Contamination From Battery Salvage Operations On The Chipola River, Florida

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Abstract: Trace elements (As, Cd, Cr, Cu, Hg, Pb, Se, and Zn) were measured in fish, clams, and sediment in 1982 to determine whether the effluents from 2 abandoned battery salvage operations were contaminating the Chipola River, Florida. Concentrations of the metals were generally low, but tended to increase downstream from plant sites. Elevated concentrations may reflect residual contamination from the battery salvage operations as well as increased land-use development and proximity to major highways. Concentrations of trace elements in samples of biota and sediments demonstrated no serious contaminant problem in the Chipola River.

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Possible contamination of the Chipola River from 2 abandoned battery salvage companies has caused concern for downstream fish and wildlife resources of the Apalachicola River and Estuary in northwest Florida. High levels of metals, sulfate, and acidity were found in drainage water and sediments in 1981 by the Florida Department of Environmental Regulation (unpubl. data) during a preliminary survey of the plant sites. Old batteries were cut open and drained, and the lead was recovered for resale during operation of these facilities. Contaminants associated with these operations were sulfuric acid (H_2SO_4), sulfate, and the metals Cd, Cu, Pb, Ni and Zn. Concentrations of Al and Mn were also high in these areas, but these metals occurred naturally and were leached from the soil under the acidic condition caused by H_2SO_4. At a battery salvage plant that operated from 1970 to 1980, north of Alford, Florida, effluents containing H_2SO_4 and associated metals drained directly into a swamp, killing the vegetation there before they entered Dry Creek, which flows 16 km to the Chipola River. This plant processed more than 50,000 batteries per week during peak operation. Another battery salvage company, which operated in 1979-1982, was about 3 km from the Chipola River and 3 km upstream from its confluence with Dry Creek. Contaminated material from this site entered the Chipola River by way of groundwater and surface runoff from unlined holding ponds constructed in porous sand.

The Chipola River originates in Alabama below Dothan and flows southward through Jackson, Calhoun, and Gulf counties, Florida, before draining into the Apalachicola River at about river mile 27. These river systems are an integral part of one of the few relatively undisturbed bottomland hardwood swamps and estuaries in the United States. Freshwater and estuarine resources associated with this system are recreationally and commercially important and contribute significantly to the economy of northwest Florida. The area is comparatively pristine; however, some agricultural developments and small towns are present in the drainage, especially in the central portion.

Contamination with metals is of particular importance to ecological systems because of their toxicity and their persistence in the environment (Miettinen 1977). Metals remain available for uptake, transportation, and transformation for a long time because of their inorganic properties (Hoover 1978). Uptake and accumulation of metals by biota vary with biotic species, metal, and water chemistry, but levels above background concentrations generally indicate contamination from anthropogenic sources. The objective of this study was to determine if toxic trace elements (metals) associated with battery salvage operations were present in sediments and biota of the Chipola River.

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Methods

Ten study sites were established along the Chipola River to assess the possible contamination contributed from the battery salvage plants. Stations 1 and 2 were above the discharge areas, stations 3 and 4 in potential discharge areas, and stations 5-10 were distributed below them; stations 8 and 9 were in Dead Lake, a small reservoir near the lower end of the river. Both Interstate Hwy. 10 and U.S. Hwy. 90 cross the Chipola River in the vicinity of station 3.

Samples of largemouth bass (*Micropterus salmoides*), spotted sucker (*Minytrema melanops*), Asiatic clam (*Corbicula manilensis*), and sediment were collected from 10 locations in the Chipola River in September 1982. Three composite samples of 5 fish each and 3 samples of clams and sediment were obtained from each station. Fish were collected by electrofishing and were weighed and measured. Tissues were extracted from the shells of clams hand-collected from the stream bottom, combined into a sample, and weighed. Individual fish and composite samples of clams were wrapped in aluminum foil. Sediment samples were collected using an Ekman grab: each sample consisted of a subsample from 3 grab samples. Sediment samples were stored in linear polyethylene bags. All samples were placed on ice after collection and frozen as soon as possible (nearly always within 8 hours).

Samples were analyzed for organochlorine insecticides and 8 potentially toxic trace elements (As, Cd, Cr, Cu, Hg, Pb, Se, and Zn). Residue analyses were conducted on whole fish. Samples were homogenized in a Hobart[1] food grinder. For organochlorine analysis, a 25-g subsample was mixed with sodium sulfate and then petroleum ether for extraction. Florisil was used to clean up the extract in part, and silica gel for additional cleanup. Measurements were made with a gas chromatograph equipped with an electron capture detector.

