

Sediment Quality in Freshwater Impoundments at Savannah National Wildlife Refuge

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Abstract. Freshwater impoundments at Savannah National Wildlife Refuge (NWR), South Carolina, provide an important habitat for wildlife species, but degraded sediment quality in the Savannah River downstream of the discharge from two impoundments have caused concern about potential contaminant problems within the impoundments. The quality of sediments from five impoundments (impoundments no. 1, 2, 6, 7, and 17) on the NWR was evaluated using physical and chemical characterization, contaminant concentrations (metals, organochlorine pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons), and toxicity testing. Survival of *Hyaella azteca* (freshwater amphipod) exposed for 28 days to solid-phase sediments was not significantly different from controls, but growth was significantly decreased at several sites. Survival in 96-hour exposures to sediment pore water was significantly decreased at most sites. Factors contributing to the toxic responses were low pH (3.7 to 4.1), ammonia (20 mg/L), and increased concentrations of cations in the pore water. The excess of simultaneously extracted metals over the acid volatile sulfides in the sediments was also typical of sites displaying decreased sediment quality. Elemental concentrations in pore water were negatively correlated with pH, and the highest concentrations were observed in impoundment no. 7. The acidic nature of the sediment in this impoundment was exacerbated by recent draining, burning, and disking, which allowed oxidation of the previously anoxic wetland sediment. Sediment disturbance and mixing of vegetation into the sediments by disking may also have contributed to the formation of ammonia caused by microbial decomposition of the fragmented organic matter. Contaminants were not detected in sediments from the impoundments, but releases of acidic water with increased levels of sediment cations from the impoundments may have contributed to the degraded sediment conditions previously observed in the river. The practice of dewatering sediments for vegetation control may exacerbate the acidification of vulnerable sediments within impoundments of this NWR.

Coastal National Wildlife Refuges (NWRs), operated by the United States Fish and Wildlife Service (USFWS), are managed to enhance habitat for wildlife species. The Savannah NWR encompasses 2180 ha of salt and freshwater marshes. Because freshwater marshes are not subjected to the salinity stresses associated with salt marshes, they support a high diversity of plants and animals (Simpson *et al.* 1983; Odum 1988) and are heavily used by birds (Mitsch and Gosselink 1993). These marshes are mosaics of plant species including a predominance of annuals whose diversity, seed production, and palatability are responsible for their value to fish and wildlife (Odum *et al.* 1978). Impoundments at Savannah NWR are managed as freshwater wetlands to provide habitat for migratory and resident bird populations, particularly waterfowl, shore birds, and wading birds (Chabreck 1980). More than 270 species of birds have been observed at this NWR. With continued loss of freshwater wetlands along the lower Savannah River related to river and harbor management, freshwater impoundments associated with the NWR become even more important in providing wildlife habitat.

During an evaluation of sediment quality in the lower Savannah River, sediments collected in the vicinity of drainage outlets from two impoundments on the Savannah NWR were found to have decreased sediment quality and were determined to be toxic to laboratory test organisms (Winger *et al.* 2000). Increased concentrations of metals, alkalinity, ammonia, polycyclic aromatic hydrocarbons (PAHs) were most likely responsible for impairment of these sediments. Because other sources of potential contamination to this portion of the Savannah River system are limited, water releases from the 2 impoundments on the NWR adjacent to and upstream of the impacted area were suspected of contributing materials to the river that may have been responsible for the toxicities observed in the evaluation of sediment quality in the river. To evaluate the potential contaminant concerns within the impoundments on the NWR, sediment quality assessments were undertaken. Sediments, serving both as a repository and a source of contaminants (Salomons *et al.* 1987), generally reflect the environmental health of aquatic ecosystems (Boyd 1995). Sediment toxicity tests have been shown to be effective tools in the assessment of habitat quality (McGee *et al.* 1999; Long *et al.* 2001), and methods have been developed for testing the tox-

Table 1. Sediment samples for toxicity testing, physical characterization, and chemical analyses collected from different management treatment sites within impoundments at Savannah NWR

Impoundment	Date Sampled	Management	
		Treatment	Implemented
1	9/14/1998	Undisturbed	Deep flooded since 2/93
2	9/14/1998	Undisturbed	Flooded since 1995; drained 10/1997
2	9/14/1998	Burned	Drained fall 1998, 1/1998
6	8/3/1998	Undisturbed	Drained/flooded 1997; drained 3/1998
6	8/3/1998	Disked	Drained fall/winter 1997, 4/98
7	8/3/1998	Undisturbed	Drained 3/1996; flooded 10/1997; drained 4/1998
7	8/3/1998	Disked	Drained spring 1998, 6/1998
7	8/3/1998	Burned	Drained spring 1998, 7/1998
17	9/14/1998	Undisturbed	Drained 3/1998
17	9/14/1998	Disked	Drained 3/1998, 4/98

icity of freshwater sediments (United States Environmental Protection Agency [USEPA] 1994, 2000). Habitat quality within the lower Savannah River has been previously evaluated using sediment quality assessments (Winger and Lasier 1995; Winger *et al.* 2000). The objectives of this study were to determine habitat quality in selected impoundments within the Savannah NWR using sediment quality-assessment procedures (sediment characterization, chemistry, and toxicity) and to identify factors that may be contributing to potentially degraded conditions within the impoundments.

Methods and Materials

The Savannah NWR is located on the eastern shore of the Savannah River in South Carolina across the river from Savannah, Georgia (Figure 1). Before being managed by the USFWS, this land was privately owned, impounded by dykes, and used for rice production. These impoundments are currently managed as freshwater marsh and open water areas for use by wintering waterfowl. Freshwater from the Savannah River is the source of water to the impoundments, and when the impoundments are drained, water is released back into the Savannah River (Little Back River). Management of the impoundments includes periodic dewatering and drying of the sediments. In addition to regulation of water levels, vegetation within the impoundments is controlled by burning, disking, and occasional application of herbicides. The history of other pesticide usage in these impoundments is unknown.

Sediment samples were collected in August and September 1998 from five impoundments (Figure 1) on the NWR and included the two (impoundments no. 6 and 7) associated with the toxic sediments in the Savannah River (Winger *et al.* 2000). The other three were characteristic of other impoundments on the NWR; impoundments no. 1 and 2 were located upriver of impoundments no. 6 and 7, and impoundment no. 17 was located downriver. The sites sampled within each impoundment represented the recent vegetation-management practices employed by the NWR: undisturbed, disked, and burned (Table 1). A total of 10 sites were sampled, and at each site three replicate sediment samples were collected. Each sediment sample consisted of a 4-L aliquot from a composite sample collected randomly over a 3-m² area with a stainless steel spoon to a depth of 20 cm (excluding the top 4 cm), placed in a stainless steel pot, and homogenized with a stainless steel paddle. Two 240-ml samples were placed in glass jars for analyses of metal and organic contaminants. Sediment samples were placed on ice for transport to the laboratory where they were stored in the dark at 4°C pending analyses. Sediment quality was assessed in the

laboratory using toxicity testing, chemical analyses, and sediment characterization.

