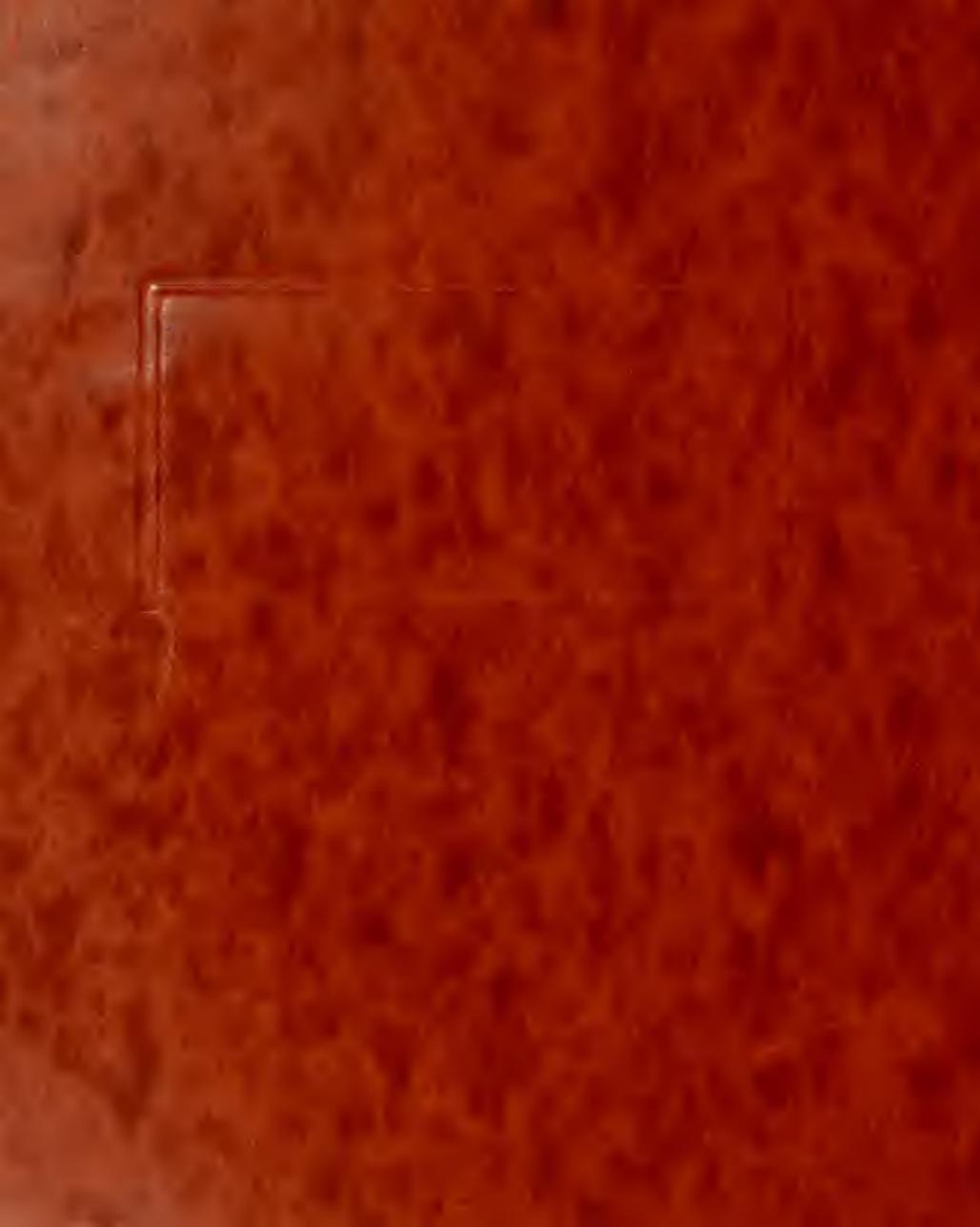


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Contaminants in Fish Food Organisms
and Duck Food Organisms from Keokuk
Pool, Mississippi River

2 November 1979

R.E. Sparks and K.E. Smith



CONTAMINANTS IN FISH FOOD ORGANISMS AND DUCK FOOD ORGANISMS
FROM KEOKUK POOL, MISSISSIPPI RIVER

for
United States Fish and Wildlife Service
Environmental Contaminants Evaluation Program
Federal Building, Fort Snelling
Twin Cities, Minnesota 55111

Prepared

2 November 1979

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INTRODUCTION

The purpose of this project was to measure contaminant levels in selected plants, benthic animals, and sediments from the Keokuk Pool, Mississippi River. Prior to this project there was virtually no information on what levels of contaminants, or even what types of contaminants, are found in the sediments and organisms of Keokuk Pool, with the exception of adult mayflies, which are collected from the pool as part of a chemical contaminant monitoring program in the Mississippi River being conducted by the Columbia National Fishery Research Laboratory of the U.S. Fish and Wildlife Service.

Contaminant levels in organisms which serve as food for fish and waterfowl are of special concern, because use of the pool by diving ducks (including the endangered canvasback duck) has been increasing in recent years (see Figure 1), and the pool supports an important commercial fishery which consistently ranks in the top 3 among all Mississippi River pools in commercial catch (Rasmussen, 1979: A1). The increasing use of Keokuk Pool by diving ducks, such as canvasbacks, may be attributable to declines in food resources in other parts of the Mississippi Flyway -- in the Illinois River, for example (Mills et al., 1966: 18-21).

Thompson and Sparks (1977: 1) reported that one important fish and duck food organism, the fingernail clam, declined significantly in the Keokuk Pool in 1976 and 1977. The specific causes for the decline were unknown, but the potential for environmental contamination from various cities, industries, and agricultural areas along the pool and upstream from the pool is great.



