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Biogeochemical response of organic-rich freshwater marshes in the Louisiana delta plain to chronic river water influx

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Abstract To help evaluate effects of Mississippi River inputs to sustainability of coastal Louisiana ecosystems, we compared porewater and substrate quality of organic-rich *Panicum hemitomon* freshwater marshes inundated by river water annually for more than 30 years (Penchant basin, PB) or not during the same time (Barataria basin, BB). In the marshes receiving river water the soil environment was more reduced, the organic substrate was more decomposed and accumulated more sulfur. The porewater dissolved ammonium and orthophosphate concentrations were an order of magnitude higher and sulfide and alkalinity concentrations were more than twice as high in PB compared with BB marshes. The pH was higher and dissolved iron concentrations were more than an order of magnitude lower in PB marshes than in BB marshes. The influx of nutrient-rich river water did not enhance end-of-year above-ground standing biomass or vertical accretion rates of the shallow substrate. The differences in porewater chemistry and substrate quality are reasonably linked to the long-term influx of river water through biogeochemical processes and transformations involving alkalinity, nitrate and sulfate. The key factor is the continual replenishment of alkalinity, nitrate and sulfate via overland flow during high river stage each year for several weeks to more than 6 months. This leads to a reducing soil environment, pooling of the phytotoxin sulfide and inorganic nutrients in porewater, and internally generated alkalinity. Organic matter decomposition is enhanced under these conditions and root mats degraded. The more decomposed root mat makes these marshes more susceptible to erosion during infrequent high-energy events (for example hurricanes) and regular low-energy events, such as tides and the passage of weather fronts. Our findings were unexpected and, if generally applicable, suggest that river diversions may not be the beneficial mitigating agent of wetland restoration and conservation that they are anticipated to be.

Keywords Alkalinity · Freshwater diversions · Organic matter decomposition · Sulfate · Wetland restoration

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Introduction

Wetlands of the Mississippi River delta plain in coastal Louisiana are eroding at annual rates of about 20 km^2, less than the rates of between 45 and 75 km^2 measured in the 1980s (Barras et al. 2003), but nonetheless substantial. The loss threatens New Orleans and other human settlements along the coast, an oil and gas infrastructure that delivers >25% of the energy needs of the United States as well as the second ranked commercial fisheries in the United States. The rapid wetland loss is occurring in part because of substantial disruptions to the inflow and distribution of freshwater and sediments (Mendelssohn et al. 1983; Turner and Cahoon 1987; Boesch et al. 1994).

The confinement of the Mississippi River behind flood-control levees in much of southeastern Louisiana mostly has eliminated the regular overbank flooding that historically brought freshwater and mineral sediments to many deltaic marshes. The input of freshwater and sediments is thought to be critical for marshes to keep pace with regional submergence that in many places averages more than 1 cm per year (Hatton et al. 1983; Boesch et al. 1994). To mitigate the loss of the economically and ecologically valuable wetlands, large-scale restoration projects are being proposed and implemented (Coastal Protection and Restoration Authority of Louisiana 2007; Day et al. 2007). One restoration approach is to divert freshwater from the Mississippi River across flood-control levees and into adjacent marshes to recreate the natural springtime overbank flooding that occurred before the levees were built. Water is taken directly from the river and either pumped over or let flow under the levees and into the adjacent estuaries. The construction and operation of freshwater diversions is integral to all coast-wide restoration plans for Louisiana.

The introduction of clays and silts, freshwater, and nutrients is assumed to nourish wetlands and enhance vertical accretion of marsh soils (Coastal Protection and Restoration Authority of Louisiana 2007; Day et al. 2007). Most of the freshwater diversions in Louisiana currently (2007) in operation or in the design phase have maximum flows of between 150 and 300 m^3 s^{-1}. Since little clay and silt is transported beyond the immediate outfall area in diversions of this magnitude (Snedden et al. 2006), diversion benefits further downstream are restricted to freshwater and nutrient inputs rather than mineral sediments. Thus, for the majority of wetlands downstream from diversions, possible benefits would accrue because of factors related to water quality, and not because of the input of mineral sediment. Freshwater inputs decrease salinity, creating habitat space for plant communities needing relatively less mineral sediment input for substrate growth and sustenance (DeLaune et al. 2003). Nutrient input also may benefit marshes. Marsh above-ground productivity was enhanced at sites receiving river water (DeLaune et al. 2005a). Lane et al. (2006) suggested marshes receiving river water accreted vertically at faster rates than control sites. McKee et al. (2007) demonstrated an increase in elevation for P-limited mangroves when fertilized with P.

Such beneficial marsh responses to freshwater diversions in coastal Louisiana may be complicated by changes in water quality of the Mississippi River since the turn of the twentieth century, when the river last regularly overflowed its banks unencumbered by flood-control levees. Since the early 1950s, the annual spring floodwaters of the Mississippi River have contained a variety of agricultural chemicals, including herbicides and fertilizers that are washed from farm fields in the Midwest (Meade 1995; Clark et al. 1999). Nitrate concentrations have increased two to threefold during this time (Turner and Rabalais 1991). Floodwaters also contain atrazine, an herbicide that inhibits root growth and is commonly used on corn and sugarcane crops. This herbicide has been shown to inhibit growth of wetland plants (Langan and Hoagland 1996). Atrazine was not present in the Mississippi River prior to the early 1960s but is detected in low concentrations offshore and in many inland coastal Louisiana locations throughout the year, and at peak concentrations during the spring (McMillin and Means 1996; Demcheck and Swarzenski 2003).

Several studies indicate a potentially negative role for nutrient additions to wetlands. Elevated nutrients and eutrophic conditions are thought to contribute to the long-term reed decline in Europe (van der Putten 1997; Clevering 1998; Cizkova et al. 1999). High nutrient concentrations may shift the balance of plant production from below- to above-ground (Ulrich and Burton 1985; Boar et al. 1989; Saarinen 1998). Boar et al. (1989) linked the decline of reed stands in some English marshes to eutrophication of surface waters.