In the laboratory, sediment samples were rehomogenized and aliquots removed for measurement of particle size distribution, acid-volatile sulfides (AVS), simultaneously extracted metals (SEM), percent moisture, and percent organic matter. Five replicates of each sediment sample and the laboratory control sediment (commercial sand that was washed and held in test water for 2 weeks before use) were prepared for solid-phase toxicity testing. For each replicate, 100 ml bulk sediment was transferred into a 300-ml, tall-form beaker with a stainless-steel, mesh-covered notch. The sediment in each beaker was then covered with 175 ml reconstituted water.

Solid-phase sediments were tested under static renewal procedures (USEPA 1994) with two renewals (70% replacement of overlying water with each renewal) daily (Zumwalt *et al.* 1994). Deionized water reconstituted to a hardness of 100 mg/L, alkalinity of 70 mg/L, pH of 8, and conductivity of 350 μ S/cm was used as the overlying and renewal water. Ten *H. azteca* (Crustacea, Amphipoda) were placed into each of the five replicate solid-phase test chambers. The animals were fed 1.5 ml (1.8 g solid/L) of a yeast, Cerophyl, and trout chow mixture daily during the 28-day exposure period. Temperature during the test was maintained at 23 \pm 1°C, and the photoperiod was 16 hours light and 8 hours dark. Survival and growth (length) were the test end points. Overlying water chemistry was monitored in the exposure chambers during the test and included dissolved oxygen, temperature, pH, alkalinity, hardness, conductivity, and ammonia. Dissolved oxygen, temperature, pH, conductivity, and ammonia were measured with the appropriate meters, and electrodes and alkalinity and hardness were determined by titration.

Pore-water samples for toxicity testing and chemical analyses (pore-water samples submitted for analytical analyses were filtered through a 0.45- μ m filter) were extracted from the remaining sediment samples using a vacuum extractor consisting of a fused-glass air stone, airline tubing, and a 60-ml syringe (Winger and Lasier 1991; Winger *et al.* 1998). Approximately 300 ml pore water was obtained from each sediment sample, aerated for 15 minutes (dissolved oxygen concentrations exceeded saturation levels during the test), and then 20 ml transferred to each of 5 replicate 30-ml plastic cups. Ten *H. azteca* and a 1-cm² piece of polyester netting (275 μ m) were placed into each cup. *H. azteca* were exposed to pore water for 96 hours under static conditions and were not fed during the test. The test exposures were maintained at 23 \pm 1°C and the 16 hours light and 8 hours dark photoperiod. The end point of the pore-water test was survival. The same basic water chemistry monitored during the solid-phase test was measured on pore water after aeration at the start of the test.

Concentrations of aluminum, arsenic, cadmium, chromium, copper, iron, magnesium, manganese, molybdenum, nickel, sulfur, lead, and

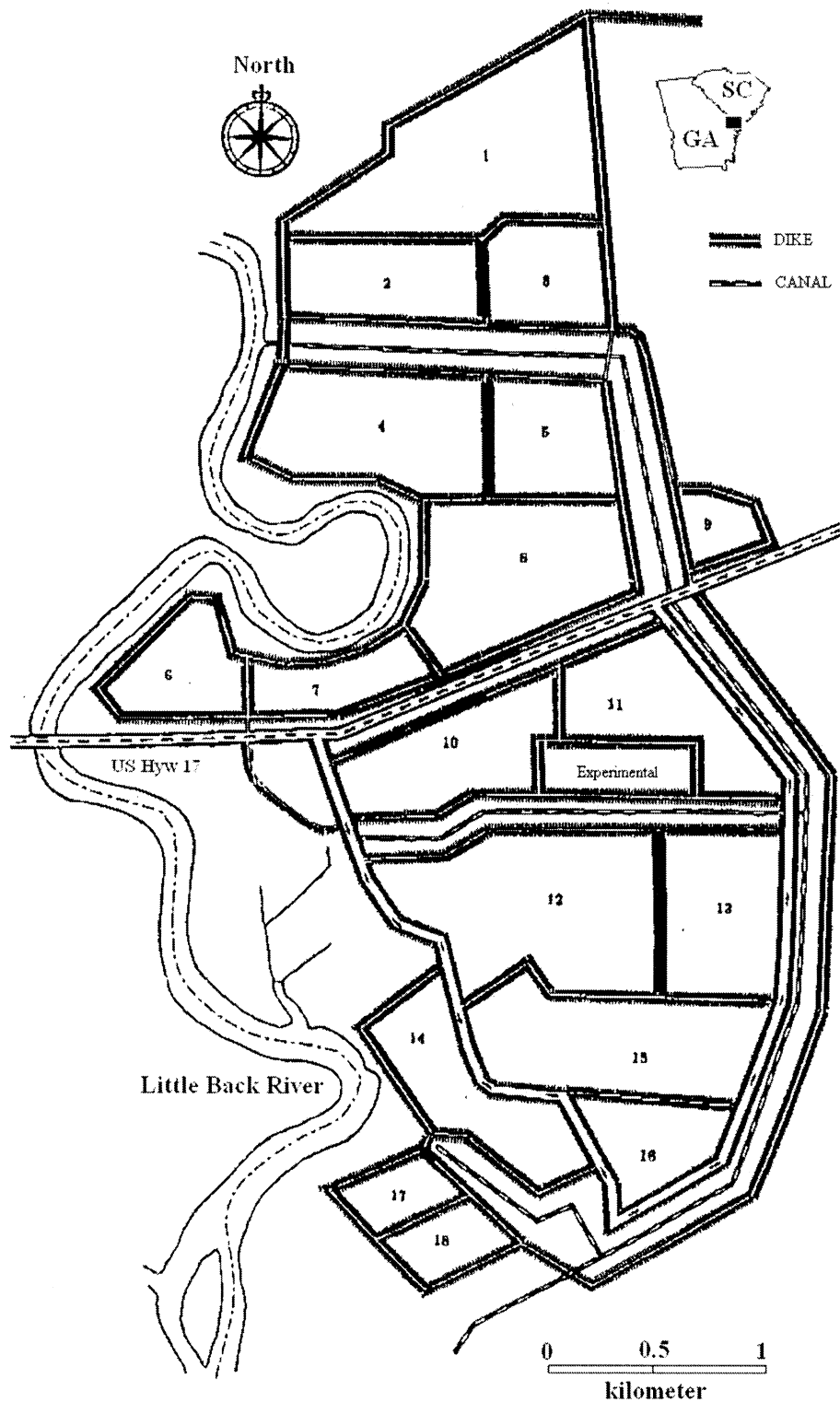


Fig. 1. Map showing the impoundment system at Savannah National Wildlife Refuge

zinc were measured in the sediment after digestion with hydrochloric acid and nitric acid using a sequential inductively coupled plasma-emission spectrometer. Arsenic and selenium in sediments were measured by graphite furnace after digestion with nitric acid and hydrogen peroxide. Samples for mercury were digested under reflux in sulfuric and nitric acids and then analyzed using a cold-vapor atomic absorp-