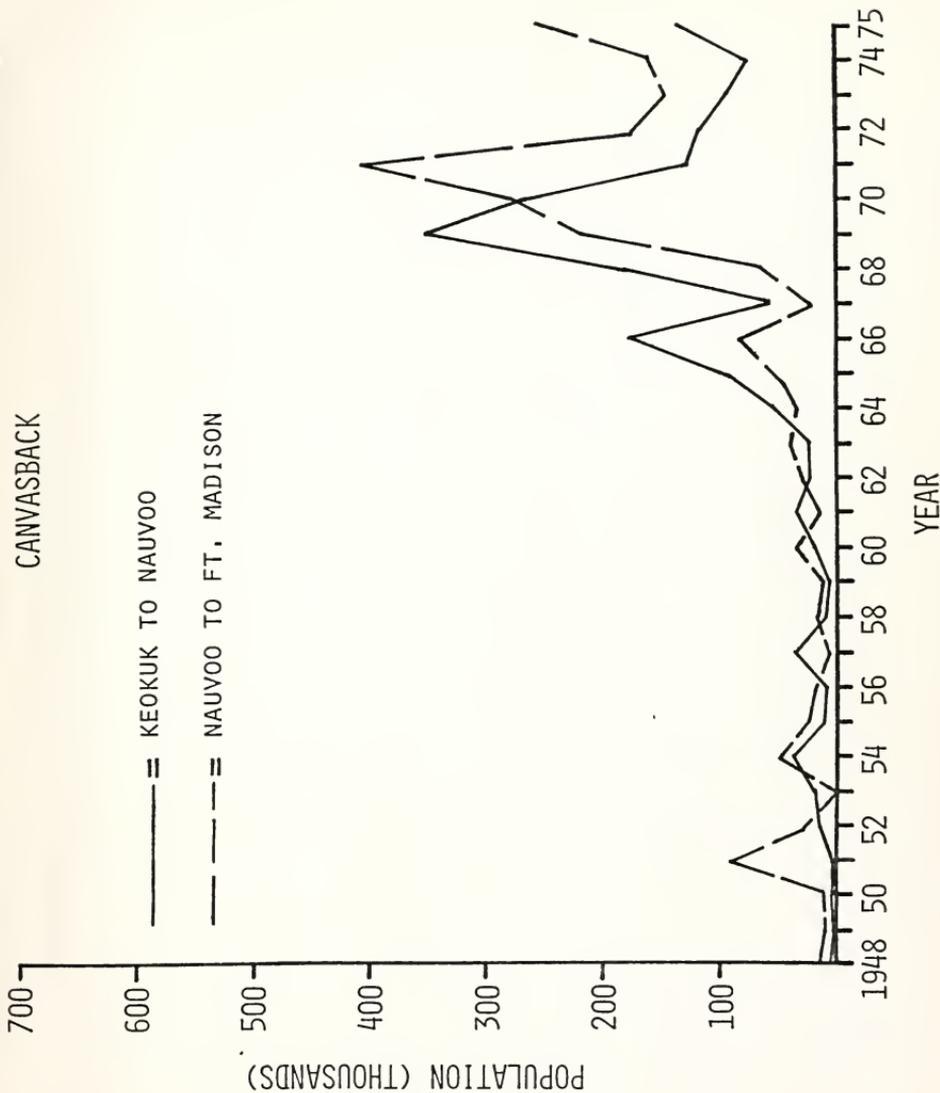


Figure 1. Canvasback duck utilization of two reaches of the Keokuk Pool, Mississippi River has increased in recent years according to aerial censuses by the Illinois Natural History Survey.

ACKNOWLEDGMENTS

This research was supported by a grant from the Environmental Contaminants Evaluation Program of the U.S. Fish and Wildlife Service, Region 3, Federal Building, Fort Snelling, Twin Cities, Minnesota 55111, as Contract Number U.S. Interior 14-16-0003-77-056. Dr. James B. Elder served as project officer for the Fish and Wildlife Service from the initiation of the project on 8 August 1977 until 18 June 1979, when Mr. Brian Cole became the project officer. Mr. Cole assisted with the supervision of the project while Dr. Elder was project officer. We are grateful to Mr. Cole for arranging cross-check analyses and a subsequent meeting between the chemists who performed the analyses. Mr. Cole also kept us apprised of other contaminant monitoring projects conducted by the U.S. Fish and Wildlife Service in the upper Mississippi River and brought several published reports to our attention. Dr. Richard Sparks designed the sampling program and collected the samples from Keokuk Pool, with Carl M. Thompson assisting in the fall of 1977 and Mr. Timothy Murphy assisting in the fall of 1978. Dr. Kenneth Smith supervised the laboratory analyses of the samples, with the assistance of Mr. Ronald E. Duzan, Ms. Patricia H. Duda and Mr. Aaron P. Griffith.

STUDY SITE

The Keokuk Pool, or Pool 19, is a 47-mile (76-kilometer) section of the Mississippi River extending from Lock and Dam 19 at Keokuk, Iowa upstream to Lock and Dam 18 above Burlington, Iowa. The upstream half of the pool is least influenced by Dam 19, and the river is relatively narrow, the

current swift, and the bottom comprised of sand in many locations. As a result of the influence of the dam, the downstream half of the pool averages one mile in width, the current velocity is reduced, and the bottom is predominantly mud. Animals which serve as food for diving ducks, such as mayflies and fingernail clams, thrive in mud bottoms where the current is not too swift. Diving ducks also feed on aquatic plants which thrive in shallow areas lateral to the main channel where the current velocity is reduced. Because the food organisms and waterfowl usage of the pool were concentrated in the downstream reach, our sampling stations were also located in this reach.

METHODS

Field Methods

Figures 2 and 3 show the location of five sampling stations established for this project (Stations 4, 8, 9, Nauvoo, and Dallas City). The stippled areas show portions of the pool which are heavily used by diving ducks during their fall migrations, based on aerial waterfowl censuses made by Frank Bellrose and Robert Crompton of the Illinois Natural History Survey. The numbered stations were established in July, 1973 for the purpose of monitoring population dynamics of benthic invertebrates. Three of these stations, 4, 8, and 9, were used in the present study to determine levels of contaminants in selected macroinvertebrates. Since the water depth at station 4 is approximately 9 feet and at station 8 approximates 12 feet, no aquatic vegetation is able to grow, so we established two other stations, one in a plant bed below Nauvoo and one in a plant bed at Dallas City, in order to obtain plants and species of snails associated with plants.

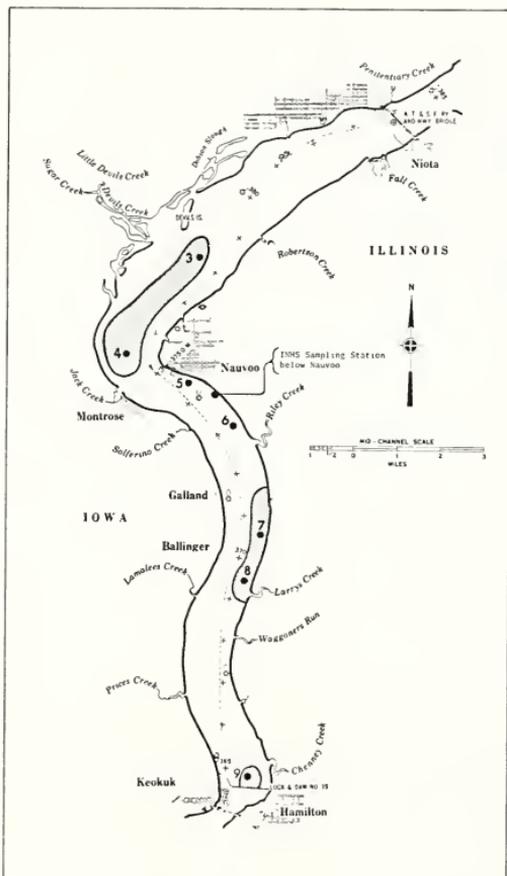


Figure 2. Map of the downstream portion of Keokuk Pool. The numbered stations are where macroinvertebrate populations are routinely sampled by the Illinois Natural History Survey. Collections were made for contaminant analysis at stations 4, 8, 9, and just below Nauvoo near the eastern shore.

