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Impacts of Coal Mining-Related Contaminants on Freshwater Mussels:

Little South Fork Cumberland River, Kentucky--

Special Report

U.S. Fish and Wildlife Service
Ecological Services
446 Neal Street
Cookeville, Tennessee 38501

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U.S. FISH and WILDLIFE SERVICE / SOUTHEAST REGION / ATLANTA, GEORGIA

U.S. Fish and Wildlife Service

Southeast Region

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by

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INTRODUCTION

Numerous species of native freshwater mussels are exposed to contaminants related to oil/gas production and coal mining. Several of these species are federally listed as endangered or threatened. In the Southern Appalachian Ecosystem, the Little South Fork Cumberland River (LSFCR) has historically supported a diverse mussel fauna and has also been subjected to impacts from oil/gas production and coal mining. The mussel populations inhabiting the LSFCR have shown substantial declines and periodic die-offs.

To investigate impacts to mussels in the LSFCR, the Fish and Wildlife Service (Service) initiated a three-pronged investigation involving: (1) a mussel survey, (2) juvenile mussel bioassays; and (3) collection and analysis of mussel and sediment samples. This project was funded through the Asheville Field Office (North Carolina) and included participation by the Service's Cooperative Research Units at Virginia Polytechnic Institute (juvenile mussel bioassays) and Tennessee Technological University (mussel survey; mussel and sediment sample collections). The Service's Raleigh Field Office (North Carolina) and Cookeville Field Office (Tennessee) provided technical support. The results of contaminant analyses on sediment and mussel samples are briefly summarized and discussed in the following sections. This report should be used only in conjunction with the results of the other two phases of the project and was prepared primarily to ensure that the reporting requirements of the Service's contaminants program are met.

RESULTS

Ten sediment and 15 composite mussel samples were collected from the Little South Fork Cumberland River (LSFCR) in July 1988 (Table 1). Mussel samples consisted of soft tissue collected from specimens of the following species: *Ellipto dilatata, Medionidus conradicus, Villosa iris, V. taeniata, Lasmigona costata, Lampsilis fasciola, Actinonaias pectorosa, Ptychobranchus fasciolaris, and Corbicula fluminea.* Samples were analyzed for the 23 metals, 23 organochlorine compounds, 11 aliphatic hydrocarbons, and 24 polycyclic aromatic hydrocarbons (PAHs) shown in Table 2.

Organochlorines and PAHs

None of the 23 target organochlorine chemicals were detected in any of the ten sediment samples or eight mussel samples which were analyzed. Of the 24 PAHs analyzed, nine were detected at low concentrations (0.01 to 0.03 ppm, wet weight) only in mussel sample LSF-M12.

Table 1. Little South Fork Cumberland River Sediment and Mussel Sample Information.

Sample Type and No.	Sample Weight (grams)		Percent Moisture	
Sediment	Field	Lab	Organics	Metals
LSF-S1	362	18.61	46.2	49.8
LSF-S2	332	14.37	30.2	32.3
LSF-S3	317	13.12	23.2	22.8
LSF-S4	346	16.26	38.5	36.5
LSF-S5	462	13.29	24.6	25.3
LSF-S6	272	16.90	40.6	37.0
LSF-S7	543	13.26	24.3	23.8
LSF-S8	383	14.12	29.2	23.6
LSF-S9	200	24.73	59.6	40.2
LSF-S10	200	25.60	60.7	41.3

Mussel Tissue	Field	Lab	Organics	Metals	Percent Lipid
LSF-M1	51.66	10.61	87.6	87.3	0.20
LSF-M2	45.62	10.00	88.7	87.5	0.14
LSF-M3	56.53	10.56	88.6	88.7	0.05
LSF-M4	62.01	10.02	90.0	86.3	0.32
LSF-M5	58.79	10.14	87.3	87.7	0.53
LSF-M8	59.29	11.59	87.0	86.9	1.16
LSF-M11	42.19	10.55	89.8	90.4	0.12
LSF-M12	28.13	5.04	88.1	88.2	2.43
LSF-M7	30.36	---	---	87.7	---
LSF-M9	38.70	---	---	89.4	---
LSF-M10	50.46	---	---	86.4	---
LSF-M13	49.13	---	---	90.7	---
LSF-M14	56.10	---	---	89.0	---
LSF-M15	64.64	---	---	89.3	---
LSF-M16	63.81	---	---	88.7	---

Table 2. Analyses Performed on Little South Fork Cumberland River Samples.