tion spectrophotometer with a mercury analyzer and a vapor generation accessory. Organochlorine pesticides (OCLs), polychlorinated biphenyls (PCBs), and PAHs were measured, after extraction and cleanup, by capillary gas chromatography with an electron-capture detector for pesticides and PCBs and mass spectrometer for PAHs (Wade *et al.* 1988).

Table 2. Mean characteristics of sediment and sediment pore water (SD) from impoundments at Savannah NWR

Impoundment and Treatment	Sediment						Pore Water					
	% Organic	% Fines	Redox (Eh)	AVS (mEq/L)	SEM (mEq/L)	SEM/AVS	pH	Alkalinity (mg/L)	Hardness (mg/L)	Conductivity (μ S/cm)	DOC (mg/L)	NH ₄ (mg/L)
1 Undisturbed	49.7 ^a	41.7 ^d	-183.4 ^b	0.02 ^a	3.45 ^a	202.8 ^a	7.5 ^a	40.0 ^{b,c}	43.0 ^b	134 ^c	95.3 ^a	0.0 ^c
SD	(5.9)	(5.0)	(47.8)	(0.01)	(1.65)	(74.75)	(0.1)	(5.2)	(3.0)	(11)	(16.5)	(0.0)
2 Burned	24.8 ^b	46.3 ^{d,c}	-239.2 ^c	0.05 ^a	2.64 ^a	126.5 ^a	7.4 ^a	58.6 ^{a-c}	31.0 ^b	184 ^{d,e}	77.7 ^a	0.0 ^c
SD	(4.6)	(4.5)	(43.0)	(0.06)	(1.50)	(118.3)	(0.1)	(7.0)	(11.7)	(30)	(36.8)	(0.0)
2 Undisturbed	2.5 ^d	49.7 ^{b-d}	-164.9 ^{b,c}	0.05 ^a	22.35 ^a	204.1 ^a	7.6 ^a	46.0 ^{b,c}	38.0 ^b	131 ^c	107.3 ^a	0.0 ^c
SD	(2.1)	(21.5)	(222.1)	(0.07)	(37.22)	(240.1)	(0.1)	(4.0)	(16.0)	(4)	(15.2)	(0.0)
6 Disked	8.9 ^{c,d}	83.7 ^{a,b}	-148.2 ^{b,c}	1.54 ^a	0.92 ^a	0.9 ^a	8.0 ^a	114.0 ^a	29.3 ^b	424 ^{d,e}	34.7 ^a	0.7 ^c
SD	(1.1)	(3.0)	(73.9)	(1.29)	(0.04)	(0.62)	(0.1)	(29.4)	(7.7)	(55)	(3.5)	(1.2)
6 Undisturbed	7.7 ^{c,d}	87.7 ^a	-126.6 ^{b,c}	0.64 ^a	0.83 ^a	2.1 ^a	8.0 ^a	98.0 ^{a,b}	46.0 ^b	509 ^d	30.0 ^a	0.0 ^c
SD	(0.8)	(1.1)	(49.9)	(0.52)	(0.25)	(1.62)	(0.2)	(38.1)	(22.0)	(73)	(9.0)	(0.0)
7 Burned	16.4 ^{b,c}	66.3 ^{a-c}	141.2 ^a	0.03 ^a	1.98 ^a	113.5 ^a	3.7 ^b	4.0 ^c	317.7 ^a	1647 ^b	69.7 ^a	11.0 ^b
SD	(2.5)	(5.8)	(22.7)	(0.03)	(0.52)	(78.20)	(0.1)	(0.0)	(133.6)	(105)	(54.8)	(2.5)
7 Disked	12.1 ^{c,d}	79.0 ^{a-c}	140.0 ^a	0.10 ^a	2.21 ^a	22.1 ^a	4.0 ^b	8.0 ^c	330.3 ^a	2116 ^a	35.0 ^a	23.1 ^a
SD	(2.1)	(9.5)	(54.7)	(0.01)	(0.26)	(3.51)	(0.3)	(3.6)	(120.3)	(92)	(15.0)	(6.5)
7 Undisturbed	14.6 ^{b,c}	74.3 ^{a-c}	-114.8 ^{b,c}	2.42 ^a	1.50 ^a	1.7 ^a	4.1 ^b	8.0 ^c	185.3 ^{a,b}	1037 ^c	31.3 ^a	0.0 ^c
SD	(2.6)	(9.4)	(74.9)	(2.02)	(0.21)	(1.99)	(0.5)	(3.4)	(45.6)	(150)	(6.5)	(0.0)
17 Disked	10.2 ^{c,d}	86.7 ^a	-121.1 ^{b,c}	1.69 ^a	24.56 ^a	13.5 ^a	4.6 ^b	19.3 ^c	171.3 ^{a,b}	1223 ^c	78.0 ^a	3.1 ^{b,c}
SD	(1.6)	(2.0)	(31.1)	(0.58)	(15.25)	(6.65)	(0.56)	(17.4)	(93.2)	(168)	(64.0)	(0.9)
17 Undisturbed	8.2 ^{c,d}	91.3 ^a	-134.5 ^{b,c}	0.06 ^a	10.92 ^a	347.7 ^a	7.1 ^a	34.7 ^{b,c}	112.7 ^{a,b}	1046 ^c	63.0 ^a	0.5 ^c
SD	(0.8)	(1.5)	(54.4)	(0.07)	(11.85)	(347.7)	(0.1)	(6.4)	(17.0)	(70)	(9.8)	(0.9)

AVS: acid-volatile sulfides, DOC: dissolved organic carbon, Eh: redox potential, NH₄: ammonia, SD: standard deviation, SEM: simultaneously extracted metals.

^{a-c} Mean values within a column that share the same superscript letter are not significantly different ($p = 0.005$).