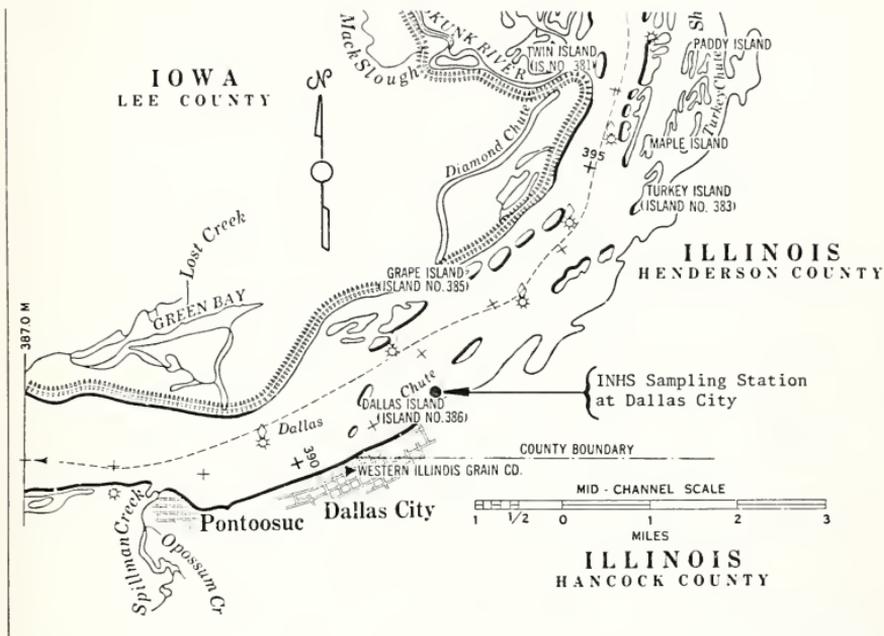


Figure 3. Map of the Keokuk Pool upstream from the Fort Madison bridge. The contaminant sampling station at Dallas City was located in a plant bed in shallow water near the eastern shore.

Station 9, located just above Dam 19, is only three to four feet deep and usually has both fingernail clams and aquatic plants.

Bottom samples were taken at stations 4, 8, and 9 with a Ponar dredge. Sediment samples were taken directly from the dredge by scooping with a glass jar. Sediment samples from the shallow stations at Nauvoo and Dallas City were scooped directly into glass jars, without using the dredge.

Sediment to be analyzed for pesticides was kept in a glass jar with an aluminum foil lined ^ccap. Sediment for metals analysis was placed in plastic bags.

At stations 4 and 8, fingernail clams, Musculium transversum, and two species of snails, Viviparus georgianus and Campeloma crassula, were separated from the mud by washing the mud through a 30-mesh screen with a 12-volt battery-operated water pump. Ponar samples repeatedly were taken and washed, until we had accumulated 25 g wet weight of each species for pesticide analysis and another 25 g for heavy metals analysis. Organisms for pesticides analysis were placed in aluminum foil, while those for metals analysis were placed in plastic bottles which had previously been rinsed with acid and distilled, deionized water. The Ponar dredge, screens, and washing equipment had all been in use since 1973, and we felt that contamination of the samples by the equipment was minimal.

At station 9 samples of Musculium transversum, Viviparus georgianus and Campeloma crassula were taken with the Ponar dredge and treated the same way as at stations 4 and 8. In addition, wild celery, Vallisneria americana, water star grass, Heteranthera dubia, and a snail which inhabited the plants, Helisoma trivolvis, were collected at station 9 by hand or with a garden rake after stopping the outboard motor and drifting into an area so as to avoid contaminating the plants with exhaust from the motor. Helisoma trivolvis, wild celery and water star grass were collected from plant beds below Nauvoo and at Dallas City by wading and picking. The samples were kept in foil or plastic bottles in the same manner as at the other stations. In the fall of 1978, wild celery could not be obtained at Dallas City, so coontail, Ceratophyllum demersum, was substituted. In addition, the aquatic vegetation

was so reduced that the plant-inhabiting snail, Helisoma trivolvis, could not be taken in sufficient quantity at station 9 and at Nauvoo so only Viviparus georgianus and Campeloma crassula were collected. In 1977 four replicate Ponar samples of mud were taken at station 9 and placed in glass jars in order to check the variability in metals analyses among samples taken from the same site on the same day.

All samples of sediment, plants and animals were placed on ice in a cooler and transported back to the laboratory where they were placed in the deep freeze. Our original schedule called for sampling in the fall of 1977 and the spring of 1978 during the waterfowl migrations. However, populations of fingernail clams declined during 1976 and 1977 and were exceptionally low in the spring of 1978 -- so low that it was impossible to obtain 25 g of fingernail clams at any of the stations. Also, no aquatic plants were available in the spring of 1978. Hence, the schedule was revised so that sampling was conducted in the fall of 1978, when aquatic plants were available and fingernail clam populations had begun a recovery.

Laboratory Methods -- Metals

All samples were kept frozen prior to freeze-drying. All samples were freeze-dried. The biological samples were pulverized prior to the removal of aliquots for weighing and analysis. The sediment samples were ground to pass a 30-mesh screen prior to removal of aliquots for analysis.

The biological samples were digested for all metals except mercury with a mixture of concentrated nitric and perchloric acids in kjeldhal flasks until the appearance of perchloric acid fumes. The solutions were centrifuged to remove insoluble silicates and diluted to volume with water in a 25-ml volumetric flask. They were then stored in plastic bottles until

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analysis. Separate aliquots of these samples were digested for mercury analysis with a mixture of concentrated sulfuric and nitric acids, potassium permanganate solution and potassium persulfate solution in a 95 C water bath with the addition of solid potassium permanganate until oxidation was complete, usually about four hours. This was signalled by no loss of the permanganate color for 30 minutes. These samples were diluted to volume with water in 100-ml volumetric flasks and analyzed the next day as described below.

The sediment samples were extracted for the analysis of all metals except mercury with a dilute (0.05N) solution of hydrochloric acid. This was done by shaking a 15-g aliquot of the sample with 30 ml of the acid for 30 minutes on a reciprocal shaker. The mixture was centrifuged and the centrifugate analyzed as below. Separate aliquots of the sediments were digested for mercury analysis by boiling with 10 ml of aqua regia followed by an acidic permanganate digestion similar to that described above. These solutions were diluted as previously described and analyzed the same day.

All metal analyses except mercury were made using an inductively coupled plasma source optical emission spectrometer (ICP-OES), a Jarrell-Ash Plasma Atomcomp Model 975. *No Ca, K, Mg work done on IL AA* Standards were prepared using high-purity metals and salts and were diluted in a matrix to match the samples. Mercury analyses were made on a Fisher Model HG-3 mercury analyzer connected to a digital integrator and a strip-chart recorder.

Laboratory Methods -- Pesticides

A frozen sample of snails, clams, sediment, or plants was weighed into a 250-ml erlenmeyer flask. The tissue of the snails and clams was not

separated from the shells, and the shells were included in the total weight. A small amount of Na_2SO_4 was added and the material was pulverized with a glass rod. One hundred ml of nanograde hexane was added to the flask and it was placed on a magnetic stirrer for two hours. The hexane solution was decanted through a funnel packed with Na_2SO_4 and the Na_2SO_4 was rinsed with an additional 100 ml of hexane. All rinsings were combined and this solution was condensed to about 5 ml on a steam bath under a Snyder column.

The extract was transferred to a previously standardized 30-gm florisil column and eluted with 90 ml of dry hexane followed by an elution with 150 ml of 10% ethyl ether in hexane. The resulting solutions were concentrated on a steam bath and placed in centrifuge tubes to await analysis.

Instrument conditions and column packing for the gas chromatography were as follows:

Instrument: Varian-Aerograph 2100 equipped with a 63 Ni electron capture detector.

Column: 6 ft x 4 mm ID glass.

Packing: 2.5% OV-210/1.5% OV-17 on 80/100 mesh chromosorb.

Temperatures: Column 180 C, Injector 220 C, Detector 250 C.

Carrier gas: Nitrogen.

Flow rate: 40 ml/min or adjusted for maximum response.