Organochlorines (23)

Aldrin	Dieldrin	Mirex
BHC (3 isomers)	Endrin	Nonachlor (2 isomers)
DDE (2 isomers)	HCB	PCBs (total)
DDD (2 isomers)	Heptachlor	Oxychlordane
DDT (2 isomers)	Heptachlor epoxide	Toxaphene
DDT (total)	Lindane	

Polycyclic Aromatic Hydrocarbons (24)

Acenapthene	Benzo(b)fluoranthene	Perylene
Acenapthylene	Benzo(k)fluoranthene	Benzo(ghi)perylene
Anthracene	Fluorene	Phenanthracene
Benzo(a)anthracene	Naphthylene	1-methyl phenanthracene
Dibenzo(a)anthracene	1-methyl naphthylene	Pyrene
Biphenyl	2-methyl naphthylene	Benzo(a)pyrene
Chrysene	2,6-dimethyl naphthylene	Benzo(e)pyrene
Fluoranthene	2,3,4-trimethyl naphthylene	Indenopyrene

Metals (23)

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

Aliphatic Hydrocarbons (11)

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

These compounds were: benzo(a)anthracene (0.03 ppm), dibenzoanthracene (0.01 ppm), chrysene (0.03 ppm), benzo(b)fluoranthracene (0.02 ppm), benzo(k)fluoranthracene (0.02 ppm), perylene (0.02 ppm), benzo(a)pyrene (0.02 ppm), benzo(e)pyrene (0.02 ppm), and indenopyrene (0.01 ppm).

In sediment samples, anthracene, dibenzoanthracene, benzo(k)fluoranthracene, and indenopyrene were not detected (<0.01 ppm, wet weight). Ten compounds were detected at low concentrations (0.01-0.05 ppm) only in sediment sample LSF-S1 (Table 3). The following three PAHs were detected in all sediment sample: 2,3,4-trimethyl napthalene (0.01-0.14 ppm), phenanthracene (0.04-0.36 ppm); and 1-methyl phenanthracene (0.02-0.16 ppm). The remaining PAHs occurred sporadically (mainly in LSF-S1 and LSF-S10) and ranged from non-detect (<0.01 ppm) to 0.51 ppm (Table 3).

Aliphatic Hydrocarbons

Dodecane (C-12) was not detected (<0.01 ppm, wet weight) in any sample while tridecane (C-13) was found in only one sediment sample (LSF-S1@0.08 ppm). Concentrations of the other aliphatic hydrocarbons analyzed were detected in all or most of the sediment samples, and ranged from 0.01 ppm to a high of 0.81 ppm (pristane in LSF-S1). In each sediment sample, pristane and phytane had higher concentrations than the other aliphatic compounds (Table 4).

Heptodecane (C-17) was detected in all mussel samples at concentrations ranging from 0.03 to 0.37 ppm, wet weight (Table 5). Of the remaining aliphatic hydrocarbons analyzed, only a trace amount (0.04 ppm) of nonadecane (C-19) was found. It was detected in a replicate aliquot taken from mussel sample LSF-M12.

Metals

Of the 23 metals analyzed, 19 (83%) were detected in the sediment samples (Table 6) and 17 (74%) were found in the mussel samples (Table 7). Antimony, molybdenum, silver, and thallium were not detected in either sediments or mussels, while beryllium and boron were not found in mussels. Mercury concentration in mussels ranged from 0.412 ppm (LSF-M8) to 1.150 ppm (LSF-M9). Mercury concentrations in mussels were 10-35 times higher than sediment mercury concentrations. Lead concentrations in mussels varied from 1.80 ppm (LSF-M14) to 3.50 ppm (LSF-M3 and LSF-M16).

Quality Assurance

Replicate, spike, and blank samples were analyzed for all the target organic parameters. Results for these samples were acceptable and did not indicate any analytical quality assurance or quality control concerns.