AVS was determined per methods described by Brouwer and Murphy (1994). Cations in pore water and metals included in the SEM (copper, cadmium, tin, mercury, lead, and zinc) obtained during the AVS determinations were measured using inductively coupled plasma-emissions mass spectrometry. Anions in pore water were determined using an ion chromatograph. Sediment particle size distribution was determined using procedures described by Miller and Miller (1987). Percent moisture was measured as the difference between original wet weight and weight after drying for 24 hours at 105°C. Percent organic matter was derived by loss on ignition at 450°C for 4 hours (Davies 1974). The pH of sediment was measured using a meter and an electrode in an equal volume-to-volume mix of sediment and deionized water. Redox potential of a sediment sample was read from the meter after allowing the redox electrode that was inserted into the sediment sample to stabilize.

Analytical analyses included procedural blanks, duplicates, spiked blanks, and standard reference material. Detection limit for OCLs was 0.05 mg/kg, for PCBs 0.1 mg/kg, and for PAHs 0.1 mg/kg. Blanks were below detection limits for the organic contaminants, and differences between duplicate samples were within normal limits as were recoveries from spiked samples. Detection limits were 10 ng/g dry weight for arsenic, chromium, selenium, and zinc; 10 μ g/g dry weight for cadmium, copper, manganese, molybdenum, nickel, and lead; and 2.5 ng/g for mercury in sediment. The limit of quantitation was 3 times the limit of detection. Recovery from spiked samples averaged $93.1 \pm 8.6\%$. Procedural blanks were generally below detection limits except for iron. Differences between duplicates were within normal limits except for cadmium, copper, and zinc, which were occasionally >20%. Results for standard reference material were within normal limits for organic contaminants and metals, except recoveries were slightly lower than normally seen for arsenic, chromium, copper, manganese, and nickel. Organic contaminants (OCLs, PCBs, and PAHs) were not detected in the sediment samples from the impoundments and are thus not included in further discussions.

Statistical analyses were conducted using Statistical Analysis Sys-

tems software (SAS 1990) and consisted of Spearman rank correlation analyses between survival in pore water and survival and length from solid-phase sediments of *H. azteca*, and these test end points were compared with water and sediment chemistry and metal concentrations in pore-water and solid-phase sediments; analysis of variance using general linear models and Dunnett's 1-tailed test for significant differences in length and survival compared with controls; and Bonferroni's pair-wise comparisons of means among sampling sites. Analyses were performed on log-transformed data.

Results

Solid-phase sediments collected from the impoundments did not decrease survival of *H. azteca* during the 28-day exposures (Figure 2); however, length was significantly decreased (compared with laboratory controls) in sediments collected from the undisturbed site in impoundment no. 7, from both management categories in impoundments no. 6 and 17, and from impoundment no. 1 (Figure 3). Sediment pore waters were significantly toxic to *H. azteca* from all sites except for those in impoundment no. 6 (Figure 2). Survival of *H. azteca* in pore water was not significantly correlated with survival or length of animals exposed to the solid-phase sediments.

Physical and chemical characteristics of the sediments and pore waters indicated that the sediments differed in percent organic matter among sites, and 4 sites (7 burned, 7 disked, 7 undisturbed, and 17 disked) were abnormally acidic (Table 2). Elemental concentrations in the pore-water and solid-phase sediments from these sites tended to reflect these acidic conditions (Tables 3 and 4).

Survival of *H. azteca* in pore water was positively corre-

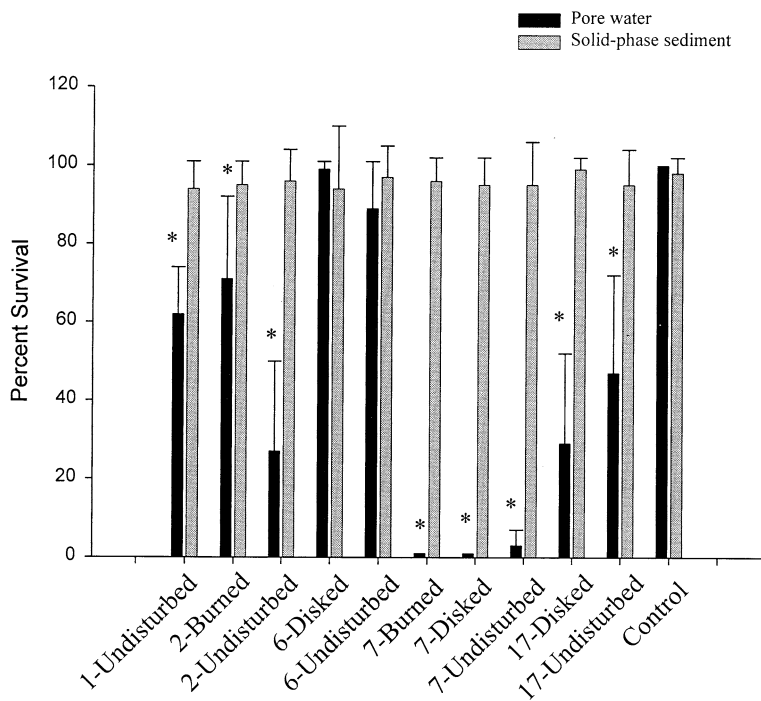


Fig. 2. Percent survival (SD) of *H. azteca* exposed to solid-phase sediment and sediment pore water from impoundments at Savannah NWR. *Significant differences from the control ($p \leq 0.05$)

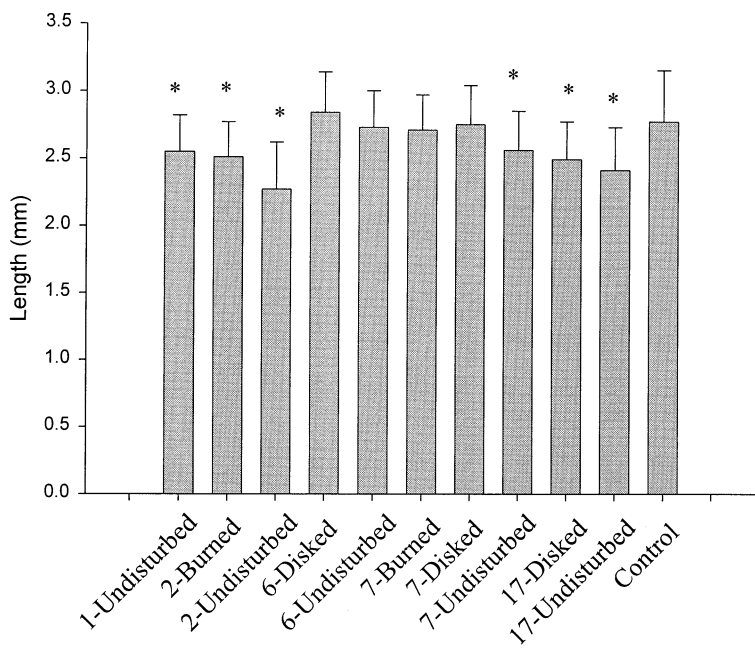


Fig. 3. Mean length (SD) of *H. azteca* exposed to solid-phase sediment from impoundments at Savannah NWR. *Significant differences from the control ($p \leq 0.05$)

lated ($p \leq 0.05$) with pore-water pH and alkalinity and negatively correlated with conductivity, ammonia, and sediment redox potential (Table 5). AVS, SEM, and the SEM-to-AVS ratios were not significantly correlated with pore-water survival, although the SEM concentrations and SEM-to-AVS ratios were generally highest at the sites that showed toxicity in the pore water (the high variability among replicates may account for the inability to detect significant differences). There were, however, significant correlations between total SEM concentrations and SEM-to-