Cellulose decomposition was faster at sites with elevated nutrient concentrations (Mendelssohn et al. 1999). Long-term nutrient additions have resulted in the loss of soil carbon in salt marsh soil (Morris and Bradley 1999), and in arctic tundra (Mack et al. 2004). Atmospheric N deposition was positively correlated with carbon loss in a study of bogs throughout Europe (Bragazza et al. 2006). Accelerated subsurface decomposition due to excess nutrient deposition may have led to decreases in bog surface elevations in northern Europe (Franzen 2006). Sulfate and alkalinity introduced by river water were identified as pollutants in Dutch fens that have highly organic soils (Roelofs 1991; Lamers et al. 1998, 2002). Sulfate reduction in anaerobic soils caused the phytotoxin sulfide to accumulate in porewater and facilitated the release of phosphate through iron-mediated reactions (termed internal eutrophication). Bacterial decomposition was favored by elevated P while plant community composition and productivity were affected by elevated sulfides. Overall, these studies indicate marsh loss is possible even when marsh gain is the intended goal of river diversion projects.

In this study, porewater and substrate quality of marshes inundated by river water annually for more than 30 years were compared with similar marshes isolated from river water inflow during the same period. Organic-rich freshwater marshes were chosen because, with a substrate typically containing more than 80% organic matter they are among the most sensitive of marsh environments to changes in water quality (Loeb et al. 2007). Organic-rich marshes occur extensively in the upper reaches of the Louisiana delta plain, with an aerial extent of about 150,000 ha (O'Neil 1949; Evers et al. 1996). They are located immediately downstream from many existing and proposed controlled river diversions.

Study area

The study area is located in coastal Louisiana at about 29°30′ N, and between 90° W and 91° W in the low-salinity (0.5 to 4 ppt) reaches of the deltaic plain of the Mississippi River (Fig. 1). Here, most emergent marshes are peat-based because of the lack of available mineral sediment (O'Neil 1949). These marshes are collectively known as flotant (Russell 1942), referring to the buoyancy of the upper 50 cm of some, but not all, of these marshes. The term peat marsh is used to refer to floating and nonfloating marshes interchangeably in this study except where specifically noted.

The Barataria basin (BB) marshes are in the Barataria Preserve of Jean Lafitte National Historical Park and Preserve, located about 15 miles south of New Orleans. The marshes have been isolated from river water influx since early in the twentieth century. Precipitation is the primary source of freshwater. There are no structural impediments to the flow of water between the Preserve and the Gulf of Mexico, about 50 km to the south. The Penchant basin (PB) marshes are located adjacent to and east of the Lower Atchafalaya River. This area has been functioning as the hydrological and ecological equivalent of a large river diversion for many years. The eastward flow is passive, due to naturally occurring gradients in water levels brought about by the annual spring flood in the river (Swarzenski 2003). In an average year, water flows into and over the marshes from January through July. The water in the Lower Atchafalaya River originates from the Mississippi River, and water quality of the two rivers is similar (Wells and Demas 1977). River water saturates porewater to at least 90-cm depth in marshes in the interior of the Penchant basin (data on file with the USGS in Baton Rouge, LA).

Methods

The sampling sites were in large expanses of interior marsh dominated by *Panicum hemitomon*, accessible only by airboat. Four interior marshes were sampled at the Barataria Preserve. Direct measurement indicated two of the four marshes were floating. Four marshes were sampled along the southeastern part of the Penchant basin, downstream from the inflowing river water, which entered the marshes along the northern and western edge of the study area. The buoyancy of these marshes was not determined. The four sampling sites within each basin were spaced 1 to 5 km apart.

Porewater and soil redox

Porewater was sampled at 15- and 45-cm depths with an acrylic tube (4-mm inside diameter) inserted into

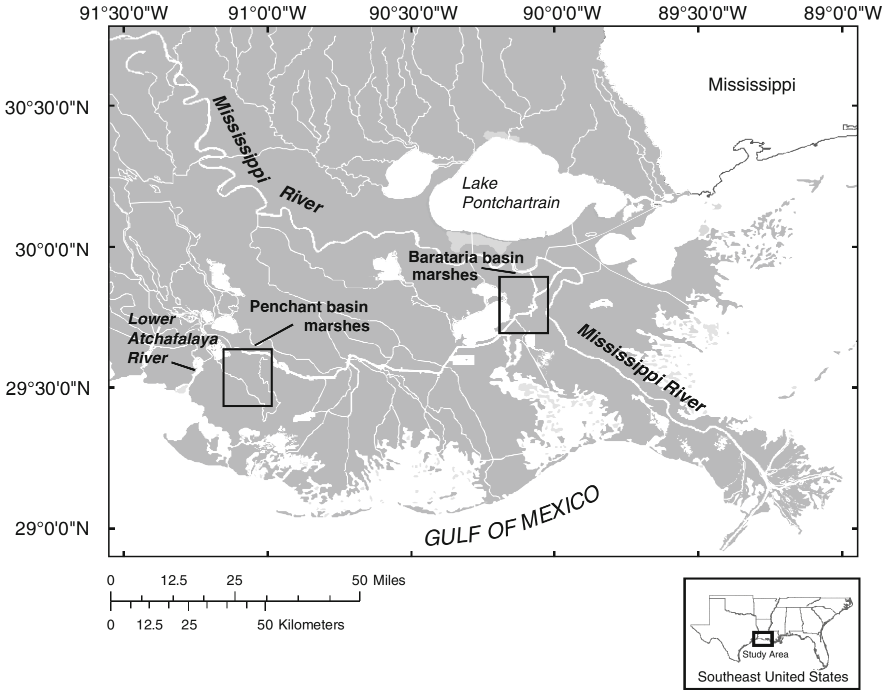


Fig. 1 Vicinity map of the Barataria and Penchant basin marshes in southern coastal Louisiana

the substrate. These depths bracket the depth at which the majority of root production occurs. Porewater was withdrawn through this tube with a plastic syringe. Porewater from three randomly chosen spots separated by no more than 15 m within each marsh site was composited in 250-ml bottles during each sampling trip. Water was either filtered in the field or in the laboratory on the same day through disposable 0.45 µm nylon filters (Whatman GD/X). Samples were chilled in the field, and shipped on ice to the USGS National Water Quality Laboratory in Denver, Colorado, within 24 h of collection. Dissolved ammonium (salicylate hypochlorite) and orthophosphate (phosphomolybdate) were analyzed using automated colorimetry (Fishman 1993). Iron was analyzed using inductively coupled plasma atomic emission spectrophotometry (USEPA 1983). Chloride and sulfate were analyzed using ion chromatography (USEPA 1983). Every 10th sample was a duplicate used for quality assurance and control. The filtration process may have oxygenated porewaters, but a bias towards low iron and phosphate numbers was not apparent.

