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Wetland Retention of Lead from a Hazardous Waste Site

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Lead (Pb) and its compounds are known to negatively affect human and animal life (Oehme, 1978; Nriagu, 1988). Some of the principal sources of Pb in the environment have been leaded gasoline, as well as contributions from storage batteries and older paint formulations (Hellawell, 1988). The area selected for this investigation was a cypress/black gum wetland named Steel City Bay in Jackson County, Florida which received large quantities of Pb carried in acid waters draining from a battery recycling facility from 1970 to 1980. The facility processed as many as 50,000 used batteries per week in 1978 (Trnovsky et al., 1988). While the plant was in operation, complaints about damage to cypress trees in adjoining wetlands in Steel City Bay were reported. After several efforts failed to correct the problem, the Florida Department of Environmental Regulation (FDER) decided to close the plant in January, 1980. Since the plant was abandoned, the residual acid and heavily contaminated soil and sediment still strongly influence the wetland ecosystem, have the potential for causing groundwater contamination, and impacting potable water supplies (Watts, 1984).

MATERIALS AND METHODS

Wetland sediment, vegetation, and surface water samples were collected for total Pb analyses from locations designated on the site map (Fig. 1), with the results to be used to evaluate the storage of Pb in the wetland ecosystem. The soil and sediment samples were also treated by sequential chemical extractions (SCE) to fractionate the chemical forms. The distribution of the chemical forms of Pb was used to predict the potential for mobilization and accumulation of Pb in the wetland sediment.

Surface water samples were collected by submerging acid-rinsed Nalgene polyethylene bottles into the standing water. Water samples for nutrients analysis were preserved in the field with 0.2% (v/v) H_2SO_4 and samples for the metal analyses were preserved with 0.2% (v/v) HNO_3. A trip blank sample bottle with deionized distilled (DDI) water was carried for Quality Assurance / Quality Control (QA/QC) purposes. All water samples were transported to the laboratory and kept refrigerated at 4 °C until analyzed. Sediment samples were collected from the same location as the surface water samples using a 4-inch stainless steel bucket auger. Sampling was conducted at three depth intervals of 0 to 15 cm, 15 to 30 cm, and 30 to 45 cm. Sediment core samples were placed in heavy-duty, plastic, zip-lock bags, stored in coolers, and transported to the laboratory and frozen until analyzed.

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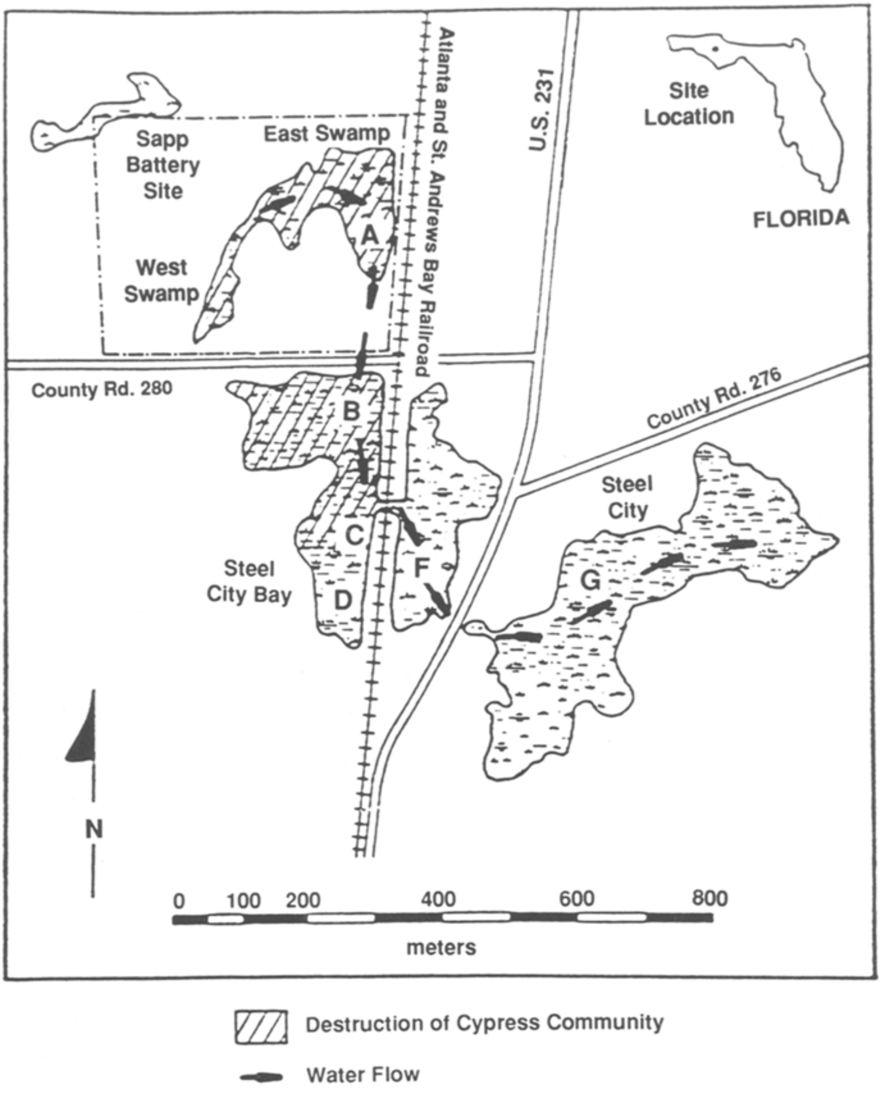