AVS ratios with length of *H. azteca* from solid-phase exposures. When the sites with low pH (7 burned, 7 disked, 7 undisturbed, and 17 disked) were excluded from the analyses, there were strong correlations between the SEM-to-AVS ratios and survival in pore water and length from the solid-phase tests (Figure 4). The acidic conditions at these four sites appeared to mask this relationship when all of the sites were included in the analysis of the pore-water exposures.

There were no significant differences in SEM concentrations

Table 3. Mean elemental concentrations (SD) in pore water from sediments collected in impoundments at Savannah NWR

Impoundment and Treatment	Al (mg/L)	As ($\mu\text{g/L}$)	Ca (mg/L)	Cd ($\mu\text{g/L}$)	Cu ($\mu\text{g/L}$)	Cr ($\mu\text{g/L}$)	Fe (mg/L)	Hg ($\mu\text{g/L}$)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Ni ($\mu\text{g/L}$)	Pb ($\mu\text{g/L}$)	Zn ($\mu\text{g/L}$)	Se ($\mu\text{g/L}$)	SO ₄ (mg/L)
1 Undisturbed	0.7 ^a	2.4 ^a	11.3 ^{a,b}	0.4 ^a	11.2 ^a	0.9 ^a	11 ^c	0.2 ^a	3.3 ^c	3.7 ^b	0.6 ^{b,c}	6.7 ^a	3.0 ^a	574 ^a	0.9 ^a	0 ^b
SD	(0.3)	(0.5)	(0.6)	(0.3)	(5.5)	(0.3)	(2)	(0.1)	(0.6)	(0.5)	(0.1)	(1.4)	(1.4)	(172)	(0.2)	(0)
2 Burned	1.2 ^a	0.9 ^a	6.5 ^{a,b}	0.1 ^a	10.3 ^a	0.8 ^a	2 ^c	0.2 ^a	1.5 ^c	3.7 ^b	0.2 ^c	1.4 ^a	1.3 ^a	1062 ^a	0.8 ^a	0 ^b
SD	(0.8)	(0.2)	(2.3)	(0.0)	(2.8)	(0.5)	(1)	(0.2)	(0.1)	(1.5)	(0.1)	(0.4)	(0.2)	(1484)	(0.2)	(0.0)
2 Undisturbed	0.4 ^a	2.8 ^a	5.5 ^{a,b}	0.1 ^a	9.2 ^a	1.3 ^a	1 ^c	0.1 ^a	1.9 ^c	6.0 ^b	0.2 ^c	2.0 ^a	1.4 ^a	209 ^a	0.9 ^a	0 ^b
SD	(0.4)	(1.9)	(3.3)	(0.1)	(5.6)	(1.5)	(1)	(0.1)	(1.1)	(2.0)	(0.1)	(1.8)	(1.5)	(136)	(0.3)	(0)
6 Disked	0.2 ^a	4.2 ^a	4.8 ^b	0.3 ^a	9.6 ^a	2.7 ^a	3 ^c	0.1 ^a	1.2 ^c	4.3 ^b	0.3 ^c	5.1 ^a	0.8 ^a	250 ^a	1.7 ^a	50 ^b
SD	(0.0)	(3.2)	(0.7)	(0.0)	(5.8)	(0.6)	(4)	(0.0)	(0.5)	(1.5)	(0.2)	(1.6)	(0.2)	(148)	(0.3)	(87)
6 Undisturbed	0.2 ^a	2.3 ^a	7.2 ^{a,b}	0.2 ^a	6.4 ^a	2.4 ^a	3 ^c	0.0 ^a	3.2 ^c	7.0 ^b	0.5 ^{b,c}	4.0 ^a	1.5 ^a	89 ^a	2.1 ^a	14 ^b
SD	(0.1)	(0.3)	(4.0)	(0.0)	(3.5)	(0.5)	(5)	(0.0)	(1.6)	(3.0)	(0.7)	(1.7)	(1.5)	(29)	(0.5)	(18)
7 Burned	1.8 ^a	30.0 ^a	49.2 ^{a,b}	1.6 ^a	9.2 ^a	1.6 ^a	229 ^a	0.0 ^a	16.3 ^{a,b}	48.7 ^a	2.9 ^{a,b}	50.7 ^a	5.2 ^a	659 ^a	2.8 ^a	1732 ^a
SD	(2.2)	(23)	(27.4)	(2.2)	(2.1)	(1.3)	(97)	(0.0)	(6.4)	(16.2)	(1.4)	(41)	(4.2)	(369)	(0.9)	(472)
7 Disked	1.1 ^a	2.8 ^a	50.1 ^a	0.7 ^a	11.7 ^a	1.6 ^a	163 ^{a,b}	0.0 ^a	20.1 ^a	51.3 ^a	2.2 ^{a-c}	23.7 ^a	17.2 ^a	786 ^a	2.7 ^a	1512 ^a
SD	(0.5)	(0.6)	(17.6)	(0.4)	(4.1)	(0.6)	(11)	(0.0)	(4.1)	(19.0)	(0.6)	(2.7)	(14.9)	(116)	(0.5)	(154)
7 Undisturbed	0.1 ^a	2.0 ^a	33.6 ^{a,b}	0.3 ^a	4.5 ^a	1.9 ^a	70 ^{b,c}	0.1 ^a	6.7 ^{b,c}	25.3 ^{a,b}	3.5 ^a	22.7 ^a	0.2 ^a	284 ^a	3.2 ^a	621 ^b
SD	(0.0)	(0.0)	(9.6)	(0.0)	(0.4)	(0.3)	(24)	(0.0)	(2.5)	(5.5)	(0.1)	(11)	(0.0)	(141)	(0.3)	(119)
17 Disked	0.1 ^a	2.2 ^a	18.8 ^{a,b}	0.2 ^a	4.4 ^a	1.9 ^a	2 ^c	0.1 ^a	6.2 ^{b,c}	31.0 ^{a,b}	0.9 ^{a-c}	3.2 ^a	0.1 ^a	302 ^a	5.6 ^a	11 ^b
SD	(0.1)	(1.1)	(10.4)	(0.1)	(2.9)	(1.7)	(1)	(0.0)	(2.7)	(16.8)	(0.5)	(3.1)	(0.1)	(18)	(3.7)	(11)
17 Undisturbed	0.1 ^a	3.2 ^a	11.4 ^{a,b}	0.2 ^a	9.7 ^a	1.9 ^a	1 ^c	0.3 ^a	6.1 ^{b,c}	21.0 ^{a,b}	0.4 ^{b,c}	2.6 ^a	0.6 ^a	290 ^a	4.3 ^a	0 ^b
SD	(0.1)	(0.6)	(2.6)	(0.0)	(3.6)	(0.4)	(1)	(0.2)	(0.3)	(2.6)	(0.0)	(1.0)	(0.4)	(199)	(0.5)	(0)