Porewater also was collected during each sampling trip at 5-, 15- and 45-cm depth for pH and sulfide determinations. Alkalinity was determined at 15-cm depth by titrating with a dilute acid using the inflection point method (Rounds and Wilde 2001). The pH was measured using a digital pH meter standardized with a two point calibration using buffers of pH 4 and 7. For sulfide measurements, standards and a dilute sodium salicylate antioxidant buffer were prepared in the laboratory prior to field trips, and stored on ice in airtight containers. In the field, 5 ml of porewater were collected and mixed with an equal volume of fresh buffer solution. Duplicate samples were collected at each depth. Samples and standards were analyzed on the same day using a sulfide-specific electrode and the digital pH meter with millivolt conversion capabilities. Readings were converted from millivolts to milligrams per liter by using a log regression standard curve. Sampling was carried out at 6–8 week intervals between fall of 1998 and summer of 2002. Marshes in Barataria and Penchant basins were visited on successive days during each sampling trip to maintain consistency in sampling conditions.

Redox potential of the substrate was measured at 2, 9, and 18 cm below the marsh surface during a subset of trips ($n = 8$) over 1 year. Five multidepth probes (Hargis and Twilley 1994a) were inserted into the soil at random points at each site and left to stabilize for 30 min. A portable voltmeter and a calomel reference probe were used to take readings in millivolts. The probes were routinely checked in a quinhydrone solution buffered to a pH of 4 to read at approximately 230 mV. When indicated, the tips were lightly sanded with emery paper to improve the contact. All five values at each site were averaged for each depth, and 230 mV added to determine the redox potential of the soil. The same five redox probes were used during the entire sampling period. In general, redox numbers are best interpreted as a relative measure of electron availability and anaerobic condition in wetland soils (Whitfield 1969; Bohn 1971).

Plant biomass and substrate sampling

Peak above-ground plant biomass was harvested during the first 3 weeks in September from 1998 to 2002 using triplicate clip-plots (area of 0.6 m^2). Plants were separated into live and dead biomass, and oven-dried at 60°C to constant weight. Results for living biomass are presented as average live above-ground standing biomass (g m^{-2}).

Substrate soil samples were collected from the surface to either 25- or 50-cm depth in 5-cm increments. Soil cores were collected from all four BB marshes, and, depending on the analysis, from three or four PB marshes. Cores were collected with a 10-cm diameter coring device with a cutting edge (Hargis and Twilley 1994b), pushed and twisted to the desired depth. Compaction was measured by comparing inside and outside surfaces during the time of collection; it was <2% for all retained cores. Soil bulk properties (dry bulk density and organic matter content were analyzed following Swarzenski et al. (1991). Substrate decomposition was assessed in three different ways. Fiber content (Lynn et al. (1974) measures the amount of material retained after mechanically fractionating the sample while washing it through a sieve (Lynn et al. 1974). The less material retained after fractionation and washing through the sieve, the more decomposed the sample is considered. Substrate decomposition of the upper 25 cm also was assessed by washing soil samples through sieves with mesh sizes of 2,000 and 63 µm and drying the residues to constant weight at 80°C. More easily fractionated and smaller size material indicates a more decomposed substrate. A third way to assess soil decomposition was to measure soil shear strength (McGinnis 1997). The torque required to shear the organic soils of PB and BB marshes was determined with a Torvane device (H-4212 1, Humbolt Manufacturing Company, Durham Geo-Enterprises, Inc.). Soil strength was measured in 5-cm increments along a vertical depth profile to 25 cm. 4-inch diameter cores were taken from the marsh and split longitudinally. The Torvane device was impressed on the flat surface of ½ of the core and the torque required to shear the intertwined root matrix measured. The less torque is needed to shear the soil, the more decomposed that soil is considered.

A portion of coarsely ground soil sample of each 5-cm increment between the surface and 25-cm depth, and plant tissue collected in 1999, were pulverized using a stainless steel Wig-L-Bug shaker and analyzed for carbon, nitrogen and sulfur content and the stable isotopes δ^{13}C, δ^{15}N and δ^{34}S (Fry 2007). Three complete culms (leaves included) of *P. hemitomon* from each of the marsh sites were coarsely homogenized with a Wiley #40 mesh and subsamples pulverized with the same shaker.

Statistical analyses

Porewater and substrate data from all sampling sites within a basin were pooled for each analyte and medium, the data transformed where necessary to meet normality and equal variance criteria, and then analyzed for significant differences between basins ($P < 0.001$, alpha of 0.05) using a paired student's *t*-test (Sigma Stat v.3.01). Transforms did not normalize the orthophosphate data, which were compared using the non-parametric Kruskal–Wallis test.

Results

Plant standing biomass and soil bulk properties in the PB and BB marshes were similar (Table 1). The PB marshes contained relatively less *P. hemitomon*. The bulk density of the upper 25 cm of substrate was low in both systems, but was slightly heavier in PB marshes ($P < 0.001$) because of the greater amount of mineral sediment.

The nitrogen and sulfur content in plant and soil material differed between the PB and BB marshes. For example, in the above-ground plant tissue, the N

Table 1 Characteristics (average ± 1 standard error) of live above-ground plant material and peat substrate (0- to 25-cm depth) in Barataria basin (four sites, without influx of river water) and in Penchant basin (three or four sites, with long-term influx of river water)

