward side of the dike; any additional subsidence could prolong flooding and worsen soil conditions for wetland plants. Plant death and peat collapse have been noted

after salt water intrusion in Louisiana brackish marshes (DeLaune et al. 1994).

Sulfide toxicity following tidal restoration in the DD marsh is much less a concern, despite greater subsidence and potentially deeper and more prolonged flooding after restoration, because the high concentrations of Fe(II) mobilized by seawater will precipitate sulfides. In addition, $\text{NH}_4\text{-N}$ concentrations after salination in our study were even higher (by sixfold) than in DF sediments, likely counteracting sulfide interference of N assimilation.

The release of millimolar Fe(II), and lesser amounts of Al, from the salinated acid sulfate DD soils could have adverse biological effects. Ferrous iron toxicity has limited the success of rice agriculture in flooded acid sulfate soils (Dent 1986) and may inhibit *Spartina* growth (Grill et al. 1985). As for sulfide, however, Fe(II) and Al phytotoxicity could be offset by abundant nutrients, especially $\text{NH}_4\text{-N}$. Aluminum can be very toxic to aquatic fauna, particularly fish (Driscoll et al. 1980); nevertheless, the rapid pH recovery of salinated microcosms, from pH < 4 to circumneutral within a few months, should reduce Al toxicity.

The potentially large mass of nutrients mobilized by increased decomposition, cation exchange, and phosphate mineral dissolution during seawater restoration could depress dissolved oxygen in surface waters by promoting algal production and organic loading. We expect a particularly large $\text{NH}_4\text{-N}$ mobilization immediately after seawater inundates diked and drained soils. This element is widely believed to limit algal production in coastal waters (Ryther and Dunstan 1971, Howarth 1988) and to be responsible for eutrophication where N loading has increased (Valiela et al. 1990). Thus, primary production may increase in receiving waters of DD soils experiencing seawater reintroduction.

CONCLUSIONS

The biogeochemical responses of diked salt marshes to tidal restoration depend on the wetland's flooding regime since original diking and the long-term effects of flooding depth and duration on substrate composition. Seasonally flooded marshes accrete freshwater wetland peat near the surface while maintaining reduced marine deposits below 30 cm. In contrast, surficial soils of drained marshes contain only a small fraction of the organic content of adjacent salt marshes; most pyrite iron and sulfur has oxidized. These comparisons alone suggest radically different responses to increased ionic strength and sulfate, and decreased redox accompanying seawater flooding.

The major changes that we observed in microcosms of resalinated, historically diked marsh soils can substantially affect estuarine plants and animals. Changes include sulfide accumulation in seasonally flooded diked peat, metal increases in drained peat, and nutrient mobilization in both seasonally flooded and diked-

drained peat. These dramatic responses emphasize the need for carefully phased tidal restoration programs that include periodic monitoring, experimentation, and assessment both within the restoration area and in receiving waters.

ACKNOWLEDGMENTS

We thank J. Wood, M. Dornblazer, and K. Regan for field and laboratory assistance and I. Valiela, C. Hopkinson, W. Bowden, and two anonymous reviewers for helpful comments. This work was supported by the National Park Service, Water Resources Division. Salary support for A. E. Giblin was provided by NSF-OCE and NOAA Sea Grant. We are indebted to Cape Cod National Seashore and the Sibley Family Trust for access to study sites.