Figure 1. Locations of the six sampling sites.

Leaves, tree stems, aquatic plants and algae in the wetland were collected as vegetation samples. Pond cypress (Taxodium ascendens), black gum (Nyssa sylvatica), water lily (Nymphaea odorate), and eel grass (Eleocharis sp.) were the species collected. Samples were placed in heavy-duty, plastic bags and stored frozen until analyzed.

Several procedures for sample pretreatment were performed. For surface water, 200 ml of acidified sample were concentrated on a hotplate to a final volume of 10 ml. Sediment and vegetation samples were dried in an oven for 24 hrs at 105°C. Dried samples were then ground and passed through a No. 40 sieve (Tyler equivalent size, 35 mesh). Nitric acid and H_2O_2 were used to digest the solid samples (Delfino and Enderson, 1978). The analytical methods used to determine the water quality parameters in this study followed those of the US Environmental Protection Agency (EPA, 1979) and/or Standard Methods (APHA et al., 1985). A sequential chemical extraction (SCE) scheme, adapted from Stover et al. (1976) and Rudd et al. (1988), is shown in Table 1 and was applied to the soil and sediment samples. All the metal analyses were performed using flame atomic absorption spectrophotometry (AAS). To insure the validity of the data, some actions were taken to meet QA/QC requirements. The QA/QC program in this study included the analysis of EPA known evaluation samples in every analysis series, running duplicate samples, and checking the recoveries of standard solution spikes. The results of analysis of EPA known evaluation samples were within the acceptable range, true value ± 95% confidence interval. The results of duplicate samples and spike recoveries were also within the 95% confidence interval (Ton, 1990).

Table 1. Conditions for sequential chemical extraction of sediment samples.

Fractions	Designated Form	Reagent (A. R. grade)	Time	Solids / Reagent
Fraction I	Exchangeable	1.0 M KNO_3	16h	1:50
Fraction II	Adsorbed	0.5 M KF(pH 6.5)	16h	1:80
Fraction III	Organically Bound	0.1 M $Na_4P_2O_7$	16h	1:80
Fraction IV	Inorganic Precipitate (Carbonate, Fe-Mn Oxides)	0.1 M EDTA(pH 6.5)	16h	1:80
Fraction V	Sulfide	6.0 M HNO_3	16h	1:50
Fraction VI	Residual	HNO_3+30%H_2O_2 Digestion		

Adapted from Stover et al. (1976) and Rudd et al. (1988).