	Above-ground material				Peat substrate (0- to 25-cm depth)			
	n	Barataria	*n*	Penchant	*n*	Barataria	*n*	Penchant
Total standing biomass live (g m^{-2})	50	538 ± 31	49	504 ± 30				
Panicum hemitomon live (g m^{-2})	50	441 ± 31*	49	337 ± 27*				
Bulk density (g cm^{-3})					26	0.051 ± 0.002*	30	0.062 ± 0.002*
Organic matter (%)					26	92.4 ± 0.5*	30	78.6 ± 1.7*
% N (nitrogen)	9	0.66 ± 0.05*	7	0.93 ± 0.06*	19	2.61 ± 0.06*	15	2.24 ± 0.08*
% S (sulfur)	9	0.17 ± 0.02*	7	0.31 ± 0.02*	19	0.88 ± 0.05*	15	1.13 ± 0.09*
% C (carbon)	9	44.7 ± 0.2	7	45.0 ± 0.1	19	48.3 ± 04*	15	39.2 ± 1.3*
C:N (molar)	9	71.2 ± 5.6*	7	49.9 ± 3.3*	19	18.7 ± 0.5	15	17.8 ± 0.8
S:C × 1,000 (molar)	9	3.8 ± 0.5*	7	6.9 ± 0.5*	19	18.2 ± 1.0*	15	27.6 ± 1.9*
δ^{15} N	9	−1.29 ± 0.11	7	−0.22 ± 0.13	19	−1.30 ± 0.11	15	0.04 ± 0.24
δ^{34} S	9	9.26 ± 0.37	7	0.17 ± 0.72	19	9.24 ± 0.29	15	−1.33 ± 0.34
δ^{13} C	9	−27.07 ± 0.19	7	−26.95 ± 0.13	19	−27.58 ± 0.07	15	−26.64 ± 0.14
Redox potential (Eh)								
2-cm depth					42	276 ± 8	32	265 ± 15
9-cm depth					42	199 ± 5*	32	169 ± 9*
18-cm depth					42	152 ± 8*	32	94 ± 7*
Torque required to shear soil (kg cm^{-2})					20	2.1 ± 0.08*	20	0.9 ± 0.09*
Fiber content								
Unrubbed[a] (% original volume)					30	89 ± 3*	20	76 ± 3*
Rubbed[b] (% original volume)					30	69 ± 4*	20	44 ± 4*
Rubbed (% unrubbed volume)					30	78 ± 5*	20	58 ± 5*

* Indicates significant difference, $\alpha = 0.05$, $P < 0.001$; isotopes not analyzed for statistical differences

[a] Unrubbed refers to volume of soil remaining after rinsing through a sieve with 0.125-mm openings

[b] Rubbed refers to soil volume remaining after mechanical fractionation of the soil and rinsing over same sieve

and S content was significantly higher in PB marshes compared with BB marshes ($P < 0.001$), by about a third for N and slightly less than half for S (Table 1). In the peat substrate, the N content of PB marshes was lower than in BB marshes ($P < 0.001$). The S content of the peat substrate followed the trends in above-ground tissue, and was significantly higher in PB marshes. When normalized for C, the N content of the peat substrate was not significantly different between the two areas, but the S content was higher in PB marshes (Table 1).

The δ^{15}N values were higher and the δ^{34}S values lower in the above-ground plant material and the peat substrate in PB marshes compared with BB marshes. In PB marshes, the δ^{15}N values were lower and the δ^{34}S values were higher in the above-ground tissue than in the peat substrate, but in BB marshes the above-ground δ^{15}N and δ^{34}S values were similar to peat substrate values (Table 1).

The redox potential of the soil decreased with depth in both PB and BB marshes (Table 1). At the 9- and 18-cm depths, the redox potential in PB marshes was significantly less than in BB marshes ($P < 0.001$). The peat substrate in PB marshes was more decomposed and the unrubbed fiber content lower compared with BB marshes ($P < 0.001$). Proportionately more material from PB marshes washed through the same sieve after manual fractionation (rubbed fiber content) as well ($P < 0.001$). Substrate particle-size distributions from marshes in both areas are shown in Fig. 2; sites differed primarily in the amount of coarse material. Only one PB marsh sample contained more than 60% material with a size greater than 2000 μm. With the exception of

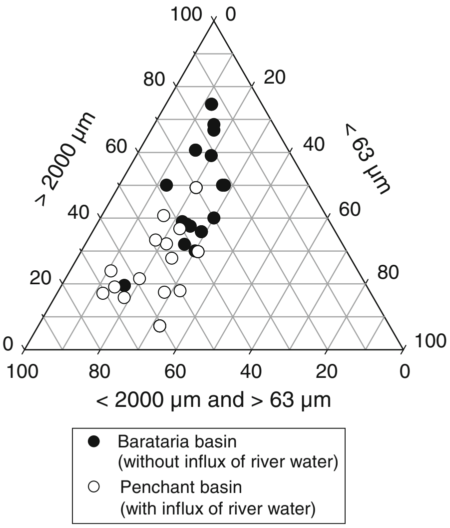


Fig. 2 Breakdown of peat substrate into particle size classes. Peat was analyzed in 5 cm increments to a depth of 25 cm from three sites each in Barataria (without influx of river water) and Penchant basins (with influx of river water)

one depth increment, at least 55% of the material of BB marshes was composed of particles greater than 2000 µm. More than twice as much torque was needed to tear the organic substrate of the BB compared with PB marshes (Table 1).

The ratio of calcium to magnesium concentrations in porewaters was similar to river water in PB marshes but not BB marshes (Fig. 3). The chloride concentrations were lower ($P < 0.001$) in porewater of PB marshes compared with BB marshes at both 15- and 45-cm depth (Fig. 4). Both marshes showed sulfate depletion in porewaters relative to sulfate in inflowing river or surface water (Fig. 4); porewater sulfide concentrations were more than twice as high in PB marshes compared with BB marshes at 15- and 45-cm depths ($P < 0.001$; Fig. 5). Dissolved ammonium and orthophosphate concentrations were higher ($P < 0.001$) in PB marshes than in BB marshes. Limited analyses for nitrate in porewater showed that concentrations were not different between basins, with values close to the detection limit of <1 mM. The dissolved iron concentrations were an order of magnitude lower in PB marshes compared to BB marshes. The pH was higher by about 0.5 units in porewater in PB marshes ($P < 0.001$); alkalinity at 15-cm depth, the only depth sampled for this constituent, was higher in PB marshes compared with BB marshes ($P < 0.001$).

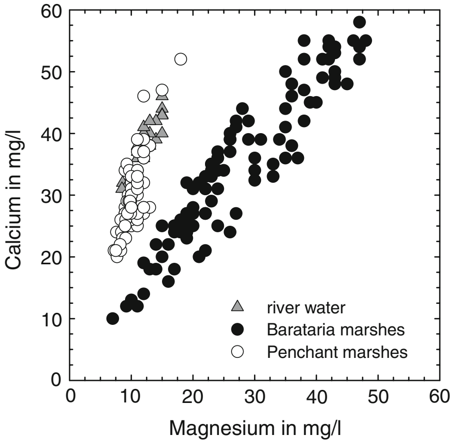


Fig. 3 Relation between calcium and magnesium concentrations in inflowing river water and in porewaters (15 and 45-cm depth) of marshes at Barataria and Penchant basins

The peat substrate δ^{15}N values were similar below 40-cm depth in the two areas, but diverged above this depth (Fig. 6). In PB marshes, values increased toward the surface until they were positive and more than 2‰ higher in the topmost 5 cm. In BB marshes, the δ^{15}N values decreased upward to 15 cm, at which depth the trend reversed. The peat substrate δ^{15}N in BB marshes is around -1‰ near the surface, similar to values observed at depths greater than 40 cm.