LITERATURE CITED

- Adams, D. A. 1963. Factors influencing vascular plant zonation in North Carolina salt marshes. *Ecology* 44:445-456.
- APHA. 1992. Standard methods for the examination of water and wastewater. 18th Edition. American Public Health Association, Washington, D.C., USA.
- Berner, R. A. 1971. Principles of chemical sedimentology. McGraw-Hill, New York, New York, USA.
- Breemen, N. V. 1976. Genesis and solution chemistry of acid sulfate soils in Thailand. Dissertation. Wageningen, The Netherlands.
- , 1982. Genesis, morphology, and classification of acid sulfate soils in coastal plains. Pages 95-108 in J. A. Kittrick, D. S. Fanning, and L. R. Hossner, editors. Acid sulfate weathering. Soil Science Society of America Special Publication No. 10.
- Bricker-Urso, S., S. W. Nixon, J. K. Cochran, D. J. Hirshberg, and C. Hunt. 1989. Accretion rates and sediment accumulation in Rhode Island salt marshes. *Estuaries* 12:300-317.
- Capone, D. G., and R. P. Kiene. 1988. Comparison of microbial dynamics in marine and freshwater sediments: Contrasts in anaerobic carbon catabolism. *Limnology and Oceanography* 33:725-749.
- Cline, J. D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnology and Oceanography* 14:454-458.
- DeLaune, R. D. 1993. Response of coastal vegetation to flooding and salinity: a case study in the rapidly subsiding Mississippi River deltaic plain, USA. Pages 211-229 in M. B. Jackson and C. R. Black, editors. Interacting stresses on plants in a changing climate. Springer-Verlag, Berlin, Germany.
- DeLaune, R. D., J. A. Nyman, and W. H. Patrick, Jr. 1994. Peat collapse, ponding and wetland loss in a rapidly submerging coastal marsh. *Journal of Coastal Research* 10:1021-1030.
- DeLaune, R. D., W. H. Patrick Jr., and N. Van Breemen. 1990. Processes governing marsh formation in a rapidly subsiding coastal environment. *Catena* 17:277-288.
- DeLaune, R. D., S. R. Pezeshki, and W. H. Patrick, Jr. 1987. Response of coastal plants to increase in submergence and salinity. *Journal of Coastal Research* 3:535-546.
- Dent, D. 1986. Acid sulfate soils: A baseline for research and development. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands.
- DeSista, R. J., and C. J. Newling. 1979. A review of mosquito control operations in Massachusetts wetlands. Regulatory Branch, New England Division, U.S. Army Corps of Engineers, Waltham, Massachusetts, USA.
- Driscoll, C. T., J. P. Baker, J. J. Bisogni, and C. L. Schofield. 1980. Effect of aluminum speciation on fish in dilute acidified waters. *Nature* 284:161-164.
- Edmond, J. M. 1970. High precision determination of titration alkalinity and total carbon dioxide content of seawater by potentiometric titration. *Deep-Sea Research* 17:737-750.
- Fenchel, T., and T. H. Blackburn. 1979. Bacteria and mineral cycling. Academic Press, New York, New York, USA.
- Ferrigno, F., and D. M. Jobbins. 1968. Open marsh water management. Proceedings of the New Jersey Mosquito Extermination Association 55:104-115.
- Focht, D. D., and W. Verstraete. 1977. Biochemical ecology of nitrification and denitrification. *Advances in Microbial Ecology* 1:135-214.
- Grill, E., E. L. Winnacker, and M. H. Zank. 1985. Phytochelatins: the principal heavy-metal complexing peptides in higher plants. *Science* 230:674-676.
- Howarth, R. W. 1988. Nutrient limitation of net primary production in marine ecosystems. *Annual Review of Ecology and Systematics* 19:89-110.
- Howes, B. L., J. W. H. Dacey, and D. D. Goehring. 1986. Factors controlling the growth form of *Spartina alterniflora*: feedbacks between above-ground production, sediment oxidation, nitrogen and salinity. *Journal of Ecology* 74:881-898.
- Howes, B. L., R. W. Howarth, I. Valiela, and J. M. Teal. 1981. Oxidation-reduction potentials in a salt marsh: spatial patterns and interactions with primary production. *Limnology and Oceanography* 26:350-360.
- Hussey, B. H., and W. E. Odum. 1992. Evapotranspiration in tidal marshes. *Estuaries* 15:59-67.
- James, B. R., C. J. Clark, and S. J. Riha. 1983. An 8-hydroxyquinoline method for labile and total aluminum in soil extracts. *Soil Science Society of America Journal* 47:893-897.
- Kemp, P. R., and G. L. Cunningham. 1981. Light, temperature and salinity effects on growth, leaf anatomy and photosynthesis in *Distichlis spicata*. *American Journal of Botany* 68:507-516.
- Koch, M. S., I. A. Mendelssohn, and K. L. McKee. 1990. Mechanism for the hydrogen-sulfide-induced growth limitation in wetland macrophytes. *Limnology and Oceanography* 35:399-408.
- Krom, M. D., and R. A. Berner. 1981. The diagenesis of phosphorus in a nearshore marine sediment. *Geochimica et Cosmochimica Acta* 45:207-216.
- Luther, G. W., III, P. A. Shellenbarger, and P. J. Brendel. 1996. Dissolved organic Fe(III) and Fe(II) complexes in salt marsh porewaters. *Geochimica et Cosmochimica Acta* 60:951-960.
- Mendelssohn, I. A., and K. L. McKee. 1988. *Spartina alterniflora* die-back in Louisiana: time-course investigation of soil waterlogging effects. *Journal of Ecology* 76:509-521.
- Mitsch, W. J., and J. G. Gosselink. 1993. Wetlands. Van Nostrand Reinold, New York, New York, USA.
- Montague, C. L., A. V. Zale, and H. F. Percival. 1987. Ecological effects of coastal marsh impoundments: a review. *Environmental Management* 11:743-756.
- Neely, W. W. 1958. Irreversible drainage—a new factor in waterfowl management. *Transactions of the North American Wildlife Conference* 23:342-348.
- Nickerson, N. H. 1978. Protection of Massachusetts' wetlands by order of conditions issued by local Conservation Commissions. Pages 69-76 in Proceedings of National Wetland Protection Symposium. U.S. Department of Interior, Washington, D.C., USA.
- Nyman, J. A., M. Carloss, R. D. DeLaune, and W. H. Patrick, Jr. 1994. Erosion rather than plant dieback as the mechanism of marsh loss in an estuarine marsh. *Earth Surface Processes and Landforms* 19:69-94.
- Parrondo, R. T., J. G. Gosselink, and C. S. Hopkinson. 1978.