The detection limits for the pesticide analyses are given in Table 1.

Cross-Checks with Other Laboratories

Portions of samples which had been taken in the fall of 1977 from Keokuk Pool were sent to the Northern Prairie Wildlife Research Station, Jamestown, North Dakota to cross-check the metals analyses, and to Raltech Scientific Services, Incorporated, Madison, Wisconsin, to cross-check the

Table 1 . Pesticide Detection Limits (Illinois Natural History Survey).
All concentrations are ppb.

	Water Star		Coontail	Wild Celery	Snails	Fingernail Clams
	Sediment	Grass				
Aldrin	0.20	0.006	0.016	0.016	0.033	0.032
Dieldrin	0.05	0.011	0.040	0.040	0.083	0.080
Chlordane	0.60	0.090	0.048	0.048	0.100	0.100
DDT	2.00	0.033	0.160	0.160	0.333	0.320
DDE	5.00	0.211	0.40	0.400	0.833	0.800
Endrin	1.00	0.017	0.088	0.088	0.183	0.176
Lindane	0.200	0.004	0.021	0.021	0.043	0.050
Heptachlor	0.100	0.002	0.008	0.008	0.017	0.02
Heptachlor Epoxide	0.700	0.010	0.056	0.056	0.117	0.112
BHC	0.001	0.020	0.020	0.020	0.300	0.550
PCB	10.0	2.658	0.800	0.800	2.000	1.600

pesticide analyses performed by the Illinois Natural History Survey. The Northern Prairie Wildlife Research Station subsequently subcontracted to Dr. Munshower of Montana State University for the metal analyses. Portions of samples taken from Keokuk Pool in the fall of 1978 were sent to Raltech to cross-check the Illinois Natural History Survey pesticide analyses and to Analytical Bio Chemistry Laboratories, Incorporated, Columbia, Missouri, to cross-check metal analyses. The U.S. Fish and Wildlife Service project officer, the principal investigator, and chemists representing the U.S. Fish and Wildlife Service, Analytical Bio Chemistry Laboratories, and Illinois Natural History Survey met on 26 June 1979 in the Natural History Survey offices at Urbana to discuss the results of the cross-checks.

In 1977 the material sent to the cross-check laboratories consisted of acid digests of samples for metals analyses and portions of the whole frozen samples for pesticide analyses. In 1978, both extracts and portions of the freeze-dried samples were sent to Analytical Bio Chemistry Laboratories as a check on the comparability of both the digestion and analytical techniques used in metal analyses. Again, portions of the whole frozen samples were sent to Raltech to cross-check the Illinois Natural History Survey pesticide analyses.

RESULTS & DISCUSSION

Changes in Keokuk Pool between 1977 and 1978

A drought occurred in the upper Mississippi basin in 1976 and 1977. When the 1977 samples for contaminant analysis were taken, the fingernail clam populations had undergone a 60% reduction in numbers and the growth of the remaining clams had been retarded (Thompson and Sparks, 1977: 1).

Since industries and municipalities continued discharging the same amount of effluent, while the flow in the river was drastically reduced as a result of the drought, it is likely that many toxic materials were at higher concentrations than in preceding years or in 1978 when the flows returned to normal. It is possible that both toxicants which accumulate in fingernail clams and toxicants which act externally on fingernail clams were at higher concentrations during the drought years. For example, Thompson and Sparks (1977: 6) reported that ammonia levels at a water intake on Keokuk Pool were higher in 1976 than in 1973.

Since there was abnormally low rainfall in 1976 and 1977, soil erosion and runoff was sharply reduced, and the upper Mississippi River became quite clear. Secchi disk transparency in Keokuk Pool in May was 21 cm in 1975, 40 cm in 1976, and 80 cm in 1977. Because of the low stable flows and increased light penetration, aquatic plants in Keokuk Pool burgeoned. Large beds of wild celery appeared above the dam for the first time in the memory of many long-term residents of the area. One species of snail which inhabits aquatic plants, Helisoma trivolvis, became abundant in 1977. With the return to more normal water flow and turbidity in 1978, the beds of aquatic plants were reduced, as were the populations of Helisoma.

Paveglio and Steffeck (1978: 39) reported that the diving ducks utilizing Keokuk Pool apparently took advantage of the availability of plant material, such as the winter buds of wild celery, and the snails, Helisoma, which inhabited the plants. It is probably fortunate that the aquatic plants increased at the time the fingernail clam populations declined, or there might have been a serious shortage of food for diving ducks in the Keokuk Pool.

Possible relationships between the changes in the Keokuk Pool between 1977 and 1978 and the results obtained in this project will be discussed below.

Results of Cross-Checks and Replicate Sampling and Analyses

Table 2 shows the results of metal analyses from four replicate Ponar grab samples of sediment from station 9. These samples were taken with the boat anchored in one place in approximately 3½ feet of water. The boat generally swings in response to wind and current on its anchor rope, and it is highly unlikely that the three grabs came from exactly the same point on the bottom. Since this is the shallowest station sampled by boat, we expected the least amount of swinging around the anchor (because the anchor rope was shorter) and hence the least variation in positioning of the Ponar on the bottom. Each of the four grab samples was treated separately in the laboratory, and three aliquots were taken from the final extract of each, except where noted in the table. The values in the table are means and standard deviations of replicate aliquots from each grab sample. Note that for some elements which were near detection limits, such as cadmium, the standard deviation of the triplicate analyses was up to 50% of the mean. The mean values for the four grab samples were generally in close agreement, and only in the case of mercury were the four grab samples significantly different.

Tables 3, 4, and 5 compare the results of the 1977 cross-checks for metals between Dr. Munshower's laboratory at Montana State University (MSU) and the Illinois Natural History Survey (INHS) laboratory. In many cases, the mean values obtained by the two labs were significantly different, but the standard deviations as a percentage of the mean were similar. These results indicate that the repeatability of instrument readings within each

Table 2 . Concentrations of metals in 4 replicate grab samples of sediment from Station 9 of the Keokuk Pool of the Mississippi River taken in Fall 1977. All concentrations are μg per g (ppm) except for mercury concentrations which are μg per kg (ppb).

	1		2		3		4		F Ratio ^c
	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	
Ag	1.9	0.5	1.9	0.4	1.9	0.3	1.7	0.1	0.21
As	2.3	1.2	1.7	0.7	2.0	0.8	1.5	0.3	0.66
B	0.98	0.24	0.96	0.24	0.90	0.09	1.1	0.1	0.63
Ba	1.4	0.2	1.4	0.1	1.2	0.2	1.5	0.1	1.94
Be	<0.06		<0.06		<0.06		<0.06		
Cd	0.40	0.21	0.32	0.12	0.38	0.19	0.26	0.10	0.49
Co	2.2	0.6	2.0	0.4	2.1	0.3	2.2	0	0.26
Cr	0.93	0.43	0.77	0.35	0.91	0.30	0.65	0.08	0.52
Cu	0.86	0.32	0.64	0.23	0.77	0.19	0.65	0.08	0.68
Hg	93	19	132	6	80	10	94	4	7.28
Mo	<0.6		<0.6		0.46 ^a		<0.6		
Ni	1.5	0.5	1.5	0.3	1.6	0.3	1.4	0.1	0.88
Pb	3.3	2.0	2.6	1.7	4.0	0.9	2.1	0.4	0.61
Rb	<0.6		<0.6		<0.6		<0.6		
Sb	1.2 ^a		<1.2		<1.2		0.47 ^b	0.11	
Se	3.0	1.1	1.7	0.8	2.0	0.8	1.4	0.2	2.24
Sn	<2.4		5.1 ^a		<2.3		<2.4		
V	0.93	0.43	0.77	0.35	0.91	0.30	0.65	0.08	0.52
Zn	3.8	0.7	4.7	1.4	4.5	1.0	4.8	1.0	0.62

^aOnly 1 replicate represented.