Discussion

In the rapidly eroding Louisiana delta plain, the most logical way to place a value on a particular restoration technique is how well it succeeds in building healthy marsh soil. It is essential that the restoration effort builds soil (1) that accretes vertically at rates fast enough to keep pace with long-term regional submergence and (2) that is resilient to chronic small and infrequent large erosive forces, for example daily tidal signals and storm surges associated with hurricanes. Organic matter is crucial to both aspects (Turner et al. 2004). Our study focused on resilience, which is related to the quality of the organic matter.

In marshes receiving the long-term influx of river water, the substrate was more reduced and the soil organic matter was more decomposed, consisting of smaller and more easily fractionated particles, and with providing less resistance to shear compared with marshes without river water influx. This was a key finding of our study. Differences in porewater

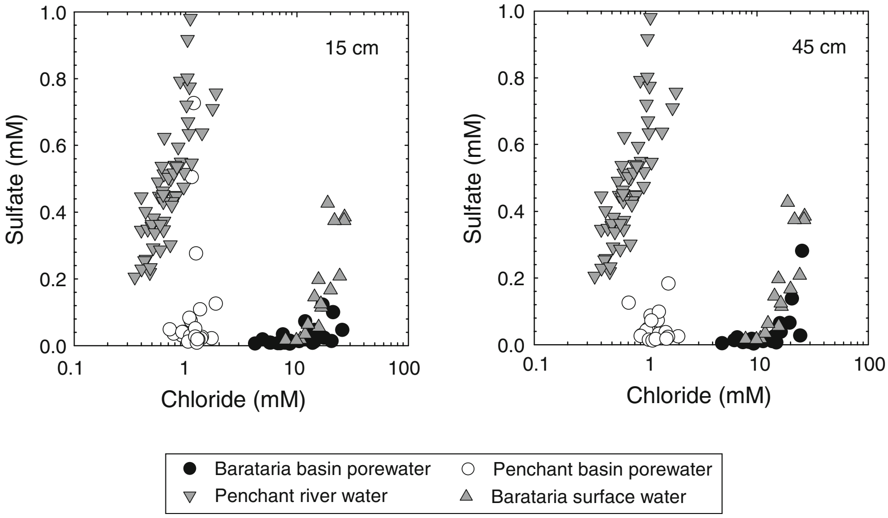


Fig. 4 Chloride:sulfate ratio in porewater of Barataria and Penchant basin marshes, in inflowing Penchant river water and in Barataria surface water. Data were collected between 1998 and 2002

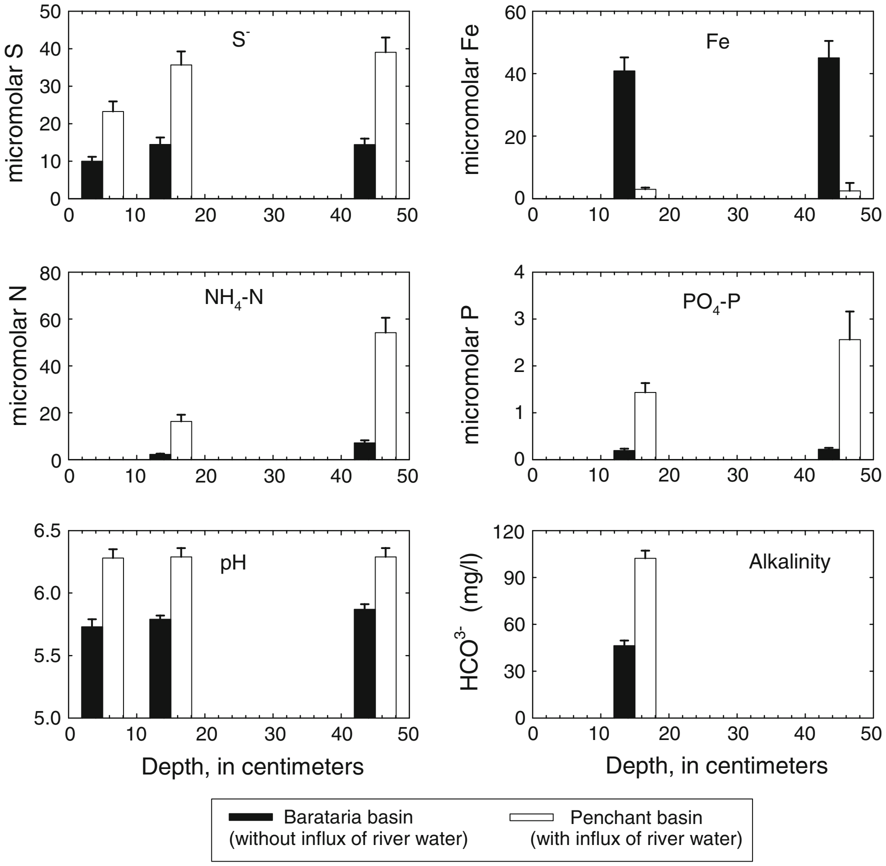
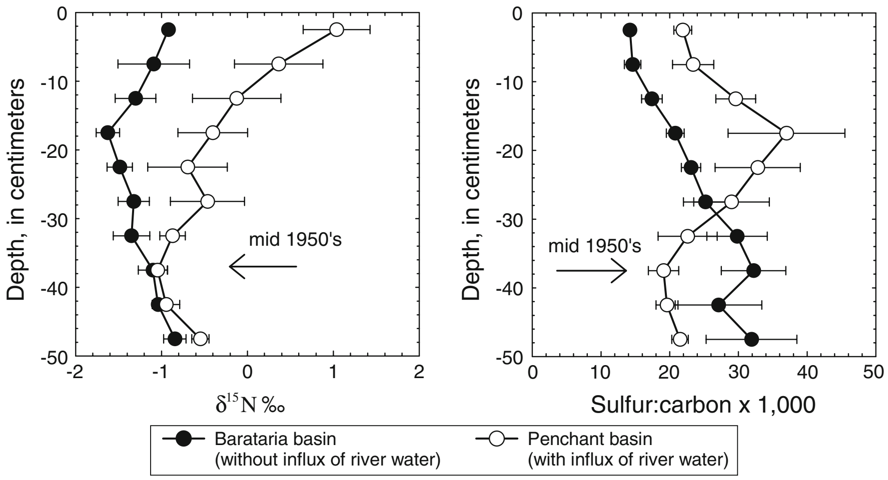