- The effect of salinity and drainage on the growth of three salt marsh grasses. *Botanical Gazette* 139:102-107.
- Portnoy, J. W. 1984. Salt marsh diking and nuisance mosquito production on Cape Cod, Massachusetts. *Journal of the American Mosquito Control Association* 44:560-564.
- . 1991. Summer oxygen depletion in a diked New England estuary. *Estuaries* 14:122-129.
- . 1996. Effects of diking, drainage and seawater restoration on biogeochemical cycling in New England salt marshes. Dissertation. Boston University Marine Program, Boston, Massachusetts, USA.
- Portnoy, J. W., and A. E. Giblin. *In press*. Effects of historic tidal restrictions on salt marsh sediment chemistry. *Biogeochemistry*.
- Portnoy, J. W., C. T. Roman, and M. A. Soukup. 1987. Hydrologic and chemical impacts of diking and drainage of a small estuary (Cape Cod National Seashore): Effects on wildlife and fisheries. Pages 253-265 in W. R. Whitman and W. H. Meredith, editors. *Proceedings of a Symposium on Waterfowl and Wetlands Management in the Coastal Zone of the Atlantic Flyway*. Coastal Management Program, Dover, Delaware, USA.
- Roman, C. T., R. W. Garvine, and J. W. Portnoy. 1995. Hydrologic modeling as a predictive basis for ecological restoration of salt marshes. *Environmental Management* 19:559-566.
- Roman, C. T., W. A. Niering, and R. S. Warren. 1984. Salt marsh vegetation change in response to tidal restriction. *Environmental Management* 8:141-150.
- Rozsa, R. 1987. An overview of wetland restoration projects in Connecticut. Pages 1-11 in *Proceedings of the Fourth Connecticut Institute of Water Resources Wetland Conference*, Hartford, Connecticut.
- Ryther, J. H., and W. M. Dunstan. 1971. Nitrogen, phosphorus and eutrophication in the coastal marine environment. *Science* 171:1008-1013.
- Satawathananont, S., W. H. Patrick, and P. A. Moore Jr. 1991. Effect of controlled redox conditions on metal solubility in acid sulfate soils. *Plant and Soil* 133:281-290.
- Soil Conservation Service. 1994. Evaluation of restorable salt marshes in New Hampshire. U.S. Department of Agriculture, Durham, New Hampshire, USA.
- Soukup, M. A., and J. W. Portnoy. 1986. Impacts from mosquito control-induced sulfur mobilization in a Cape Cod estuary. *Environmental Conservation* 13:47-50.
- Stookey, L. L. 1970. Ferrozine—A new spectrophotometric reagent for iron. *Analytical Chemistry* 42:779-781.
- Stumm, W., and J. J. Morgan. 1981. *Aquatic chemistry*. J. Wiley and Sons, New York, New York, USA.
- Taylor, N. 1939. Salt tolerance of Long Island salt marsh plants. *New York State Museum Circular* 23. Albany, New York, USA.
- Thom, R. M. 1992. Accretion rates of low intertidal salt marshes in the Pacific Northwest. *Wetlands* 12:147-156.
- Valiela, I., J. Costa, K. Foreman, J. M. Teal, B. Howes, and D. Aubrey. 1990. Transport of groundwater-borne nutrients from watersheds and their effects on coastal waters. *Biogeochemistry* 10:177-197.
- Warren, R. S., and W. A. Niering. 1993. Vegetation change on a northeast tidal marsh: interaction of sea-level rise and marsh accretion. *Ecology* 74:96-103.