RESULTS AND DISCUSSION

The Sapp Battery site is located on a topographically high area relative to the elevation of the surrounding swamps and streams. The general area of the study site receives rainfall as its major water source. Surface water, including acid discharge from the Sapp Battery site, drains to the south and east into the West and East Swamps and then flows into Steel City Bay (Fig. 1). Eventually, the series of cypress swamps empty into Little Dry Creek approximately 1.6 km away. The surface water flow rate varied with seasonal changes and storm events. Watts (1984) indicated the flow discharge to Little Dry Creek to be 2.83 L sec^{-1} (0.1 ft^3 sec^{-1}) in May, 1983. However, the creek may cease to flow and dry up on occasion. As shown in Figure 1, samples were taken from upstream near the original source of Pb and in a series going downstream, including sampling of an area lateral to the main flow, i.e. site D. Site E was selected for another study not related to the spatial distribution of Pb in the main flow regime. Therefore, six sample sites ranging from A to G, excluding E, were included in this study. The water quality conditions in the study area are shown in Table 2. The distance indicates an approximate measurement away from the discharge point at the Sapp Battery site, i.e. the sampling site A. The concentration of Pb in surface water decreased significantly from 0.28 mg L^{-1} to less than 0.01 mg L^{-1} in less than 450 m from the discharge point (Table 2). The same trend of Pb concentration decline was also observed in soil and sediment samples but with less of a gradient, ranging from 484 to 100 $\mu g\ g^{-1}$ within 900 m from the discharge point (Table 3).

Table 2. Water quality of sampling sites that received discharge from the Sapp Battery Superfund site, Jackson County , Florida

	A*	B	C	D	F	G
Distance (m) **	0	240	444	587	459	> 900
pH	3.4	3.6	3.8	4.4	4.5	3.9
Temperature (°C)	32	31	32	28	29.5	-
Water Depth (cm)	51	52	64 - 89	> 90	38 - 51	31 - 51
Conductivity (µmho/cm-25°C)	322	106	76	31	48	77
Nitrite/Nitrate (mg-N/L)	0.08	0.01	0.02	0.04	0.04	0.02
Ammonia (mg-N/L)	3.76	0.18	0.08	0.16	0.35	0.16
TKN (mg-N/L)	5.08	1.43	2.06	3.60	2.31	1.08
Total P (mg/L)	0.03	0.07	0.09	0.20	0.08	0.02
Total Pb (mg/L)	0.28	0.03	<.01	<.01	0.01	0.01

* See Fig. 1 for the locations of the sampling sites.
** Distance measured from sampling site A.
\- Indicates no data available.

Table 3. Lead content in sediment/soil profiles of Steel City Bay, Jackson County, Florida.

	Location*											
	A		B		C		D		F		G	
	1**	2	1	2	1	2	1	2	1	2	1	2
Depth (cm)												
0 -15	287	485	345	76.8	228	240	53.5	65.2	147	30.2	88.5	100
15 -30	18.6	18.6	566	100	158	41.9	41.9	30.2	123	18.6	18.6	18.6
30 -45	6.90	18.6	438	18.6	100	30.2	6.90	18.6	41.9	18.6	30.2	18.6

* See Fig. 1 for the locations of the sampling sites.
**Numbers 1 and 2 indicate two different sampling locations,15 m apart from each other, at each sampling site.
All data are in units of µg/g (ppm, dry weight).

These results show that most of the Pb is bound to soil and sediment, rather than remaining in the water column. The Pb distribution gradient in this wetland area indicated that the removal of lead from the water column occurred through mechanisms operating along the gradient. Sedimentation, adsorption, chelation, and precipitation are likely the most important mechanisms for removing the lead from the water column. The sediment-water interface was the apparent site for Pb removal since the organic-rich sediment likely served as a strong binding agent. Lead adsorbed, complexed or precipitated with organic colloids has been reported elsewhere (Huang et al., 1977; Florence and Bately, 1980; Chan et al., 1982; Aiken et al., 1985). Vertical profile data for Pb in sediment/soil samples are listed in Table 3. The distribution of Pb in the soil and sediment profiles indicates that most of the Pb has accumulated in the top layer of soil and sediment, i.e. 0 to 15 cm (except location B). This phenomenon may suggest the reduced potential for groundwater contamination. Considerable spatial heterogeneity existed in the study area as seen by differences between samples 1 and 2 at each sampling site. A number of the sediment samples in the study site were well decomposed organic matter (OM) or black muck, while some sediments were only partially decomposed. Chan et al. (1982) pointed out that dead but not decomposed litter was able to adsorb heavy metals directly from the water. Furthermore, decomposed litter releases humic acids that act as metal chelators and can effectively immobilize metal pollutants. Data for total Pb concentration in vegetation samples were insufficient to show the same trend of lead accumulation along the surface water drainage channel. However, the shallow-rooted, most highly exposed submerged aquatic plant, Eleocharis sp., contained the highest detected Pb content in tissue, i.e. 487 $\mu g\ g^{-1}$ (Table 4). This result indicates the possibility for bioaccumulaton of Pb from contaminated sediment.