Fig. 5 Concentrations (average ± 1 standard error) of selected constituents in porewater of Barataria and Penchant basin marshes sampled at 4–6 week intervals between September 1998 and June 2002. Four locations within each basin were sampled each time. Differences in concentrations at individual depths are all significant ($\alpha = 0.05$, $P < 0.001$) except for sulfide at 5-cm depth

chemistry between the two areas were consistent with the influx of river water as causing the degradation of the peat, through transformations and biogeochemical processes involving nitrate, sulfate and alkalinity. This interpretation of the data is supported by stable isotope and elemental soil depth profiles, which indicate a shift in nitrogen and sulfur cycling coincident with the period when river water first

Fig. 6 Profiles of δ^{15}N and sulfur:carbon ratios (±1 standard error) with depth in peat samples from Barataria basin ($n = 4$, without river water influx) and from Penchant basin ($n = 3$, with river influx) marshes



started to infiltrate the Penchant marshes. The field observations match results from published greenhouse studies, which link alkaline river influx and soil organic matter breakdown. Our results suggest that controlled river diversions may in some instances contribute to marsh breakup rather than the envisioned restoration and land building.

Evidence for long-term river influx into PB marshes

The patterns in δ^{15}N values and sulfur:carbon ratios in the peat substrate (Fig. 6) suggest a fundamental change in the way nitrogen and sulfur cycled in the marshes in PB above the 35- to 40-cm depth. At this depth, which dates to the mid-1950s (Cs-137 soil accretion data from the same sites, on file with the USGS in Baton Rouge, LA), the δ^{15}N values started trending positive in PB marshes, and diverged from values and trends in BB marshes. Higher δ^{15}N values are expected for areas heavily influenced by river water, which has abundant nitrate with an average δ^{15}N near 8‰ (Fry and Allen 2003). Sulfur began to accumulate at the same depth in PB but not BB marshes. The observed changes in nitrogen and sulfur cycling are consistent with increased river influence in the PB marshes after the mid-1950s.

Porewater chemistry

Porewater quality reflects both the source of the inflowing water, and in-situ soil biogeochemical processes. Because porewater is much less transient than surface waters, analysis can provide useful context into processes which control the soil environment, and which influence organic matter quality and plant vigor.

Porewater calcium:magnesium ratios indicated that river water saturated the substrate to at least 45 cm depth. This influx into PB marshes resulted in lower porewater chloride concentrations compared with BB marshes. Low chloride concentrations are a precondition for the occurrence of plants such as *Panicum hemitomon* that can build their own substrate with minimal mineral sediment input. Habitat space with low ambient chloride concentrations is of value for restoration efforts because many parts of the Mississippi River delta plain are beyond the reach of regular mineral sediment input. Other differences in porewater chemistry suggest a compromised soil environment with river influx. Sulfate, inorganic nutrients, and alkalinity figure prominently.

Sulfide concentrations in porewater were twice as high in PB compared with BB marshes. Sulfide is a phytotoxin for wetland plants (Smolders and Roelofs 1995; Lamers et al. 1998, 2002), including *Panicum hemitomon* (Koch and Mendelssohn 1989). Toxicity can be acute or chronic. Sulfide inhibits root uptake of inorganic nutrients. Damage due to chronic exposure can range from root deformation and decay to mortality (Armstrong and Armstrong 2001). In addition to direct toxicity, sulfate reduction can mobilize phosphate by interfering with the binding with iron-hydroxides, an effect termed "internal eutrophication," because the increased nutrient concentrations occur without additional external input

(Roelofs 1991; Lamers et al. 1998; Smolders et al. 2006). Phosphate can stimulate bacterial mineralization and contribute to organic matter degradation when plant P uptake is reduced due to sulfide toxicity. Finally, even small amounts of sulfur can effectively promote organic matter oxidation when soils reduce and re-form sulfate under changing soil redox conditions (Wieder et al. 1992).

The porewater inorganic nutrient concentrations were greater by as much as an order of magnitude in marshes receiving long-term influx of river water. The elevated concentrations in PB marshes probably resulted from internal eutrophication, and from a combination of increased external supply, inhibition of plant uptake caused by increased sulfide concentrations and more rapid mineralization rates of the peat. A compromised soil environment of PB marshes is suggested not so much by absolute high values and direct toxicity, but by the unused pools of inorganic nutrients. Large pools of unused nutrients may indicate a system imbalance; nitrogen typically is limiting in low-salinity Louisiana marshes dominated by *Panicum hemitomon* (DeLaune et al. 1986). The enhanced nutrient pools in the peat substrate can stimulate microbial activity and enhance degradation of organic matter (Mendelssohn et al. 1999).

Porewater pH and alkalinity were higher in marshes exposed to the long-term influx of river water than those fed by rain water. Even small increases in pH and alkalinity can accelerate decomposition rates of the substrate organic matter. Increasing the pH resulted in a more humified substrate in some German moors (Kuntze et al. 1990). The higher porewater alkalinity concentrations in PB marshes likely originated externally through the influx of alkaline river water (e.g. Roelofs 1991) and internally because alkalinity is generated during sulfate and nitrate reduction (Lamers et al. 2002; Smolders et al. 2006). The elevated alkalinity buffers the trend to more acidic conditions which could slow down organic matter decomposition. Alkalinity in porewater rapidly increased after the first spring flood pulse whether river alkalinity was increasing (2001) or remained stable (2002) (Fig. 7). The higher summer values and the much greater fluctuations in the PB marshes suggest a higher level of microbial activity there compared with BB marshes and could indicate microbial activity involved with organic matter degradation (Smolders et al. 2006).