Table 3. Polycyclic Aromatic Hydrocarbons (PAHs) Detected* in LSFCR Sediment Samples (July 1988).

Sample	Fluoranthracene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthracene	Benzo(a)pyrene	Benzo(e)pyrene	Perylene	Biphenyl
LSF-S1	0.04	0.04	0.03	0.06	0.03	0.02	0.05	<0.01	0.06
LSF-S2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
LSF-S3	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
LSF-S4	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	0.05	<0.01
LSF-S5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
LSF-S6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
LSF-S7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
LSF-S8	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
LSF-S9	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
LSF-S10	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	0.02	0.01

*ppm, wet weight

Table 3. Continued.

Sample	Benzo(ghi)perylene	Naphthalene	1-Methylnaphthalene	2-Methylnaphthalene	2,6-Dimethylnaphthalene	2,3,4-Trimethylnaphthalene
LSF-S1	0.02	0.30	0.44	0.51	0.14	0.14
LSF-S2	<0.01	0.01	<0.01	<0.01	0.01	0.04
LSF-S3	<0.01	<0.01	<0.01	<0.01	<0.01	0.06
LSF-S4	<0.01	<0.01	<0.01	<0.01	<0.01	0.05
LSF-S5	<0.01	<0.01	<0.01	<0.01	0.01	0.04
LSF-S6	<0.01	<0.01	<0.01	<0.01	<0.01	0.03
LSF-S7	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
LSF-S8	<0.01	<0.01	<0.01	<0.01	<0.01	0.02
LSF-S9	<0.01	<0.01	<0.01	<0.01	<0.01	0.03
LSF-S10	<0.01	0.04	0.04	0.05	0.02	0.02

*ppm, wet weight.

Table 3. Continued.

Sample	Acenaphthalene	Acenaphthene	Fluorene	Phenanthracene	1-Methylphenanthracene
LSF-S1	0.01	0.03	0.05	0.36	0.16
LSF-S2	<0.01	<0.01	<0.01	0.07	0.04
LSF-S3	<0.01	<0.01	<0.01	0.13	0.07
LSF-S4	<0.01	<0.01	<0.01	0.08	0.04
LSF-S5	<0.01	<0.01	<0.01	0.07	0.03
LSF-S6	<0.01	<0.01	<0.01	0.06	0.03
LSF-S7	<0.01	<0.01	<0.01	0.04	0.02
LSF-S8	<0.01	<0.01	<0.01	0.05	0.03
LSF-S9	<0.01	<0.01	<0.01	0.06	0.04
LSF-S10	<0.01	<0.01	<0.01	0.06	0.03

*ppm, wet weight.

Table 4. Aliphatic Hydrocarbons Detected* in Sediment Samples From LSFCR (July 1988).

	C-13	C-14	C-15	C-16	C-17	Pristane	C-18	Phytane	C-19	C-20
LSF-1	0.08	0.14	0.25	0.19	0.33	0.81	0.11	0.41	0.09	0.09
LSF-2	<0.01	0.03	0.08	0.12	0.11	0.41	0.04	0.28	0.01	0.07
LSF-3	<0.01	0.04	0.10	0.19	0.14	0.75	0.07	0.52	0.03	0.02
LSF-4	<0.01	0.03	0.08	0.11	0.04	0.57	0.05	0.48	0.03	0.03
LSF-5	<0.01	0.03	0.07	0.11	<0.01	0.48	0.05	0.34	0.01	0.08
LSF-6	<0.01	0.02	0.05	0.11	0.02	0.38	0.04	0.29	0.02	0.08
LSF-7	<0.01	<0.01	0.03	0.06	<0.01	0.25	0.03	0.19	0.09	0.05
LSF-8	<0.01	0.02	0.06	0.10	<0.01	0.34	0.04	0.27	0.12	0.05
LSF-9	<0.01	0.01	0.04	0.08	0.01	0.26	0.04	0.25	0.10	0.03
LSF-10	<0.01	0.02	0.03	0.05	0.21	0.15	0.02	0.11	0.08	<0.01

*reported in ppm (wet weight) as normal alkane concentrations.