Table 4. Lead content in vegetation samples in Steel City Bay, Jackson County , Florida .

		Location†					
Vegetation	Item	A	B	C	D	F	G
	Bark	112*	56.3*	75*	< 5.0#	< 5.0	12.5*
Cypress	Stem(0-3 cm)	37.5*	12.5*	175*	12.5	< 5.0	< 5.0
Taxodium ascendens	Leaves	-	< 5.0	< 5.0	< 5.0	< 5.0	-
	Bark	-	-	-	18.8	-	25.0
Black gum	Stem(0-3 cm)	-	-	-	< 5.0	-	37.5
Nyssa sylvatica	Leaves	-	12.5	-	-	-	12.5
Water lily	Stem & leaves	-	75.0	12.5	12.5	12.5	-
Nymphaea odorate	Root	-	62.5	12.5	-	50.0	-
Eelgrass		487	-	-	-	-	-
Eleocharis sp.							
Algae		-	-	-	-	150	-

† See Fig. 1 for the location of the sampling sites.
*Indicates dead tree.
#Detection limit : 5.0 µg/g (0.05 mg/L equivalent in solution).
- Indicates no data due to lack of specimen in the sampling area.
The leaf samples(B, C, D) were collected from live trees on the edge of the swamp.
All data are in units of µg/g (ppm, dry weight).

Total metal concentrations have been used to assess the ecological impacts of heavy metals (Oehme, 1978; Påhlsson, 1989; Tyler, 1989; Tyler et al., 1989). However, many studies suggested that the ecological influences of metals were more determined by the specific chemical forms rather than total metal concentrations (Hoover, 1978; Venugopal and Luckey, 1978; Schalscha et al., 1982; Calmano et al., 1986). In this study, specific chemical reagents were used to fractionate Pb into different chemical forms. Exchangeable, adsorbed, organically bound, inorganic precipitate (carbonate, Fe-Mn oxides), sulfide, and residual were the categories used to identify the different chemical forms which were indicated by fraction I to fraction VI, respectively. Fractions I and II were considered as active forms, i.e. readily bioavailable, while the other fractions (III, IV, V, VI) have been stated to be less active and less bioavailable forms (Schalscha et al., 1982). Based on sequential chemical extractions, the fractionation of Pb in sediment and soil samples is indicated in Table 5. Fraction III (organically bound Pb) was found to be the most abundant chemical form in the soil and sediment. The data also indicated that the chemical forms of Pb decreased in the following order of abundance: fraction III > fraction IV > fraction I > fraction V > fraction VI > fraction II. The high organic content in the soil/sediment profile could have released humic substance fragments as degradation occurred (Aiken et al., 1985). Lead is known to complex with organic ligands, followed by the possible adsorption of these complexes by hydrous oxide solids or organic particulates (Huang et al., 1977). The maximum adsorption of complexing ligands onto oxide surface sites was observed at the pH approximately equal to the pKa of the ligands

Table 5. The distribution of chemical forms of Pb in sediment and soil samples after treatment by sequential chemical extractions, Steel City Bay, Jackson County, Florida.