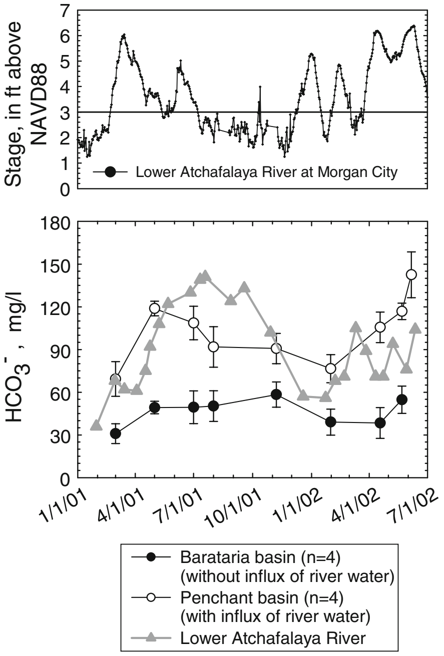


Fig. 7 Discharge of the Lower Atchafalaya River (LAR) at Morgan City and alkalinity concentrations (±1 standard error) in porewater (15-cm depth) in Barataria and Penchant basins and in the Atchafalaya River. Overland flow dominates in the Penchant basin when stage of the LAR is above 3 ft NAVD88

There are few data from long-term field studies that could be used to assign a specific level of impairment to the observed values of porewater constituents. Concentrations that are insignificant in acute terms may have a lasting effect on marsh stability when exposure is chronic. When viewed in isolation, none of the porewater constituents appeared to reach thresholds critical to long-term marsh sustainability. Taken as whole, porewater parameters consistently pointed to reduced quality in PB marshes when compared to BB marshes.

Above-ground plant biomass and substrate

End of season above-ground standing biomass of marshes did not differ between the two areas. Assuming similar turnover rates in the two areas, the above-ground productivity benefit ascribed to freshwater diversions in other coastal Louisiana locations (DeLaune et al. 2003; Lane et al. 2006) did not hold for the Penchant area, with its large inflow of nutrient rich river water. This was surprising considering the large standing pools of inorganic nutrients in porewater of

PB marshes. A probable explanation is that plant productivity was suppressed, through the accumulation of the phytotoxin sulfide in porewater, and perhaps other organic matter decay products which were not measured, such as fatty acids (Cizkova et al. 1999; Armstrong and Armstrong 2001).

Another benefit attributed to freshwater diversions is an increased rate of vertical accretion (Lane et al. 2006). In our study vertical accretion rates did not differ significantly between the BB and the PB marshes (see Fig. 5). Placing this lack of difference into context is difficult because changes in marsh elevation and relations to long-term water level trends were not concurrently measured in the two areas. In many coastal wetlands, accretion rates may respond as much to changes in relative water level as to increases in fertility and root biomass accumulation. Although root production and decay was not measured directly, PB marshes did not appear to have more or less soil carbon than BB marshes. The organic matter density of the upper 25 cm of substrate, which represents the most recent 30–35 years of peat accumulation appeared to be similar between the two areas (see Table 1). This result should be interpreted cautiously because it is not known what happens to soil physical properties such as bulk density when carbon is lost from a soil profile. Direct field measurements of soil respiration in both systems over long periods could be a better approach to determine the long-term soil carbon balance.

The sulfur content of the above-ground plant material and peat substrate, normalized for carbon, was greater in the PB marshes than BB marshes (see Table 1). This difference was completely unexpected. Sulfur usually enters coastal freshwater wetlands in the form of sulfate from marine sources, whether carried by sea spray or through inflowing tidal water, and not from freshwater influx. The low porewater chloride values in the Penchant area, and the low δ^{34}S values of the peat indicate that the elevated sulfur does not originate from marine sources. Instead, the observed pattern of higher stored S in the PB marsh substrate appears to result from chronic river influx during overland flow, which provides a higher sulfate supply rate to PB marshes.

The N content of the shallow peat substrate normalized for carbon did not differ between the two areas even though the regular overland flow of river water in the Penchant basin should provide a large subsidy of nitrogen not available to the BB marshes. Nitrogen apparently is not stored in PB marsh peat in excess over concentrations observed in BB marshes. Rather than being incorporated into the peat substrate a large portion of the nitrogen may exit the Penchant system, most likely through denitrification. DeLaune et al. (2005b) estimated the capacity of similar marshes to remove between 30 and 100 mg N m^{-2} d^{-1} of inflowing nitrate in this manner. Although marshes may reduce the amount of nitrogen flowing downstream and into offshore waters and help reduce the development of an offshore hypoxic zone, this potential environmental gain may be partially offset by the release to the atmosphere of large amounts of nitrous oxide, an effective greenhouse gas, during denitrification.

Finally, the organic-rich substrate of *P. hemitomon* marshes exposed to the chronic long-term influx of river water was more reduced, contained more fine particles and fractionated more easily than the peat substrate of BB marshes, where rain water was the primary source of freshwater. The substrate of PB marshes required less than ½ the amount of force to shear than did the substrate of BB marshes. All these data point to a more decomposed substrate in PB marshes compared with BB marshes. The more decomposed organic matter in PB compared with BB marshes has the most far-reaching implications for wetland restoration of all the differences between the marshes in the two watersheds. Because peat makes up 80% or more of the shallow substrate, any process that increases decomposition and weakens the organic matter makes this marsh type more susceptible to erosion and break up. Hydraulic energy in the form of waves or even a daily tidal signal may facilitate gradual interior erosion and marsh breakup. Occasional high hydraulic energy events such as rapid wind-induced water-level fluctuations and storm surges for example through hurricanes likely will have similar effects.

The chronic influx of nutrients, sulfate and alkaline waters to organic-rich marshes from river water should promote higher rates of organic matter degradation than in marshes where precipitation is the primary source of fresh water. Both nitrate and sulfate are terminal electron acceptors and are reduced under flooded, anaerobic soil conditions in the presence of bio-available organic matter. Organic matter, an electron donor, is oxidized during both nitrate and sulfate reduction (Lamers et al. 2002; Smolders et al. 2006). The peat substrate is degraded in the process. In organic-rich freshwater marshes, sulfate and nitrate concentrations typically are low and supply is limited (Mitsch and Gosselink 2000). Decomposition and degradation of organic matter is slow and peat accumulates. When the supply of nitrate and sulfate to freshwater marshes increases or becomes chronic, as for example through freshwater diversions, the organic matter may degrade faster (Wieder et al. 1992; Lamers et al. 1998).

Linking river water influx to organic matter degradation

A link between the influx of alkaline river water, sulfide toxicity, and organic matter degradation has been shown experimentally in the laboratory and in the field for organic-rich wetlands in Europe (for example Eggelsmann 1960; Roelofs 1991; Brouwer et al. 1999; Loeb et al. 2007). The data from this study suggest a similar link occurs in the organic-rich marshes of the Louisiana delta plain. Hydrology, soil biogeochemical processes and a positive feed-back mechanism are thought to be important contributing factors.