Table 5. Heptodecane Concentrations* in Mussel Samples from Little South Fork Cumberland River, Kentucky (July 1988).

Samples	Heptodecane (C-17)
LSF-M1	0.36
LSF-M2	0.28
LSF-M3	0.03
LSF-M4	0.10
LSF-M5	0.28
LSF-M8	0.37
LSF-M11	0.07
LSF-M12	0.32

*ppm, wet weight.

Table 6. Metals (ppm, dry wt.) and Total Volatile Sulfides (TVS-%) in LSFCR Sediment Samples (July 1988).

	LSF-S1	LSF-S2	LSF-S3	LSF-S4	LSF-S5	LSF-S6	LSF-S7	LSF-S8	LSF-S9	LSF-S10
Aluminum (%)	0.95	0.69	0.335	1.22	0.26	0.65	0.44	0.47	0.74	0.95
Arsenic	26.50	6.60	10.40	13.10	5.10	6.00	4.60	5.90	16.40	14.10
Barium	64.90	27.10	18.50	58.30	12.20	24.20	19.60	21.90	56.40	60.60
Beryllium	1.20	0.89	0.32	0.79	<0.33	<0.40	<0.33	0.33	0.42	0.94
Boron	5.08	<3.69	<3.24	8.58	<3.35	5.95	<3.28	<3.27	5.85	<4.26
Cadmium	<0.50	<0.37	0.32	0.39	<0.33	1.11	<0.33	<0.33	<0.42	<0.43
Chromium	47.40	34.60	45.80	20.90	34.10	16.40	17.70	29.60	22.20	17.60
Copper	14.10	3.47	<1.62	6.77	<1.67	3.41	2.30	2.55	4.93	9.54
Iron (%)	5.02	1.61	1.74	1.67	1.45	1.02	0.98	1.16	1.83	1.72
Lead	8.47	7.83	6.93	9.13	2.54	4.76	4.13	<1.96	8.44	13.60
Magnesium	1260	739	395	2490	268	1020	604	648	1100	1700
Manganese	1580	1130	587	1010	357	221	193	287	3500	1370
Mercury	0.068	<0.037	<0.032	<0.039	0.033	<0.040	<0.033	<0.033	<0.042	0.055
Nickel	26.70	29.20	8.74	13.40	4.08	7.46	5.71	7.00	10.30	35.30
Selenium	0.400	0.300	<0.130	<0.160	0.270	<0.160	0.390	<0.130	0.330	0.340
Strontium	26.30	21.50	26.90	42.20	13.20	33.70	15.00	38.00	69.80	80.80
Tin	8.76	5.91	7.32	4.25	6.36	6.83	8.33	3.99	6.86	8.60
Vanadium	36.40	16.50	15.90	22.80	11.11	11.50	8.40	11.40	18.10	16.70
Zinc	59.00	52.30	22.10	43.90	17.10	26.40	19.00	24.10	41.00	72.70
TVS (%)	5.14	2.65	1.68	5.03	0.67	3.19	1.34	3.03	4.25	5.66

Table 7. Metals Results (ppm, dry weight) for LSFCR Mussel Samples (July 1988).