^bOnly 2 replicates represented.

^cCritical value = 5.25

Table 3 . Comparison of 1977 cross-check sample results between Montana State University (MSU) and Illinois Natural History Survey (INHS) for Keokuk Pool Sample 23, Sediment-Station 9. All concentrations are mg/kg.

	MSU				INHS				Paired t		
	1&2	3&4	5&6	\bar{x}	σ	1&2	3&4	5&6		\bar{x}	σ
Ca	3,580	3,710	4,230	3,840	344	3,380	3,470	3,970	3,610	318	13.829 ^b
Mg	1,420	1,380	1,460	1,420	40	1,350	1,250	1,150	1,250	100	2.357
Na	107	94.0	92.5	97.8	8.0	13.0	12.0	12.1	12.4	0.6	19.31 ^b
K	21.3	-	21.9	21.7	0.3	43.8	41.9	43.2	43.0	1.0	-29.36 ^b
Ag	0.17	0.11	0.10	0.13	0.04	1.68	1.78	2.17	1.88	0.26	-10.51 ^b
Ba	<2.0	<2.0	<2.0	<2.0	-	0.6	0.5	0.6	0.6	0.1	-
Cd	0.21	0.20	0.22	0.21	0.01	0.69	0.63	0.72	0.68	0.05	-22.58 ^b
Cu	2.6	2.5	2.5	2.6	0.06	2.4	2.2	2.2	2.3	0.1	7.940 ^a
Fe	1,630	1,534	1,570	1,578	48	1,700	1,550	1,500	1,560	104	-0.131
Hg	0.007	0.005	0.004	0.005	0.002	0.185	0.170	0.173	0.176	0.008	-44.40 ^b
Mn	181	181	183	182	1	155	145	135	145	10	5.766 ^a
Ni	1.85	1.68	1.78	1.77	0.09	2.27	2.36	2.32	2.32	0.05	7.276 ^a
Pb	1.99	1.87	2.03	1.96	0.08	5.35	5.56	7.03	5.98	0.92	-8.080 ^a
Zn	11.3	11.0	11.5	11.3	0.3	10.9	11.6	11.6	11.4	0.4	-0.346

^aCritical value $t_2 = 4.303$ ($p < 0.05$).

^bCritical value $t_2 = 9.925$ ($p < 0.01$).

Table 4. Comparison of 1977 cross-check sample results between Montana State University (MSU) and Illinois Natural History Survey (INHS) for Keokuk Pool Sample 11, Water star grass - below Nauvoo. All concentrations are mg/kg.

	MSU					INHS					Paired t	
	\bar{x}	σ										
Ca	1,480	1,670	1,570	1,570	1,570	95	1,380	1,450	1,450	1,430	40	3.951 ^a
Mg	293	378	409	360	360	60	331	362	396	363	32	-0.131
Na	148	271	293	237	237	78	370	370	446	395	44	-4.439 ^a
K	888	1,600	1,670	1,386	1,386	433	724	869	1,140	911	211	2.862
Ag	0.09	0.09	0.08	0.09	0.09	0.01	0.48	0.92	0.80	0.73	0.23	-4.831 ^a
Ba	20.2	26.8	30.4	25.8	25.8	5.2	39.4	55.3	63.5	52.7	12.2	-6.588 ^a
Cd	0.15	0.22	0.13	0.17	0.17	0.05	0.05	0.43	0.13	0.20	0.20	-0.401
Cu	0.72	0.82	0.91	0.82	0.82	0.10	0.49	0.76	0.79	0.68	0.17	2.736
Fe	395	374	438	402	402	33	257	376	423	352	86	1.131
Hg	0.014	0.008	0.030	0.017	0.017	0.011	0.0008	0.014	0.012	0.012	0.012	0.866
Mn	1,460	1,380	1,610	1,480	1,480	117	837	1,180	1,380	1,130	272	2.576
Ni	0.54	0.81	0.98	0.78	0.78	0.22	0.76	1.32	1.48	1.19	0.38	-4.374 ^a
Pb	0.35	0.28	0.53	0.39	0.39	0.13	1.43	3.00	3.61	2.68	1.12	-3.780
Zn	3.58	4.20	5.57	4.45	4.45	1.02	2.69	5.16	6.64	4.83	2.00	-0.538

^aCritical value $t_2 = 4.303$ ($p < .05$).

Table 5. Comparison of 1977 cross-check sample results between Montana State University (MSU) and Illinois Natural History Survey (INHS) for Keokuk Pool Sample 39, Snails-Dallas City. All concentrations are mg/kg, except Ca which is in weight percent.

	MSU					INHS					Paired t
	\bar{x}	σ	\bar{z}	\bar{x}	σ	\bar{x}	σ	\bar{z}	\bar{x}	σ	
Ca	12.3%	11.8%	11.7%	11.9%	0.32%	11.5%	11.6%	11.3%	11.5%	0.15%	2.646
Mg	579	605	617	600	19	662	598	608	623	34	-0.736
Na	366	486	471	441	65	799	953	920	891	81	-45.39 ^b
K	67	89	84	80	12	1,680	1,410	1,110	1,400	285	-7.790 ^a
Ag	0.37	0.37	0.34	0.36	0.02	8.51	8.49	7.68	8.23	0.47	-29.87 ^b
Ba	15.3	27.2	28.4	23.8	7.4	22.7	23.9	19.4	22.0	2.3	0.372
Cd	0.67	0.22	0.19	0.36	0.27	1.37	0.84	0.85	1.02	0.43	-28.58 ^b
Cu	2.06	2.24	2.17	2.16	0.09	3.31	3.48	3.33	3.37	0.09	-42.32 ^b
Fe	327	372	328	342	26	343	394	339	359	31	-5.137 ^a
Hg	0.012	0.025	0.031	0.023	0.010	0.018	0.001	-	0.0095	0.012	0.600
Mn	167	158	126	150	22	172	160	134	156	19	-2.867
Ni	0.97	0.86	0.64	0.82	0.17	1.94	2.06	2.06	2.02	0.07	-9.211 ^a
Pb	0.96	1.03	0.88	0.96	0.08	13.5	14.6	14.3	14.1	0.60	-41.01 ^b
Zn	6.95	7.89	9.38	8.07	1.23	5.05	6.39	8.26	6.56	1.61	6.631 ^a

^aCritical value $t_2 = 4.303$ ($p < .05$).

^bCritical value $t_2 = 9.925$ ($p < .01$).

of the labs was similar. In general, INHS had higher values for metals than MSU.

The INHS values for mercury in sediments were higher those of MSU probably because an extraction was used on sediment samples for mercury analysis which decomposed mercury sulfide. This digest was separate from the dilute acid extraction used for other metals in sediments. Only the dilute acid extract was provided to MSU. Mercury analysis of the stronger digest provides a better indication of the total amount of mercury in the sediment. Analysis of the stronger digest probably provides a more realistic measure of the potential for contamination of the food chain from the sediment because all the mercury in the sediment eventually can be methylated, although the methylation may occur slowly.

