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Contaminant Analyses of Water and Sediment at Key Cave, Lauderdale County, Alabama

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by

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EXECUTIVE SUMMARY

Water and sediment samples were collected from Key Cave and analyzed for 20 metals and 78 organic chemicals. Results indicated the presence of p,p'-DDE and elevated concentrations of seven metals (Al, B, Be, Fe, Mn, Ni, Zn) in sediment. Restrictions on land application of sewage sludge, implementation of an integrated pest management program, and a 12-month monitoring program are recommended.

INTRODUCTION

The endangered Alabama cavefish (*Speoplatyrhinus poulsoni*) is known to occur only in Key Cave, Lauderdale County, Alabama. Only nine specimens are known to exist in scientific collections, and few individuals have been observed in the wild. Considering the limited distribution, and the few specimens seen or collected, this species appears to be one of the rarest of all North American freshwater fish.

The watershed in which Key Cave occurs is a sinkhole plain of about 10,000 acres which has been used to produce cotton, soybeans, and corn. The limestone karst area contains numerous sinkholes which allow rapid movement of surface water runoff to the underground cave systems. The application of agricultural chemicals such as insecticides, herbicides, and fertilizers, coupled with soil erosion and surface water runoff, raised concerns about impacts to the Alabama cavefish and its habitat, including Key Cave Lake and Key Spring. The Southeast Region of the U.S. Fish and Wildlife Service (Service) funded this project to conduct a preliminary assessment using water and sediment samples. The Service is considering this area for inclusion in the National Wildlife Refuge system (Figure 1).

Key Cave is also used as a maternity cave by the endangered gray bat (*Myotis grisescens*). A survey conducted in 1993 estimated the population to be over 41,000. Two species of blind crayfish (*Procambarus pecki* and *Cambarus jonesi*) also inhabit the cave.

METHODS AND MATERIALS

Water and sediment samples were collected and placed in clean glass and plastic containers for organic analyses and metal analyses, respectively. Sediment samples were collected using clean stainless steel scoops, spoons, and buckets. Water samples collected for metal analyses were preserved with 2 ml of concentrated, ultrapure nitric acid. All samples were transported on wet ice and stored under refrigeration until shipped to the laboratory for analysis.

All samples were analyzed using standard procedures approved by the Patuxent Analytical Control Facility at the Patuxent Wildlife Research Center. Water and sediment samples used for metal analyses were acid-digested in Teflon-lined microwave vessels and analyzed using inductively coupled plasma emission (ICP) spectrometry. Metal analyses were performed by Research Triangle Institute in Research Triangle Park, North Carolina.

For organic analyses, water and sediment samples were extracted with methylene chloride, ethyl ether, and petroleum ether. They were then fractionated using florisil, silica gel and silicic acid columns, and benzene/hexane. Organophosphate and carbamate analyses were performed on samples extracted with acetone and methylene chloride. Analyses were performed using gas chromatography with megabore capillary columns and appropriate detectors. Organophosphate and carbamate analyses were performed by the Patuxent Wildlife Research Center in Patuxent, Maryland. Organochlorine, chlorophenoxy acid herbicides, and aliphatic hydrocarbon analyses were performed by the Mississippi State Chemical Laboratory.

QUALITY ASSURANCE/QUALITY CONTROL

Analytical accuracy, as measured by spiked sample recoveries and reference material analysis, were generally acceptable. The recovery values for antimony, silver, and tin by ICP analyses were typically low, thus these results should be used with caution. Precision, as measured by duplicate sample analysis, was acceptable. Results of calibration check samples and method blank samples indicated acceptable performance of the analytical instruments.