		Fraction													
Sample*	Total	I**	%	II	%	III	%	IV	%	V	%	VI	%	Sum	T %
A1a#	287	75.8	**23.9**	0.06	**0.0**	139	**43.9**	69.4	**21.9**	21.7	**6.8**	10.8	**3.4**	317	**110.5**
A2a	485	105	**24.9**	11.6	**2.7**	196	**46.4**	80.9	**19.2**	21.7	**5.1**	7.24	**1.7**	422	**87.2**
B1a	345	86.7	**29.3**	0.06	**0.0**	92.5	**31.2**	80.9	**27.3**	21.7	**7.3**	14.5	**4.9**	296	**85.9**
B1b	566	65.0	**13.0**	11.6	**2.3**	185	**36.9**	196	**39.1**	28.9	**5.8**	14.5	**2.9**	501	**88.5**
B1c	438	43.4	**11.1**	11.6	**3.0**	139	**35.4**	162	**41.3**	21.7	**5.5**	14.5	**3.7**	392	**89.5**
B2a	76.8	14.5	**18.3**	0.06	**0.1**	23.2	**29.3**	23.2	**29.3**	7.26	**9.2**	10.8	**13.7**	79.0	**102.8**
B2b	100	14.5	**15.6**	0.06	**0.1**	28.9	**31.2**	34.7	**37.5**	7.26	**7.8**	7.24	**7.8**	92.7	**92.6**
C1a	228	25.3	**12.3**	0.06	**0.0**	63.6	**30.9**	80.9	**39.3**	21.7	**10.5**	14.5	**7.0**	206	**90.2**
C1b	158	18.1	**13.3**	0.06	**0.0**	34.7	**25.5**	57.8	**42.5**	14.5	**10.6**	10.8	**8.0**	136	**85.9**
C1c	100	7.26	**10.7**	0.06	**0.1**	23.2	**34.0**	23.2	**34.0**	7.26	**10.6**	7.24	**10.6**	68.1	**68.1**
C2a	240	21.7	**11.5**	11.6	**6.1**	63.6	**33.6**	63.6	**33.6**	14.3	**7.5**	14.5	**7.6**	189	**78.8**
D1a	53.5	7.26	**13.7**	0.06	**0.1**	23.2	**43.7**	11.6	**21.9**	7.26	**13.7**	3.63	**6.8**	53.0	**99.0**
D2a	65.2	7.26	**10.1**	0.06	**0.1**	23.2	**32.3**	23.2	**32.3**	7.26	**10.1**	10.8	**15.1**	71.7	**110.0**
F1a	147	28.9	**23.2**	0.06	**0.0**	46.3	**37.2**	34.7	**27.9**	7.26	**5.8**	7.24	**5.8**	124	**84.8**
F1b	123	14.5	**14.2**	0.06	**0.1**	34.7	**34.0**	34.7	**34.0**	7.26	**7.1**	10.8	**10.6**	102	**82.7**
G1a	88.5	14.5	**16.5**	0.06	**0.1**	17.4	**19.8**	23.2	**26.4**	21.7	**24.8**	10.8	**12.4**	87.6	**99.0**
G2a	100	14.5	**13.3**	0.06	**0.1**	23.2	**21.3**	34.7	**32.0**	21.7	**20.0**	14.5	**13.3**	109	**108.4**
AVG			**16.2**		**0.9**		**33.3**		**31.7**		**9.9**		**8.0**		**92.0**
SD			**5.7**		**1.7**		**7.3**		**7.0**		**5.3**		**4.1**		**11.6**

*See Fig. 1 for the locations of sampling sites.

**(Fraction I: exchangeable; II: adsorbed; III: organically bound; IV: Inorganic precipitate; V: sulfide; VI: Residual; %: percent of total Pb concentration; T %: total percent recovery)

a, b, c indicate the depth of sediment sample: a: 0-15 cm; b: 15-30 cm; c: 30-45 cm.

All data are in units of µg/g (ppm, dry weight) except for the % data.

(Davis and Leckie, 1978). The pH of the study area's surface water, i.e. pH 3.4 to 4.5, was similar to the pKa of natural humic acid, i.e. pH 2.5 to 4.5 (Tipping et al., 1988). The high percentage of organically bound Pb in this wetland might have been due to the adsorption of the Pb-humic acid complexes onto colloidal organic matter or inorganic species.

The analyses of total Pb in soil and sediment samples in the vicinity of Steel City Bay provided a distribution profile of Pb in those matrices. The concentration of Pb decreased with depth as most of the Pb was accumulated in the upper layers. Due to the high organic content in the sediments of the study area, Pb appeared to be bound at the upper sediment layer (0-15 cm). The fractionation of Pb in the environment is an important factor in the assessment of the potential hazards associated with the metal. The data indicated that generally less than 20-25% of the total Pb in the soil and sediment was readily bioavailable, adsorbed, or in the exchangeable form, and over 80% of the total Pb in the soil and sediment is stable and immobilized. These results suggest that the wetlands at the study site are capable of retaining and filtering Pb from a contaminated inflow source.

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