The INHS values for potassium, silver, cadmium, and lead in sediment were much higher than the MSU values, while the INHS sodium values were much lower. Even though there were significant differences between MSU and INHS values for 5 other metals, according to a t test, the means were very close. For example, MSU obtained a mean of 2.6 mg/kg copper in sediment, while INHS obtained 2.3 mg/kg (Table 3). INHS obtained higher values for sodium, silver, barium, nickel, and lead in plants than MSU, and lower values for calcium, while the values for other metals in plants were not significantly different (Table 4). Nine of 14 values reported for metals in snails were significantly different between the two laboratories. INHS had higher values for sodium, potassium, silver, cadmium, nickel, and lead, and lower values for zinc and mercury.

It was the consensus of the chemists at the 26 June, 1979 meeting that the samples analyzed by Dr. Munshower at Montana State University had

been stored too long (8 months) for reliable comparison with the INHS data. Furthermore, since aliquots of a standard reference sample, or a sample spiked with known amounts of several metals had not been submitted to both laboratories, it was impossible to determine whether the MSU values were too low or the INHS values too high for the 1977 cross-checks.

The samples used in the 1978 cross-checks of metal analyses between Analytical Bio Chemistry Laboratories (ABC) in Columbia, Missouri and the Illinois Natural History Survey Laboratory (INHS) purposely were stored approximately the same length of time at both labs, to rule out differences in results due to differences in storage times. Table 6 shows that the sediment concentrations reported by ABC and INHS agreed closely. The INHS values for water star grass are close to, but generally higher than the ABC results. The INHS value for lead in water star grass was much higher (7.58 $\mu\text{g/g}$) than the ABC value (0.34 $\mu\text{g/g}$). The greatest differences between labs occur in results for fingernail clam extracts and whole fingernail clams. For example, the INHS chromium value for fingernail clam extract is 16 times greater than the ABC value. The ABC nickel value for whole fingernail clams is more than twice the INHS value. INHS values for whole fingernail clams were higher than ABC values for copper, cadmium, chromium, lead, and mercury, and lower for nickel and zinc. INHS values for extracts of fingernail clams were higher than ABC values for copper, cadmium, chromium, and zinc. ABC did not analyze clam extracts for lead, mercury, and nickel. The replicates analyzed by ABC (Table 6) show less variation than the results between labs, indicating real differences exist between the two laboratories that are greater than instrument reading errors.

Since no spiked samples were analyzed by both ABC and INHS, it is again

Table 6 • Comparison of 1978 cross-checks for trace metals. All concentrations are in $\mu\text{g/g}$ (ppm), except for mercury concentrations which are ppb. ABC = Analytical Bio Chemistry Laboratories. INHS = Illinois Natural History Survey.

Sediment (Extract) (46)	Water Star Grass (64) (Extract) Station 9		Fingernail Clams (42) (Extract) Station 4		Fingernail Clams (48) (Whole) Station 8				
	<u>ABC</u>	<u>INHS</u>	<u>Replicate 1</u> <u>ABC</u>	<u>Replicate 2</u> <u>INHS</u>	<u>ABC</u>	<u>INHS</u>	<u>ABC</u>	<u>INHS</u>	
Cu	0.40	0.33	1.46	1.76	2.56	2.14	5.34	3.46	4.40
Cd	0.20	0.16	0.06	0.11	0.69	0.08	0.91	0.15	0.73
Cr	0.40	0.57	1.61	2.31	3.77	0.16	2.62	0.29	2.12
Pb	0.60	0.35	NA	0.34	7.58	NA	12.4	2.29	10.3
Hg	NA ^a	337	NA	6.78	7.4	NA	29.6	7.41	23.3
Ni	3.39	2.66	NA	2.29	3.09	NA	1.56	2.87	1.22
Zn	8.56	8.19	12.96	9.61	12.2	4.95	8.27	8.50	7.17

^aNA = not analyzed.

impossible to determine whether INHS values were high or ABC values low. INHS values for whole clams were probably higher than ABC values because INHS used a stronger digestion, for a longer time, than ABC. This does not explain why INHS and ABC values differed for aliquots of the same extract. The different analytical instruments used at the two laboratories may have contributed to differences in results. INHS used a Fisher mercury analyzer for mercury and a Jarrell-Ash inductively coupled plasma source optical emission spectrometer for all other metals. ABC used an atomic absorption unit. The viscous perchloric acid provided by INHS may have caused some problems in sample nebulization by ABC. It seems unlikely that samples or aliquots of samples were heterogeneous enough to influence the results, at least to the extent observed in Table 6.

The chemists at the 26 June, 1979 meeting agreed that all three laboratories -- MSU, INHS, and ABC -- seemed to have internally consistent results (see Tables 2-5 and 6, which show results obtained on replicate samples within labs), and that the INHS data could be used to discuss relative differences in metal concentrations between sampling stations, sampling times, and between sediments and the different organisms. The INHS values for most of the toxic metals were consistently higher than values obtained at the other two laboratories. If INHS data actually were higher than the "real" values, use of INHS data in evaluating contaminant problems in Keokuk Pool would err on the side of safety, by over-estimating the potential hazard, rather than under-estimating. The chemists at the 26 June, 1979 meeting agreed that the INHS data should be interpreted and evaluated with these considerations in mind.

Table 7 shows that the results from Raltech and INHS for pesticides were in close agreement in both 1977 and 1978.

Metals

Table 8 compares the concentrations of metals in sediment along the main stem of the Mississippi River with samples from the Illinois River, Fox Lake, non-industrial streams in Illinois, and Lake Michigan. Concentrations of toxic metals in the sediments of Keokuk Pool were generally below those of the Illinois River, non-industrialized tributary streams of the Illinois River, the Fox Chain of Lakes, and even below concentrations found in the surficial sediments of Lake Michigan. Fingernail clams died out in the Illinois River in 1955 and have never recolonized. It is possible that there is a link between the relatively high concentrations of metals in the sediments of the Illinois and the die-off of fingernail clams.

Sediment concentrations of arsenic, boron, barium, cadmium, copper, molybdenum, lead, rubidium, and selenium in Keokuk Pool decreased substantially between 1977 and 1978. Silver, beryllium, chromium, antimony, and vanadium either changed very little or went up at some stations and down at others. Cobalt, mercury, nickel, tin, and zinc increased substantially from 1977 to 1978.

A comparison of sediment metal concentrations in Tables 8 and 9 shows no marked differences between the shallow plant beds (station 9, Dallas, Nauvoo) and the deeper main-channel stations (stations 4 and 8).