	M1	M2	M3	M4	M5	M7	M8	M9	M10	M11	M12	M13	M14	M15	M16
Al (%)	0.067	0.041	0.137	0.080	0.069	0.045	0.137	0.045	0.049	0.082	0.104	0.017	0.038	0.045	0.046
As	3.90	1.60	2.70	1.50	1.60	1.60	1.50	0.94	0.71	1.00	4.20	<1.10	0.91	<0.93	<0.88
Ba	300	354	286	313	192	1210	343	1140	1260	526	18.80	1370	955	1170	1170
Cd	2.60	2.32	2.30	1.75	2.20	2.11	1.83	1.51	2.87	2.40	2.66	3.44	3.55	2.80	1.77
Cr	4.65	5.12	9.29	4.60	3.90	6.83	7.56	6.23	7.43	5.62	5.93	7.31	6.00	5.70	6.64
Cu	11.40	13.80	16.70	12.30	17.30	5.12	13.70	6.89	6.54	13.00	85.40	4.84	7.00	6.64	6.55
Fe (%)	0.291	0.211	0.403	0.270	0.297	0.778	0.360	0.821	0.700	0.348	0.212	0.838	0.646	0.693	0.713
Mg (%)	0.168	0.184	0.202	0.172	0.159	0.189	0.192	0.181	0.181	0.250	0.138	0.189	0.162	0.187	0.185
Mn (%)	0.494	0.720	0.735	0.683	0.398	1.110	0.622	1.140	1.300	0.793	0.047	1.200	0.897	1.140	1.190
Hg	0.748	1.020	0.566	0.445	0.675	0.886	0.412	1.150	0.860	0.958	NA*	0.989	0.964	0.953	1.040
Ni	3.86	4.72	4.60	<2.92	<3.25	<3.25	4.58	5.09	3.68	<4.17	<4.84	<4.30	<3.64	<3.74	<3.54
Pb	3.10	3.20	3.50	2.20	2.40	2.40	2.30	1.90	2.20	2.10	3.40	3.20	1.80	1.90	3.50
Se	6.30	7.20	5.30	4.40	3.30	4.10	5.30	3.80	3.70	4.20	NA*	5.40	3.60	7.50	7.10
Sr	458	530	790	617	375	467	526	433	457	746	88.50	509	393	460	457
Sn	10.40	12.00	11.80	11.80	12.80	6.34	10.00	<4.72	10.40	<5.21	8.72	14.30	<4.55	10.80	8.94
V	<3.94	<4.00	4.78	3.80	<4.07	5.28	4.35	4.91	5.96	<5.21	<6.05	<5.38	<4.55	5.23	5.40
Zn	243	477	372	303	320	185	345	195	229	450	192	186	190	189	183

*NA- Not analyzed due to insufficient sample.

Blank, duplicate, and reference material samples were also analyzed for metals. Results for these quality assurance/quality control samples were generally acceptable, except for the following:

1) the amount of LSF-M12 was insufficient to complete selenium and mercury analyses;

2) the relative percent difference for the ten duplicate analyses was out of acceptable range (51%); and

3) the recovery for the barium and tin spike analyses were out of acceptable range (75% and 73%, respectively).

DISCUSSION

Overall, the concentrations of organochlorine chemicals and PAHs in these sediment and mussel samples do not appear to represent a significant threat to mussels in the LSFCR (Eisler 1987). Water samples were not analyzed in this phase of the study and the results of the juvenile mussel toxicity tests should be consulted for a more complete evaluation. Concentrations measured in mussels were similar to those found in sediment.

The effects of the aliphatic hydrocarbons found in the mussel samples is uncertain. The concentrations appear to be fairly low, and were not notably higher than those found in the sediment samples. Comparisons with the results of the mussel survey and toxicity tests may provide additional information.

Based on a comparison with Kelly and Hite (1984), total volatile sulfides were not elevated at any of these ten sampling locations. Most sediment metal concentrations were within normal ranges expected in soils of the eastern United States (Shacklette and Boerngen 1984). Several notable exceptions included: arsenic at five sites (1, 3, 4, 9 and 10); iron and copper at Site 1; nickel at Sites 1 and 2; and manganese at five sites (1, 2, 4, 9 and 10). Manganese also approached or exceeded the limit of tolerance values established for Canada (Jaagumagi 1992, Persaud et al. 1989) at these same five sites. Based on unpublished USEPA (1977) guidelines, the six sites where manganese exceeded 500 ppm (Table 6) would be considered heavily polluted.

Mercury was only detected in sediment samples from Sites 1 and 10, however, it was found in all mussel samples, except M12, at an average concentration of 0.833 ppm. Mercury concentrations exceeded 1.0 ppm in samples from Sites 1 and 9 and would be considered moderately polluted based on USEPA (1977) unpublished guidelines. On average, mercury concentrations in mussel samples were about 14 times greater than those in sediment. While it has been widely noted that mussels accumulate a variety of metals, the effects of these body burdens is not certain.

Overall, our results indicate that some heavy metals may be impacting mussel populations in LSFCR. The primary metals of greatest concern are arsenic, manganese, and mercury. The contaminant analyses obtained from this portion of the project should be used in conjunction with results from the mussel survey and the juvenile mussel toxicity tests.

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