Mean concentrations within a column that have the same superscript letter are not significantly different ($p = 0.05$).

Table 4. Mean elemental concentrations in $\mu\text{g/g}$ dry weight (SD) in sediments collected from impoundments at Savannah NWR

Impoundment and Treatment	Al	As	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Mo	Ni	Pb	Se	Zn
1 Undisturbed	21925 ^a	3.3 ^{a-c}	0.57 ^a	21.3 ^c	23.7 ^a	21593 ^{a,b}	0.07 ^a	667 ^{c,d}	192 ^a	4.1 ^a	8.7 ^a	14.7 ^{c-e}	1.3 ^a	39.5 ^{b,c}
SD	(584)	(1.4)	(0.3)	(2.0)	(4.0)	(2016)	(0.01)	(52)	(53)	(1.7)	(1.5)	(1.5)	(0.3)	(5.6)
2 Burned	12074 ^{a,b}	1.6 ^{b,c}	0.24 ^a	13.7 ^{c,d}	12.0 ^{b,c}	12716 ^{b,c}	0.07 ^a	495 ^d	107 ^{a-d}	4.5 ^a	6.1 ^{a,b}	12.0 ^{d,e}	0.7 ^{a,b}	33.7 ^{d,e}
SD	(6122)	(0.8)	(0.0)	(6.3)	(5.2)	(5510)	(0.00)	(217)	(24)	(0.8)	(1.7)	(13.0)	(0.2)	(12.8)
2 Undisturbed	2566 ^b	0.3 ^c	0.57 ^a	4.0 ^d	4.0 ^c	2691 ^c	0.03 ^a	581 ^{c,d}	17 ^c	1.5 ^a	2.1 ^b	6.7 ^c	0.1 ^b	10.9 ^d
SD	(1301)	(0.1)	(0.37)	(1.7)	(1.7)	(2058)	(0.01)	(401)	(8)	(0.5)	(0.7)	(3.2)	(0.0)	(0.6)
6 Disked	18370 ^a	4.5 ^{a,b}	0.57 ^a	56.7 ^a	21.0 ^{a,b}	22877 ^{a,b}	0.11 ^a	2858 ^a	172 ^{a-c}	3.1 ^a	9.8 ^a	28.7 ^{a-d}	0.1 ^b	69.2 ^a
SD	(3117)	(1.4)	(0.23)	(2.5)	(1.0)	(1933)	(0.06)	(281)	(19)	(2.2)	(1.7)	(2.5)	(0.0)	(4.9)
6 Undisturbed	19082 ^a	3.4 ^{a-c}	0.52 ^a	46.3 ^{a,b}	20.0 ^{a,b}	23376 ^{a,b}	0.06 ^a	2167 ^{a,b}	180 ^{a,b}	1.8 ^a	10.9 ^a	26.7 ^{b-c}	0.2 ^b	59.1 ^{a-c}
SD	(1069)	(0.9)	(0.02)	(0.5)	(2.6)	(3649)	(0.03)	(148)	(17)	(0.1)	(1.0)	(0.5)	(0.0)	(4.1)
7 Burned	21847 ^a	5.4 ^{a,b}	0.88 ^a	39.3 ^b	24.0 ^a	26886 ^{a,b}	0.06 ^a	1661 ^b	94 ^{c-e}	4.4 ^a	7.9 ^a	28.7 ^{a-d}	0.2 ^b	60.2 ^{a,b}
SD	(2939)	(1.4)	(0.17)	(2.5)	(1.7)	(5701)	(0.01)	(166)	(22)	(1.6)	(1.9)	(1.5)	(0.0)	(11.9)
7 Disked	21331 ^a	4.1 ^{a-c}	0.41 ^a	40.0 ^b	23.0 ^a	22023 ^{a,b}	0.07 ^a	1669 ^b	81 ^{d,e}	3.1 ^a	8.6 ^a	48.0 ^a	0.3 ^b	66.8 ^a
SD	(2264)	(0.7)	(0.27)	(1.0)	(1.0)	(4517)	(0.01)	(167)	(10)	(0.7)	(1.0)	(2.0)	(0.2)	(4.3)
7 Undisturbed	18031 ^a	3.7 ^{a-c}	0.81 ^a	37.7 ^b	21.3 ^{a,b}	32799 ^a	0.08 ^a	1445 ^{b,c}	118 ^{a-d}	3.8 ^a	10.7 ^a	41.0 ^{a,b}	0.3 ^b	57.7 ^{a-c}
SD	(1184)	(0.4)	(0.73)	(3.0)	(1.1)	(2237)	(0.03)	(91)	(2)	(1.7)	(0.4)	(3.6)	(0.1)	(4.7)
17 Disked	21470 ^a	4.3 ^{a,b}	0.45 ^a	38.3 ^b	18.3 ^{a,b}	21440 ^{a,b}	0.09 ^a	2091 ^{a,b}	101 ^{b-e}	4.5 ^a	9.8 ^a	31.7 ^{a-d}	0.3 ^b	48.6 ^{a-c}
SD	(318)	(0.7)	(0.20)	(4.5)	(1.5)	(3616)	(0.01)	(248)	(1.5)	(0.8)	(0.3)	(3.0)	(0.1)	(2.6)
17 Undisturbed	22488 ^a	6.1 ^a	0.26 ^a	40.7 ^b	20.0 ^{a,b}	24922 ^{a,b}	0.08 ^a	2628 ^a	109 ^{a-d}	2.2 ^a	10.2 ^a	34.0 ^{a-c}	0.2 ^b	50.2 ^{a-c}
SD	(2627)	(0.7)	(0.15)	(2.0)	(2.6)	(3057)	(0.02)	(308)	(8.9)	(0.8)	(1.6)	(7.9)	(0.0)	(4.7)

^{a-c} Mean concentrations within a column that share the same superscript letter are not significantly different ($p = 0.05$).

or the SEM-to-AVS ratios among sites, but the pH values measured in the pore water at the three sites in impoundment no. 7 and the disked site in impoundment no. 17 were significantly lower than those at the other stations (Table 2). Alkalinity in pore water was significantly correlated ($p < 0.05$) with pH and was lowest at the sites where pH was lowest (impoundments no. 7 and 17). Hardness and conductivity were also highest at these sites.