Table 10 shows that metal concentrations in water star grass and wild celery were greater in 1978 at the downstream station 9 than at the upstream stations at Nauvoo and Dallas City, with the exception of barium in both plants and mercury in water star grass. With the exception of nickel, metal

Table 7 . Comparison of 1977 and 1978 cross-check results between Raltech (RT) and Illinois Natural History Survey (INHS) for organics in sediment, plants, and snails from Keokuk Pool, Mississippi River. Concentrations are $\mu\text{g}/\text{kg}$ (ppb).^a

	Sediment		Water Star Grass		Snails		Fingernail Clams					
	Station 4	Station 9	Nauvoo(69)	Station 9	Station 9	Nauvoo(67)	Station 9 (83)					
	1977	1977	1978	1977	1977	1978	1978					
	RT	INHS	RT	INHS	RT	INHS	RT	INHS				
Aldrin	nd ^b	nd	nd	nd	nd	nd	nd	nd				
Dieldrin	nd	0.4	nd	1.1	nd	1.2	3.4	nd	1.9	nd	0.3	
Chlordane	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
DDT	nd	nd	nd	6.8	nd	nd	nd	nd	5	5.8	nd	nd
DDE	nd	nd	nd	0.7	nd	nd	nd	nd	25	30.3	nd	11.9
Endrin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Lindane	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor Epoxide	nd	4.8	nd	1.1	nd	1.0	4.2	nd	nd	nd	nd	0.8
BHC	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCBs	nd	3.4	nd	23.0	nd	nd	185	nd	nd	nd	nd	14.5

^a Raltech detection limits were 5 ppb for chlorinated insecticides and 10 ppb for PCBs and toxaphene. INHS detection limits are given in Table 1.

^b nd = not detectable.

Table 8 . Comparison of Metal Concentrations ($\mu\text{g/g=ppm}$) in Sediment.

	Keokuk Pool, Mississippi River ^f										Non- industrial streaming, Ill.	L.Mich. ^d	
	Station 9		Station 8		Station 4		Ill.R. ^a		Ill.R. ^b				Fox L. ^c
	1977	1978	1977	1978	1977	1978	1977	1978	1977	1978			
Ag	2.1	2.36	2.8	1.89	1.9	2.02							
As	2.5	0.653	2.9	<0.28	1.4	0.015			11.9				15.00-25.0
B	0.9	<0.10	0.40	<0.10	1.2	<0.10			35.8	21			10.00-70.0
Ba	1.4	0.805	2.3	0.874	1.4	0.921							
Be	<0.06	<0.020	<0.06	0.037	<0.06	0.042			2.70	<1			0.50-3.0
Cd	0.40	0.298	0.40	0.011	0.32	0.162	2.0		8.8	<0.9	0.4		
Co	2.5	4.94	1.3	3.76	2.4	6.05	6		12.1	<3.6	6		6.00-24.0
Cr	0.9	1.05	1.3	0.277	0.71	0.573	17		158.3		6		20.00-120.0
Cu	0.67	0.421	0.79	0.231	0.57	0.326	19		61.4	19.8	7.7		20.0-100.0
Hg ^e	179	378	263	308	150	337			250				50-400
Mo	0.40	0.258	0.60	0.044	<0.6	0.155				<2.9			
Ni	1.7	1.92	1.5	1.64	1.6	2.66	27		56.3	20.7	16		20.0-60.0
Pb	3.2	1.57	4.5	<0.52	2.2	0.345	28		146.4	37	17		25.00-175.0
Rb	<0.6	0.01	<0.6	0.01	<0.6	0.02							
Sb	<1.2	2.09	0.9	<1.0	<1.1	<1.0							
Se	2.1	0.325	2.7	<0.40	1.3	<0.40							
Sn	1.0	6.15	0.89	<4.6	2.2	<4.6							
V	0.87	1.06	1.1	0.494	0.63	0.819	81		82.9	31	30		20.0-80.0
Zn	3.7	6.66	1.4	5.75	4.6	8.19	81		448	81.7			75.00-400.0

^aMathis and Cummings, 1973: 1574.^bCollinson and Shimp, 1972: 15. Samples from main channel of Peoria Lake, Illinois River.^cKothandaraman et al., 1977: 26. Fox Lake is one of the chain of lakes in the Fox River system in Illinois.^dCollinson and Shimp, 1972: 16.^eppb.^fKeokuk data are means from 3 aliquots of the same extract.

Table 9 . Metal Concentrations^a ($\mu\text{g/g}=\text{ppm}$), Keokuk Pool Sediment, 1978.

	<u>Dallas City</u>	<u>Nauvoo</u>
Ag	2.23	2.31
As	0.971	0.268
B	<0.10	<0.10
Ba	0.555	0.541
Be	<0.020	<0.020
Cd	0.141	0.061
Co	5.24	3.40
Cr	0.767	0.622
Cu	0.412	0.330
Hg ^b	234	570
Mo	0.225	<0.16
Ni	1.98	1.54
Pb	0.909	0.582
Rb	0.01	0.01
Sb	1.52	0.946
Se	0.406	0.142
Sn	7.69	4.93
V	0.568	0.775
Zn	6.04	3.42

^aMeans from 3 aliquots of the same extract.

^bppb.

Table 10 . Metal Concentrations^a ($\mu\text{g/g-ppm}$), Keokuk Pool.

	Water Star Grass, <i>Heteranthera dubia</i>				Wild Celery, <i>Vallisneria americana</i>				Coontail, <i>Ceratophyllum demersum</i>		
	Dallas City		Nauvoo		Station 9		Nauvoo		Station 9		Dallas City
	1977	1978	1977	1978	1977	1978	1977	1978	1977	1978	1978
Ag	0.68	0.89	0.73	1.21	0.70	1.00	1.2	1.35 \uparrow	0.94	1.48	1.36
As	6.5	11.4	5.8	6.93	4.2	29.8	26	7.77 \downarrow	8.3	16.8	23.7
B	1.8	4.81	2.1	3.03	1.3	7.38	6.6	4.26 \downarrow	2.1	5.04	12.5
Ba	19	45.5	5.3	61.7	8.0	38.0	50	70.6 \uparrow	22	41.8	86.8
Be	0.02	0.044	0.02	0.023	0.02	0.123	0.08	0.020 \uparrow	0.02	0.069	0.092
Cd	0.37	0.297	0.20	0.254	0.43	0.686	1.0	0.242 \downarrow	0.41	0.476	0.640
Co	2.3	6.67	2.5	4.35	1.8	14.2	9.8	7.03 \downarrow	3.3	8.69	13.1
Cr	1.1	1.84	0.60	1.21	0.88	3.77	3.3	1.26 \downarrow	1.3	2.79	3.09
Cu	1.2	1.58	0.68	1.01	1.0	2.56	2.4	1.25 \downarrow	1.5	2.11	2.58
Hg ^b	8.0	33.5	12	19.8	3.5	7.4	17.7	30.1	9.0	50.0	8.7
Mo	0.63	0.562	0.71	0.499	0.57	0.997	1.9	0.509 \downarrow	0.74	0.751	1.00
Ni	1.8	1.67	1.2	2.12	1.8	3.09	2.8	1.83 \downarrow	3.1	2.73	4.44
Pb	3.2	3.64	2.7	3.56	3.9	7.58	11	3.00 \downarrow	4.3	5.01	7.66
Rb	0.96	1.91	2.8	1.61	0.9	3.72	2.3	2.57 \uparrow	1.5	5.06	3.19
Sb	1.0	4.89	0.67	3.46	1.0	11.6	3.3	2.78 \uparrow	1.4	7.19	10.6
Se	2.4	2.17	2.4	1.80	2.2	4.86	7.6	1.59 \downarrow	3.3	3.01	4.62
Sn	1.0	35.7	1.0	23.1	1.0	94.8	3.3	21.6 \uparrow	1.3	52.3	74.4
V	1.8	3.11	1.2	1.75	1.2	7.18	4.8	1.87 \downarrow	2.1	4.46	5.77
Zn	5.2	6.96	4.8	5.75	3.4	12.2	16	4.19 \downarrow	3.7	7.78	13.5

^aMeans from 3 aliquots of the same extract.^bppb.

concentrations in wild celery were higher at the upstream station at Nauvoo in 1977 than at downstream station 9. Although several metals in water star grass occurred at lower levels in station 9 in 1977 than at the upstream station, the differences are not as pronounced as in the wild celery. With the exception of cobalt, nickel, selenium, mercury, and tin the sediments in 1978 at station 9 contained higher levels of metals than at Dallas City and Nauvoo. It is possible that the water star grass and wild celery accumulate metals in proportion to what is available in the sediment. There appeared to be little difference among species of plants in metal accumulation.