Samples for Cd, Cr, Cu, Pb, Hg, and Zn analysis were prepared by refluxing with nitric acid. Samples for As and Se determinations were digested with a nitric-perchloric acid mixture. Using atomic absorption spectroscopy techniques, As and Se were analyzed by hydride generation, Hg by a cold-vapor technique, and a graphite furnace was used for Cd, Cr, and Pb. Cu and Zn were determined by inductively coupled argon plasma emission spectroscopy.

Analysis of variance and Duncan's multiple range test, available on the Statistical Analysis System (Helwig and Council 1982) at the University of Georgia computer center, were used to analyze transformed data ($\log x + 1$) by species among stations.

Results and Discussion

Metal concentrations in sediments and biota of the Chipola River were not considered excessively high, but levels generally increased downstream from the background levels at the 2 upstream stations (Table 1). The downstream increase of As, Cd, Cr, Pb, and Zn was particularly noticeable in clam and sediment samples. Elevated levels may reflect residual contamination from the abandoned battery salvage operations as well as increased land-use developments (agriculture and urbanization) and proximity to highways, which has been shown to cause significant increases in metal levels (Von Hassel et al. 1980).

Concentrations of As, Cd, and Se in fish from the Chipola River were similar to those measured in biota from the Apalachicola River (Winger et al. 1984). Pb levels in clams were higher in the Chipola River than reported in the Apalachicola River. Concentrations of Hg in largemouth bass and spotted suckers from the Chipola River were <0.5 ppm, the concentration generally accepted as natural in unpolluted environments (Abernathy and Cumbie 1977), and substantially less than the 1 ppm (methyl mercury) action level allowed in fish for human consumption (U.S. Food and Drug Adm. 1984).

The higher concentrations of As in *Corbicula* than in fish demonstrated that As bioaccumulates in this mollusk, but does not biomagnify. Arsenic is generally accu-

[1]Reference to trade names or manufacturers does not imply U.S. Government endorsement of commercial products.

Table 1. Organochlorine and metal residues (ppm whole body, wet weight) in biota and sediment from the Chipola River, Florida, 1982.[1]