Survival of *H. azteca* in pore water was positively correlated with manganese in solid-phase sediments and negatively correlated with lead in solid-phase sediments and concentrations of iron, magnesium, manganese, nickel, and zinc in the pore water (Table 5). The only cation in pore water that was correlated with survival in the solid-phase test was copper. Length of *H. azteca* was positively correlated with the following sediment cations—chromium, copper, manganese, and zinc—

Table 5. Spearman rank correlations

Characteristics	Pore-Water Survival	Solid-Phase Survival	Solid-Phase Length
Sediment			
Organic matter (%)	-0.137	-0.203	0.215
Fines (%)	-0.076	0.102	0.512 ^a
Redox potential	-0.557 ^a	0.007	0.229
AVS	0.165	0.106	0.227
SEM	-0.236	0.160	-0.512 ^a
SEM/AVS ratio	-0.185	0.074	-0.483 ^a
Pore-water			
pH	0.882 ^a	0.138	0.168
Alkalinity	0.902 ^a	0.102	0.228
Hardness	-0.671 ^a	-0.037	0.152
Conductivity	-0.579 ^a	0.049	0.215
DOC	-0.026	-0.123	-0.550 ^a
NH ₄	-0.629 ^a	0.122	-0.629 ^a
Sediment			
Aluminum	-0.155	0.047	0.125
Arsenic	-0.164	0.199	0.235
Cadmium	-0.080	-0.195	0.264
Chromium	0.282	0.102	0.608 ^a
Copper	-0.258	-0.209	0.493 ^a
Iron	-0.167	-0.140	0.333
Mercury	0.146	-0.107	0.216
Magnesium	0.245	0.171	0.300
Manganese	0.669 ^a	-0.134	0.383 ^a
Molybdenum	-0.205	-0.080	0.156
Nickel	0.159	-0.112	0.203
Lead	-0.467 ^a	-0.018	0.278
Selenium	0.085	-0.211	-0.036
Zinc	-0.04	-0.005	0.728 ^a
Pore-water elements			
Aluminum	-0.060	-0.123	0.232
Arsenic	-0.213	-0.025	0.140
Cadmium	-0.322	-0.240	0.534 ^a
Chromium	0.160	-0.170	0.273
Copper	0.019	-0.383 ^a	0.068
Iron	-0.583 ^a	-0.149	0.327
Mercury	0.251	0.063	-0.539 ^a
Magnesium	-0.744 ^a	0.085	0.083
Manganese	-0.626 ^a	-0.184	0.262
Molybdenum	0.421 ^a	-0.093	-0.390 ^a
Nickel	-0.480 ^a	-0.200	0.542 ^a
Lead	-0.114	-0.127	0.312
Selenium	-0.337	-0.131	0.057
Zinc	-0.395 ^a	-0.301	0.269

Correlations describe relationships between sediment and pore-water toxicity to *H. azteca* and the physical and chemical characteristics of solid-phase sediments and pore water in samples collected from impoundments at Savannah NWR.

^a Significant correlation ($p \leq 0.05$).

and the following cations in pore water—cadmium and nickel. Length was negatively correlated with mercury and molybdenum in the pore water.

The proportion of fines (silt and clay components) in the sediments varied from a low of 41% to a high of 91% among sites (Table 2). No pattern with regard to management option or impoundment was apparent for percent organic matter or percent fines. The sediments were reducing (redox ≤ 100 mV) except at the disturbed sites (disked and burned) in impoundment no. 7.

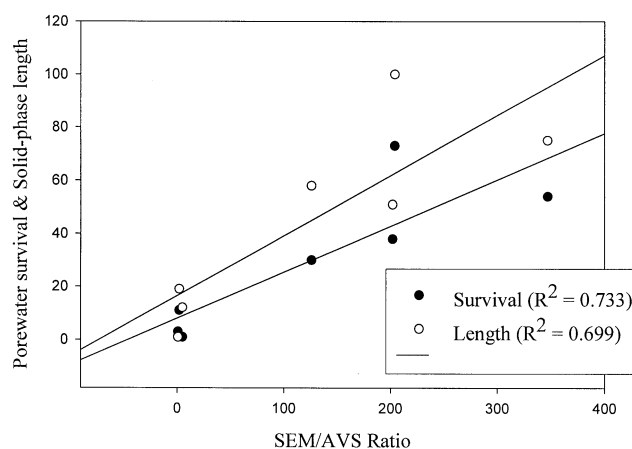


Fig. 4. Relationship between toxicity (survival in pore water and length from solid-phase exposures proportionally ranked) and SEM/AVS ratios (proportionally ranked) when acidic sites were omitted from the analysis

Discussion

Contaminants (metal concentrations in the sediments) do not appear to be the major factors responsible for the decreased sediment quality found in several of the impoundments at the Savannah NWR. OCLs, pesticides, PCBs, and PAHs were not detected in sediments collected from the impoundments, and metals were generally within normal ranges. Elements in the solid-phase sediments appeared to be similar to those reported for other wetland sediments (Lindau and Hossner 1982; Ghuman and Menon 1984), although chromium and lead exceeded consensus-based sediment-quality guidelines at a few sites (MacDonald *et al.* 2000). Chromium concentrations exceeded the guideline (43.4 $\mu\text{g/g}$) at the 2 sites sampled in impoundment no. 6, and lead exceeded the 35.8 $\mu\text{g/g}$ guideline at the disked and undisturbed sites in impoundment no. 7 (Table 4).

Ammonia and pH appear to be important factors associated with decreased survival of *H. azteca* in the pore waters from impoundment no. 7 and the burned site in impoundment no. 17. Hydrogen ion toxicity to *H. azteca* has been shown to occur at pH levels < 5.5 (France and Stokes 1987), and ammonia is generally toxic to *H. azteca* at concentrations ≥ 10 mg/L (Ankley *et al.* 1990). Management practices used at the NWR to control vegetation may influence these 2 factors. Ammonia concentrations were significantly higher at the disturbed sites (disked and burned) in impoundments no. 7 and 17 than at the other stations. The increased amount of organic matter associated with the sediments, because of the disking and burning at these sites, probably enhanced microbial activity and the build up of ammonia concentrations.