RESULTS

Six water samples and two sediment samples were collected from the Key Cave area and analyzed for 20 metals, 25 organophosphate compounds, six carbamates, six chlorophenoxy acid herbicides, 28 organochlorine chemicals, and 13 aliphatic hydrocarbons (Table 1). Of the 78 organic chemicals analyzed, only p,p'-DDE was detected (0.09 ppm, wet weight) in the sediment sample from Key Spring. No organic chemicals were detected in the sediment sample from Key Cave or in any of the water samples. For water samples, the following detection limits were used: 2 μg/l (organophosphates); 20 μg/l (carbamates); and 5 μg/l (chlorophenoxy acid herbicides, organochlorine chemicals, and aliphatic hydrocarbons). For sediment samples, the following detection limits were used: 0.5 μg/g (organophosphates); 1.0 μg/g (carbamates); and 0.01 μg/g for all chlorophenoxy herbicides, aliphatic hydrocarbons and organochlorines except PCBs and toxaphene (0.05μg/g).

Of the 20 metals analyzed, six (Sb, Be, Cd, Pb, Mo, Ag) were not detected in water samples, and four (Sb, Mo, Ag, Sn) were not detected in the sediment samples. In water samples, Co and Sn were detected only at Key Spring while the remaining 12 metals were found at both Key Cave and Key Spring (Table 2). In sediment samples, Cu and Pb were not detected at Key Spring while the remaining 14 metals were found at both locations (Table 3). Detection limits for water and sediment samples are shown in Table 4 for each metal analyzed.

Although Al and Fe concentrations were slightly higher in water samples from Key Spring, metal concentrations were generally similar at both Key Cave and Key Spring. Sediment metal concentrations were consistently higher at Key Cave, and several metals (including Al, Cd, Cu, Pb, Mg, Mn, Sr, Zn) were 2-3 times greater in Key Cave sediments as compared to Key Spring.

DISCUSSION

While our limited sampling and analysis of 78 organic chemicals indicated only the presence of p,p'-DDE in sediment, a variety of agricultural chemicals are known to have been used in the vicinity of Key Cave (Table 5). Metal concentrations in Key Spring sediment were generally representative of normal concentrations in soils and sediment from the Eastern United States. Several metals (Al, B, Be, Fe, Mn, Ni, Zn) were considered to be elevated in Key Cave sediment, possibly reflecting input from previous land disposal of sewage sludge. Although organic carbon and particle size analyses were not conducted on the sediment samples, it is thought that the fine-grained, clay and silt components comprised a smaller portion of the spring sediment and a larger portion of the cave sediment.

Implementation of a regular monitoring program over a 12-month period, with emphasis on storm events, would provide a much better characterization of organic chemical and metal loading to Key Cave. If the Service establishes Key Cave as a National Wildlife Refuge, then implementation of the Southeast Region Integrated Pest Management Program, and associated Pesticide Use Proposal process, would help provide additional protection. Should the area not be brought into the refuge system, then restricted pesticide use and appropriate land management practices should be pursued through cooperative agreements with landowners. In either case, it is recommended that land disposal of sewage sludge in this area be eliminated. This would help to protect the recharge areas identified by Ozark Underground Laboratory (Figure 2).

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Table 1. Analyses Performed on Key Cave Samples.

Metals (20)

Aluminum (Al)	Cadmium (Cd)	Lead (Pb)	Silver (Ag)
Antimony (Sb)	Cobalt (Co)	Magnesium (Mg)	Strontium (Sr)
Barium (Ba)	Chromium (Cr)	Manganese (Mn)	Tin (Sn)
Beryllium (Be)	Copper (Cu)	Molybdenum (Mo)	Vanadium (V)
Boron (B)	Iron (Fe)	Nickel (Ni)	Zinc (Zn)

Organophosphates (25)

Acephate	Dimethoate	Methamidophos
Azinphos-methyl	Disulfoton	Methyl parathion
Chlorpyrifos	Dursban	Mevinphos
Coumaphos	EPN	Monocrotophos
Demeton	Ethoprop	Parathion
Diazinon	Famphur	Phorate
Dichlorvos	Fensulfothion	Terbufos
Dicrotophos	Fenthion	Trichlorfon
	Malathion	