Hydrologically, river water has to enter and saturate the organic substrate in sufficient quantity to have an effect on marsh quality. The naturally occurring hydraulic gradient between the Lower Atchafalaya River and water levels in the Penchant basin interior during the seasonal flood peak ensures the steady influx of river water to PB marshes for several weeks to months each year (Swarzenski 2003). Porewater calcium:magnesium data demonstrated the saturation of the organic substrate in PB marshes. Overland flow of the river water provides a continuous supply of the oxidizing agents nitrate and sulfate to the marshes and leads to reducing conditions in the marsh. During overland flow, uptake of nitrate and sulfate occurs (Fig. 8). When nitrate and sulfate are reduced, organic matter is mineralized and sulfide accumulates in porewater. Porewater alkalinity is generated when organic matter is mineralized (Kuntze et al. 1990; Brouwer et al. 1999; Smolders et al. 2006). Alkaline river water influx also contributes to peat mineralization directly (Roelofs 1991). The larger swings in porewater alkalinity in PB marshes suggest higher microbial activity there compared to BB marshes.

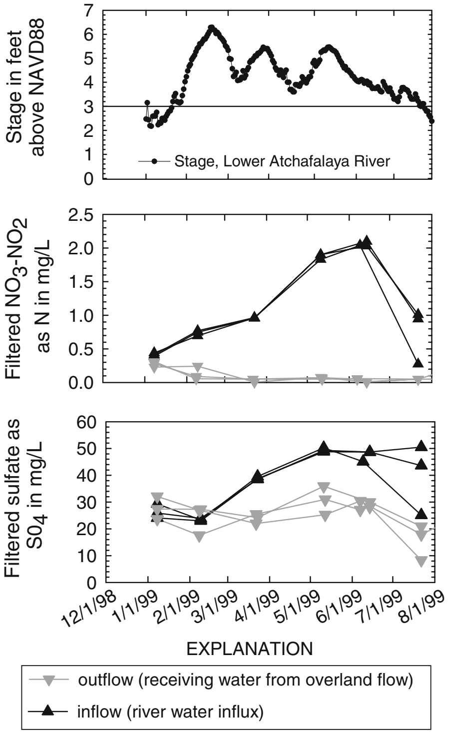


Fig. 8 Discharge of the Lower Atchafalaya River at Morgan City and concentrations of filtered nitrate-plus-nitrite and sulfate in inflowing river water ($n = 3$) and in waterways immediately down-stream of marshes receiving overland flow ($n = 3$), in Penchant Basin. Overland flow dominates in the Penchant Basin when stage of the LAR is above 3 ft NAVD88

The reducing conditions and decay of the substrate organic matter initiated and sustained by the chronic influx of river water may become self-reinforcing and contribute to further declines in marsh vigor and organic matter quality (Cizkova et al. 2001; Santrucková et al. 2001). Dissolved iron, a possible buffer in this cycle because it can bind with sulfide and phosphate (Smolders and Roelofs 1995; van der Welle et al. 2006), is in short supply in PB marsh porewater, presumably because it is used up in the biogeochemical reactions catalyzed by river influx. BB marshes have high iron concentrations in porewater (Fig. 5).

Summary

The substrate of marshes exposed to river water was more reduced, more decomposed, fractionated more easily and sheared at lower torque than that of similar marshes with rain as the primary source of freshwater. The influx of river water promoted the accumulation of sulfur in the peat and sulfide in porewater in excess of levels found in marshes isolated from river water influx. Alkalinity and pH were higher and large standing pools of inorganic N and P were present in porewaters of PB but not BB marshes. Rates of vertical marsh accretion were similar in the two areas. Thus, while river water influx was associated with more decomposed soil organic matter and generally poorer porewater quality, the chronic influx of nutrient rich river water did not appear to promote marsh accretion rates above those found in nutrient-poor settings. Chronic influx of river water with high nutrient concentrations also did not promote greater end-of-year above-ground plant biomass compared to marshes growing without this nutrient subsidy.

The patterns of porewater sulfide concentrations and peat sulfur content confounded expectations for freshwater diversions. One of the primary benefits envisioned for freshwater diversions is to reduce marine influence, of which sulfate influx and sulfide toxicity are major components. While river water introductions may be successful at decreasing chloride concentrations and increasing habitat space for organic-rich freshwater marshes, they also appear to make conditions unsustainable in the long-run for the same marsh type, by promoting sulfur accumulation.

To establish cause and effect of river water influx and organic matter degradation, carefully controlled experiments are needed linking organic matter degradation to specific pollutants contained in river water. Even then, extrapolating from relatively short-term laboratory studies may overestimate concentrations needed to provoke a system response. The data collected during this 4-year study represent field conditions of two well-defined systems alike in all important attributes except for their source of fresh water. The study provides insight into environmentally relevant concentrations of pollutants that appear to provoke a system response. If our interpretations about the importance of sulfate are correct, the data suggest that even relatively low concentrations may affect the freshwater wetlands provided the exposure is frequent and continues for many years.

We studied diversions of a scale where changes to water-quality and not mineral sediment additions were the primary effect. The main objective of using such diversions for marsh building has been on restoring the natural process of overbank flooding during high water wherever possible. The tacit assumption in this approach is that river water quality has not changed appreciably since the river last flowed unencumbered into the estuaries. This assumption does not always hold. For example, nitrate concentrations are threefold higher than historical back-ground concentrations (Turner and Rabalais 1991) and if sulfate concentrations measured in the Mississippi River at New Orleans in 1905 and 1906 (in Dole 1909) are representative of that time period in general, average sulfate concentrations since the 1950s may be twice as high. Herbicides, which we did not evaluate in this study, were only introduced post-1950s. More than previously, marshes have to rely on the organic matter being incorporated into the soil of the Louisiana delta plain marshes to keep pace with rapid regional subsidence (Turner et al. 2004). It seems likely that the quality of the inflowing river water is an important variable to consider in how delta plain marshes respond to diversions.

Currently, structural, hydrological and even human constraints determine the placement of controlled river diversions along the Mississippi River. Soil type and the organic matter that gives the marsh soil its structure and resilience to perturbations have not been considered. The results from this study suggest that the type of marsh, the soil environment and the organic matter quality of the wetlands also be given careful consideration with respect to the construction and operation of controlled river diversions. In addition to their cost, controlled river diversions, once implemented, may have an outcome that will not be known for many years, and which, if not as envisioned, may not be easily reversed.

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