Increased concentrations of metals in pore waters from impoundments no. 1 and 2 and the undisturbed site in impoundment no. 17 may have contributed to the observed decreased survival and growth of *H. azteca* in pore-water and solid-phase exposures, respectively. The high ratios of SEM to AVS shown for these sites are consistent with these observations (Table 2). SEM-to-AVS ratios > 1 indicate that metals exceed the available acid volatile sulfides and may be a potential source of toxicity (Di Toro *et al.* 1992). Metals in excess of sediment

AVS may be bioavailable in the pore water, although other entities in the pore water—such as colloids and dissolved organic carbon—could bind with the metals and ameliorate their toxicities (Temminghoff *et al.* 1997).

The acidic nature of the sediments in impoundment no. 7 also appears to be responsible for the high concentrations of elements in the pore water (Table 3). Increased concentrations of ions in soil solutions are characteristic of low-pH systems (Gambrell 1994). Total concentrations of elements in the pore waters (particularly aluminum, iron, magnesium, and manganese) from sediments in impoundment no. 7 were one order of magnitude higher than those from the other impoundments. Pore waters from this impoundment also had the highest hardness concentrations and conductivities, demonstrating that more ions were in solution than at the other sites (Table 2). The limited supply of AVS present in the sediments, which could potentially bind with some of the metals, may also have been a contributing factor to the higher concentrations of metals in the pore water. Associated with this low pH was also a correspondingly low alkalinity, which reflects decreased acid-neutralizing capacity.

A number of factors and interrelated processes may contribute to the acidic conditions exhibited in the sediments at several sites within the impoundments on the NWR. For example, decomposition of organic matter may lead to reduced pH through the formation or release of humic and fulvic acids (Williams *et al.* 1994). Oxidation–reduction reactions are also known to control many of the chemical processes that occur in sediments (Gambrell 1994). During the reduced phase, when sediments are flooded, oxygen is depleted by microbial respiration. As conditions become anoxic, alternative electron acceptors such as nitrate, manganic manganese, ferric iron, sulfate, and other oxidized materials are used, and redox potential decreases accordingly. The pH of sediment under reduced conditions is generally between 6.5 and 7, and metals are effectively immobilized and unavailable (Gambrell 1994). When the sediments are exposed to oxygen during withdrawal of water and drying, they become oxidized, and redox potential increases. The pH of sediments, particularly organic wetland sediments, decreases during oxidation and may reach levels that inhibit plant growth and enhance metal mobility and bioavailability (Gambrell 1994).

The chemistry related to ferrololysis may also explain the low pH observed in sediments from impoundments at the Savannah NWR. This condition develops under the alternate oxidation–reduction processes associated with drying and flooding of the sediments (Brinkman 1969/1970; Ponnampetuma 1972). Under normal conditions, the pH of submerged soils is circumneutral; however, during flooding sediments become reduced and cations displaced from exchange sites by iron (Fe^{2+}), are lost (migrate out of the reduced zone). When the sediment is drained and oxidized, the iron that was reduced under flooding is reoxidized (Fe^{3+}) and precipitates. With the loss of iron from exchange sites on sediment surfaces, H^+ ions become the dominant cation, and the sediment is acidified, thus resulting in low pH and loss of alkalinity.

When sediments are oxidized, sulfide minerals formed under reducing conditions are dissolved and released to the pore water or overlying water (Cooper and Morse 1998). The exposure of reduced sediment to oxygen can lead to the decom-

position of metal sulfides and release of associated ions and sulfuric acid to the pore waters (Saeki *et al.* 1993; William *et al.* 1994). The release of cations is characteristic of sediments when redox potential increases and pH decreases (DeLaune and Smith 1985; Gambrell and Patrick 1988; Anisfeld and Benoit 1997). The oxidation–reduction processes (redox potential and the associated pH) associated with the oxidized conditions present at the 2 disturbed sites in impoundment no. 7 (areas with the highest concentrations of most cations) undoubtedly influenced the mobility and availability of the divalent cations (copper, cadmium, magnesium, nickel, lead, and zinc).

Sediments in the impoundments at the NWR also have the possibility of being acid-sulfate soils, which have been reported from coastal areas. The transition of potentially acid-sulfate soils developed under anaerobic or reduced (submerged) conditions to the acid-sulfate soils formed under the oxic/oxidized (dewatered) state produces sulfuric acid, which could contribute to the decreased pH levels measured in the pore water (Sundström *et al.* 2002). When potential acid-sulfate soils in coastal areas are drained and aerated (oxidized), pyrite is oxidized to sulfuric acid, and the sediment is acidified, thus resulting in $\text{pH} < 4$ (Satawathananont *et al.* 1991). Acid-sulfate soils are identified by the following criteria: pH of the sediment mixed with peroxide < 3 ; sediment sulfur concentrations $> 0.74\%$; and pH of the oxidized sediment < 3.5 (Boyd 1995). The pHs of sediments from the NWR impoundments mixed with peroxide were < 3 . However, the pHs of the sediments after they were oxidized were not < 4 . Total sulfur in the sediments ranged from 0.10% to 0.31%, only approximately one fourth of the concentration characteristic of acid-sulfate soils. Therefore, the sediments in the impoundments would at most be considered marginally acid-sulfate soils. Nevertheless, cations such as hydrogen, aluminum, and iron could accumulate and concentrations in acid-sulfate soils occasionally exceed lethal concentrations (DeLaune and Smith 1985). Transport of acidic water and metals in drainage from acid-sulfate soils has been shown to impact downstream aquatic systems (Sundström *et al.* 2002). Releases of water from impoundments on the NWR with acidic conditions could have contributed to the decreased quality of sediments in the downgradient reaches of the river that were identified during the previous study (Winger *et al.* 2000).

Contaminants (metals) could be marginally responsible for the impaired conditions at several sites within the impoundments of the Savannah NWR and potentially impact resident biota. However, decreased sediment quality, as indicated by the sediment and pore-water toxicity and chemistry from sediment collected in the impoundments, appears to be more related to the acidic conditions associated with oxidation of the wetland sediments during periodic dewatering. Disking of the vegetation in the impoundments appeared to contribute to the increased concentrations of ammonia by enhancing the amount and availability of organic matter for decomposition. The processes associated with the dewatering, drying, and oxidation of the sediments appear to be the major factors contributing to the acidic conditions and cation concentrations in the pore water in impoundment no. 7. Cook *et al.* (2000) highlighted the importance of drainage in the acidification of vulnerable sediments and asserted that

extended flooding could ameliorate the acidic conditions. Drainage from the impoundments with decreased pH and increased availability of metals could account for the increased concentrations of metals in the downgradient sediments, and the management practices currently employed apparently exacerbate the acidification of the sediments.

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