Sample and Station	Average weight (g)	Lipid (%)	Organochlorines			Metals							
			Total DDT	PCB	Other[2] Organic	As	Cd	Cr	Cu	Hg	Pb	Se	Zn
Largemouth bass (N=3 composite samples of 5 fish each)													
1	194	2.53^{abc}	0.07^{cd}	ND^{d}	ND^{a}	0.05^{a}	0.04^{a}	0.47^{bc}	0.78^{a}	0.48^{a}	0.07^{a}	0.40^{abc}	13.98^{ab}
2	241	1.64^{bc}	0.04^{d}	ND^{d}	ND^{a}	0.05^{a}	0.04^{a}	0.32^{d}	0.71^{a}	0.46^{a}	0.05^{a}	0.46^{abc}	11.89^{b}
3	446	1.21^{c}	0.14^{ab}	0.20^{a}	0.03^{a}	0.05^{a}	0.17^{a}	0.59^{a}	0.81^{a}	0.38^{a}	0.06^{a}	0.51^{ab}	15.65^{a}
4	320	1.31^{bc}	0.06^{d}	0.08^{bcd}	0.01^{a}	0.06^{a}	0.04^{a}	0.54^{ab}	0.74^{a}	0.28^{a}	0.09^{a}	0.53^{a}	16.23^{a}
5	333	1.93^{abc}	0.05^{d}	0.03^{cd}	0.01^{a}	0.05^{a}	0.05^{a}	0.46^{bc}	0.53^{a}	0.25^{a}	0.05^{a}	0.41^{abc}	14.43^{a}
6	425	3.21^{a}	0.10^{abcd}	0.04^{cd}	0.01^{a}	0.05^{a}	0.05^{a}	0.42^{c}	0.54^{a}	0.38^{a}	0.08^{a}	0.50^{ab}	14.32^{a}
7	406	2.73^{ab}	0.07^{bcd}	ND^{d}	0.01^{a}	0.05^{a}	0.19^{a}	0.47^{bc}	0.52^{a}	0.43^{a}	0.07^{a}	0.38^{bc}	13.93^{ab}
8	503	3.34^{a}	0.13^{abc}	0.13^{abc}	0.03^{a}	0.07^{a}	0.05^{a}	0.49^{abc}	0.89^{a}	0.33^{a}	0.43^{a}	0.33^{c}	15.17^{a}
9	462	2.18^{abc}	0.08^{bcd}	0.07^{bcd}	0.01^{a}	0.09^{a}	0.17^{a}	0.59^{a}	0.65^{a}	0.37^{a}	0.05^{a}	0.39^{abc}	15.67^{a}
10	638	6.61^{d}	0.15^{a}	0.14^{ab}	ND^{a}	0.05^{a}	0.05^{a}	0.48^{abc}	0.73^{a}	0.42^{a}	0.11^{a}	0.50^{ab}	14.14^{ab}
Spotted sucker (N=3 composite samples of 5 fish each)													
1	394	6.48^{a}	0.06^{bcd}	ND	ND^{a}	0.06^{b}	0.07^{a}	0.33^{e}	0.71^{b}	0.15^{a}	0.05^{a}	0.50^{bcd}	15.42^{d}
2	532	4.08^{ab}	0.05^{cd}	ND	0.03^{a}	0.07^{a}	0.07^{a}	0.37^{de}	0.66^{b}	0.21^{a}	0.08^{a}	0.77^{a}	16.50^{cd}
3	449	3.89^{ab}	0.09^{abc}	0.17^{a}	0.06^{a}	0.06^{a}	0.04^{a}	0.41^{cd}	0.74^{b}	0.10^{a}	0.17^{a}	0.51^{bcd}	17.15^{cd}
4	467	3.34^{b}	0.13^{a}	0.14^{a}	0.04^{a}	0.06^{a}	0.09^{a}	0.57^{a}	3.13^{a}	0.38^{a}	0.31^{a}	0.61^{ab}	20.24^{a}
5	472	3.74^{ab}	0.08^{abcd}	ND	0.03^{a}	0.11^{a}	0.07^{a}	0.46^{bc}	0.64^{b}	0.11^{a}	0.08^{a}	0.53^{bc}	17.17^{cd}
6	588	4.12^{ab}	0.11^{ab}	ND	0.04^{a}	0.08^{a}	0.05^{a}	0.35^{a}	0.86^{b}	0.17^{a}	0.10^{a}	0.42^{cd}	16.67^{cd}
7	654	4.22^{ab}	0.04^{d}	ND	ND^{a}	0.07^{a}	0.18^{a}	0.55^{a}	7.56^{a}	0.15^{a}	0.88^{b}	0.51^{acd}	19.65^{ab}
8	642	6.03^{ab}	0.06^{bcd}	ND	0.01^{a}	0.06^{a}	0.05^{a}	0.44^{bcd}	0.77^{b}	0.11^{a}	0.05^{a}	0.34^{d}	17.66^{bc}
9	497	5.31^{ab}	0.04^{d}	ND	ND^{a}	0.06^{a}	0.05^{a}	0.49^{ab}	0.88^{b}	0.11^{a}	0.05^{a}	0.39^{cd}	20.05^{a}
10	433	10.90^{c}	0.12^{a}	0.16^{a}	0.02^{a}	0.05^{a}	0.05^{a}	0.44^{bcd}	0.88^{b}	0.13^{a}	0.07^{a}	0.39^{cd}	15.69^{d}
Asiatic clam													
1	91[3](142)[4]	1.17^{c}	0.01^{b}	ND	ND	0.28^{f}	0.42^{ab}	1.09^{de}	6.74^{a}	0.18^{abc}	0.27^{a}	NA	23.35^{a}
2	80(164)	1.14^{c}	0.01^{b}	ND	ND	0.63^{de}	0.50^{ab}	1.86^{abcd}	10.73^{a}	0.18^{abc}	0.28^{a}	NA	22.76^{a}
3	161(209)	1.33^{c}	0.01^{b}	ND	ND	0.55^{ef}	0.22^{c}	2.81^{a}	8.17^{a}	0.08^{c}	0.46^{a}	0.81^{b}	23.00^{a}
4	95(199)	1.24^{c}	0.01^{b}	ND	ND	0.94^{bcd}	0.44^{ab}	2.31^{ab}	13.14^{a}	0.09^{bc}	0.63^{a}	1.02^{a}	24.81^{a}
5	42(102)	0.64^{d}	ND^{b}	ND	ND	NA	0.52^{a}	2.75^{a}	8.83^{a}	NA	0.25^{a}	NA	20.97^{a}
6	80(171)	1.21^{c}	0.01^{b}	ND	ND	0.77^{cde}	0.38^{b}	2.04^{abc}	19.23^{a}	0.19^{ab}	1.18^{a}	NA	29.89^{a}
7	37(42)	1.30^{c}	ND^{b}	ND	ND	NA	0.47^{ab}	1.57^{bcde}	18.17^{a}	NA	1.02^{a}	NA	26.29^{a}
8	118(110)	1.85^{b}	0.01^{b}	ND	ND	1.10^{abc}	0.27^{c}	1.88^{abcd}	8.30^{a}	0.20^{a}	0.41^{a}	0.83^{b}	21.40^{a}
9	127(78)	1.87^{b}	0.01^{b}	ND	ND	1.37^{ab}	0.16^{c}	1.20^{cde}	12.67^{a}	0.13^{abc}	0.60^{a}	0.65^{c}	20.20^{a}
10	106(94)	2.49^{a}	0.08^{a}	ND	ND	1.50^{a}	0.23^{c}	0.92^{e}	8.64^{a}	0.08^{c}	0.18^{a}	0.75^{bc}	21.78^{a}