Carbamates	**Chlorophenoxy Acid Herbicides**
Aldicarb	Dicamba
Carbaryl	Dichlorprop
Carbofuran	2,4,-D
Methiocarb	Silvex
Methomyl	2,4,5-T
Oxamyl	2,4-DB

Organochlorines (28)

BHC (4 isomers)	Dieldrin	Nonachlor (2 isomers)
Chlordane (2 isomers)	Endrin	Octochlorostyrene
DDE (2 isomers)	HCB	PCBs (total)
DDD (2 isomers)	Heptachlor epoxide	Oxychlordane
DDT (2 isomers)	Mirex (6 isomers)	Toxaphene

Aliphatic Hydrocarbons (13)

n-dodecane	n-pentadecane	n-octadecane
n-tridecane	nonylcyclohexane	phytane
n-tetradecane	n-hexadecane	n-nonadecane
octylcyclohexane	n-heptadecane	n-eicosane
	pristane	

Table 2. Metals Results (mg/l) for Water Samples.

	Key Cave			Key Spring		
	KC-1B	KC-2B	KC-3B	KS-1B	KS-2B	KS-3B
Al	0.032	0.154	0.797	0.267	0.964	1.86
Ba	0.016	0.017	0.029	0.023	0.034	0.036
B	0.007	0.008	0.031	0.015	0.010	0.011
Co	<0.002	<0.002	<0.002	<0.002	<0.002	0.002
Cr	0.006	0.005	0.005	0.005	0.004	0.009
Cu	0.002	0.005	0.003	0.002	0.005	0.004
Fe	0.092	0.182	0.693	0.220	0.762	1.62
Mg	1.43	1.52	3.31	1.75	1.81	1.81
Mn	0.007	0.015	0.053	0.012	0.023	0.140
Ni	<0.004	<0.004	0.007	<0.004	0.005	0.006
Sr	0.071	0.074	0.054	0.097	0.100	0.076
Sn	<0.012	<0.012	<0.012	0.019	<0.012	<0.012
V	<0.001	<0.001	0.002	0.001	0.002	0.005
Zn	0.022	0.025	0.013	0.017	0.025	0.048

Table 3. Inorganic Results ($\mu g/g$, dry weight) for Sediment Samples.

Element	Key Spring	Key Cave
Al	2240	6750
Ba	230	282
Be	0.684	1.77
B	56.0	76.3
Cd	0.597	3.10
Co	10.6	11.9
Cr	32.0	59.3
Cu	<2.50	13.7
Fe	16300	26900
Pb	<12.0	17.9
Mg	47.5	321
Mn	561	1300
Ni	17.8	58.7
Sr	13.1	58.6
V	53.8	82.5
Zn	71.1	353
% Moisture	22.0	36.2

Table 4. Detection Limits (ppm) for Metals Analyzed in Water and Sediment Samples.

Element	Water	Sediment (ppm, dry weight)
Al	0.015	50
Sb	0.025	50
Ba	0.001	2.0
Be	0.001	0.2
B	0.002	3.5
Cd	0.001	0.5
Co	0.002	2.0
Cr	0.002	3.0
Cu	0.002	2.5
Fe	0.010	30
Pb	0.008	12
Mg	0.015	30
Mn	0.002	1.0
Mo	0.004	6.0
Ni	0.004	5.0
Ag	0.005	10
Sr	0.001	0.8
Sn	0.012	35
V	0.001	1.0
Zn	0.005	5.0

Table 5. Insecticides and Herbicides Applied in Lauderdale County, Alabama.*

Bladex	DSMA	Phorate
Caparol	Lasso	Probe
Carbaryl	Lorax	Sulfan
Carbofuran	Lorsban	Treflan
Cotoran	MSMA	

*Provided by Mr. Mack A. Pugh, Cooperative Extension Program, Alabama A&M University, Normal, AL 35762.