Sample and Station	Average weight (g)	Lipid (%)	Organochlorines			Metals							
			Total DDT	PCB	Other[2] Organic	As	Cd	Cr	Cu	Hg	Pb	Se	Zn
Sediment[6] (N=3/station)													
1	100	19.7[5]	ND[a]	ND	ND	0.60[cd]	0.08[a]	6.71[a]	0.65[b]	0.05[a]	2.97[c]	NA	5.57[c]
2	100	24.6	ND[a]	ND	ND	0.77[cd]	0.18[a]	11.09[a]	1.02[b]	0.05[a]	4.32[bc]	NA	8.21[bc]
3	100	23.8	ND[a]	ND	ND	1.12[bc]	0.17[a]	9.63[a]	1.90[b]	0.05[a]	10.18[a]	NA	15.19[ab]
4	100	20.7	ND[a]	ND	ND	0.50[d]	0.14[a]	7.24[a]	0.94[b]	0.05[a]	3.75[bc]	NA	9.07[bc]
5	100	20.3	ND[a]	ND	ND	0.50[d]	0.12[a]	5.95[a]	0.76[b]	0.05[a]	3.09[c]	NA	7.24[bc]
6	100	30.0	ND[a]	ND	ND	1.77[ab]	0.28[a]	12.63[a]	2.00[b]	0.05[a]	8.52[ab]	NA	16.28[ab]
7	100	39.9	ND[a]	ND	ND	0.50[d]	0.27[a]	10.37[a]	1.91[b]	0.05[a]	14.65[a]	NA	19.10[ab]
8	100	42.2	0.03[a]	ND	ND	0.82[cd]	0.20[a]	10.28[a]	1.86[b]	0.05[a]	11.47[a]	NA	25.33[ab]
9	100	54.4	0.01[a]	ND	ND	1.86[ab]	0.23[a]	18.88[a]	7.69[a]	0.06[a]	13.37[a]	NA	35.13[a]
10	100	30.3	ND[a]	ND	ND	2.00[a]	0.09[a]	14.51[a]	4.84[a]	0.05[a]	9.93[a]	NA	26.76[a]

NOTE: ND = not detected
NA = not analyzed
[1] Values with the same superscript within a column and sample group are not significantly different ($P<0.05$)
[2] α BHC, *trans* nonachlor, *cis* nonachlor, mirex, α chlordane, γ chlordane
[3] Mean weight of sample
[4] Mean number of Asiatic clam excluding shell
[5] Mean percentage moisture
[6] Concentrations in sediments expressed on a wet-weight basis

mulated at higher concentrations in animals of lower trophic level than fish (Sphehar et al. 1980).

Copper concentration varied considerably, especially in spotted sucker and sediment samples. This variability may be attributed to the use of copper-based herbicides in the control of aquatic vegetation in the Chipola River. Compared with records from the National Pesticide Monitoring Program (Lowe et al. 1985), trace elements in fish from the Chipola River were generally below the 85th percentile (concentrations exceeding this level are considered high and may indicate a problem), except for Hg (85th percentile 0.18 ppm) and occasionally Cd (0.06 ppm), Cu (0.90 ppm), and Pb (0.25 ppm).

Organochlorine and PCB residues were low throughout the Chipola River (Table 1). They were not detected in sediment samples, except for DDT at stations 8 and 9. Although DDT residues were low in samples of fish and clams, they were found at all stations (except in clams at stations 5 and 7). Other organochlorine insecticides and PCBs were occasionally detected, but concentrations were low. Somewhat elevated concentrations at stations 3 and 4 appeared to be related to more intensive land-use activities (agriculture, highways, and urbanization). Compared with mean levels measured in the National Pesticide Monitoring Program (Schmitt et al. 1983), the concentrations of organochlorines and PCBs were low in fish from the Chipola River. Organic residues in the Chipola River were also lower than these reported for biota in the Apalachicola River in 1978 (Winger et al. 1984).

Dead Lake may serve as a sink for contaminants passing through the Chipola River. Concentrations of most metals in sediment samples were higher at station 9 (lower Dead Lake) than at station 10, near the mouth of the river. The only organochlorine pesticides found in the sediment samples were in Dead Lake (station 8 and 9).

Although contamination from the abandoned battery salvage plants may have contributed toxic trace metals to the Chipola River during and shortly after operation, our samples reflect no serious contamination in 1982.

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