Table 11 shows that metals in fingernail clams declined between 1977 and 1978 with the following exceptions: rubidium at stations 8 and 4, mercury at station 4, antimony at all stations, and tin at all stations. In the fall of 1977, when the body burdens of metals in the clams were high (in comparison to the fall of 1978), the numbers of fingernail clams had declined, in comparison to 1975 (Thompson and Sparks, 1977: 1). Not only did the number of clams decline during the period 1976-77, but the growth of the survivors was reduced. In 1976, the maximum shell length was only 8.3 mm as compared to 12.4 mm in both 1974 and 1975 (Thompson and Sparks, 1977: 5). Fingernail clams begin to reproduce when they reach about 5 mm in shell length (Gale, 1969). In 1974 and 1975, the reproductive population was reduced to less than 1,000 per square meter (Thompson and Sparks, 1977: 5).

There may be a link between the 1976-77 drought in the upper Mississippi basin, the body burdens of metals in the clams, and the 60% decline in numbers of fingernail clams between 1975 and 1976-1977. While the body

Table 11. Comparison of Metal Concentrations ($\mu\text{g./g}=\text{ppm}$) in Fingernail Clams.

	Keokuk Pool, Mississippi River ^a						Fox R. ^b
	Station 4		Station 8		Station 9		
	1977	1978	1977	1978	1977	1978	
Ag	10	4.93	14	4.37	17	5.25	
As	15	10.5	12	6.05	9.6	5.72	
B	2.3	2.7	1.1	1.58	2.2	1.48	
Ba	32	13.6	18	5.88	21	4.46	
Be	0.13	0.066	0.06	0.050	0.06	0.057	
Cd	1.4	0.907	1.0	0.732	0.56	0.860	1.99
Co	6.8	4.58	3.7	2.36	4.5	2.14	
Cr	3.4	2.62	3.5	2.12	3.4	2.36	
Cu	8.4	5.34	9.4	4.40	7.9	3.70	10.06
Hg ^c	15.6	29.6	50.8	23.3	4,259	28.0	
Mo	1.4	0.857	1.0	0.653	<2	0.740	
Ni	2.2	1.56	1.7	1.22	1.1	1.40	
Pb	14	12.4	12	10.3	10	12.6	32.18
Rb	5.9	7.8	5.2	5.4	5.6	5.3	
Sb	4.6	14.7	3.7	11.7	2.8	13.8	
Se	5.9	3.78	5.0	2.78	<8	3.17	
Sn	4.9	65.9	8	50.6	<8	57.9	
V	5.5	3.07	4.6	2.20	4.5	2.34	
Zn	14	8.27	14	7.17	15	5.70	61.07

^aFingernail clams were Musculium transversum. Tabled values are means of 2 aliquots from the same sample.

^bAnderson, 1977: 348. Fingernail clams identified to genus Sphaerium.

^cppb.

burdens of metals in the clams may not have been high enough to harm the clams directly, it is possible that the clams were sensitized to other stresses such as increased ammonia concentrations and oxygen stratification in Pool 19 (Anderson et al., 1978: 79). The return to more normal flows in the upper Mississippi in the spring of 1978, the decreasing body burdens of metals in clams in Pool 19, and the recovery of the clam populations similarly may be linked.

Concentrations of cadmium, copper, lead, and zinc were much lower in fingernail clams from Keokuk Pool than in fingernail clams from the Fox River (Table 11). The body burden of silver in fingernail clams and snails in the Keokuk Pool (up to 20 ppm, see Tables 11 and 12) seems surprisingly high. However, the INHS values for silver were consistently higher than the values obtained by another laboratory (MSU), and need to be confirmed before one can conclude that silver may be a significant contaminant in Keokuk Pool. Silver is known to be orders of magnitude more toxic to fish than lead. We were not able to locate any published information on the toxicity of silver to fingernail clams or on body burdens of silver in clams or snails in other rivers.

Tin concentrations in fingernail clams increased by an order of magnitude between 1977 and 1978 in Keokuk Pool (from less than 10 ppm to 50-100 ppm). We have no explanation for this large increase, and we could find no published information on tin toxicity to molluscs, or tin levels in molluscs. Biesinger and Christensen (1972: 1691) reported that .35 ppm tin in Lake Superior Water caused a 16 percent decrease in the number of young produced by Daphnia magna. In terms of reproductive impairment of Daphnia, tin was more toxic than arsenic. The extremely high mercury concentration of 4,259 ppb at station 9 in 1977 appears anomalous because it is so much higher than the other stations and the

same station in 1978.

Table 12 shows that metal concentrations in snails followed the same pattern as in fingernail clams, i.e. much lower in 1978 than 1977. Exceptions to the general rule were: mercury, rubidium, tin, and antimony. Results for lead, cobalt, and boron in both snails and clams were mixed: the concentrations at different sampling stations increased, decreased, or remained the same between 1977 and 1978. As in fingernail clams, the silver concentrations in snails appear surprisingly high. Tables 11 and 12 show that concentrations of zinc in clams and snails were considerably higher in the Fox River than in the Mississippi, while concentrations of cadmium and copper were almost the same. Concentrations of lead in fingernail clams were approximately 3 times higher in the Fox River than in the Mississippi, while lead in snails was practically the same in the two rivers.

There did not seem to be a pronounced upstream-downstream trend in metal concentrations in the fingernail clams or snails within the study reach of Keokuk Pool. Nor did any one station stand out as a "hot spot".

Organics

Table 13 shows that at stations where samples were taken in both 1977 and 1978 the concentration of dieldrin in sediment increased from 1977 to 1978, while heptachlor epoxide showed decreases at 2 stations and an increase at station 8. Tables 14 and 15 show that dieldrin apparently did not accumulate in plants or mollusks to levels much greater than in the sediments. In contrast, PCBs occurred at much higher levels in water star grass (10 to 20 times) than in the sediments and in 1977 PCB levels

Table 12 . Comparison of Metal Concentrations ($\mu\text{g}/\text{g}=\text{ppm}$) in Snails.

	Keokuk Pool, Mississippi River ^a							
	Station 4		Station 8		Station 9		Fox R. ^b	Jubilee Creek ^c
	1977	1978	1977	1978	1977	1978		
Ag	18	6.00	20	6.54	18	6.15		
As	23	12.6	18	14.3	18	10.2		
B	4.9	4.64	2.6	5.46	5.2	4.88		
Ba	65	25.1	44	39.4	82	22.5		
Be	0.15	0.080	0.12	0.088	0.10	0.071		
Cd	1.8	1.07	1.5	1.20	1.8	0.962	1.76	
Co	9.2	6.74	6.8	9.17	12	5.87		
Cr	6.5	3.38	5.0	3.81	4.4	3.29		
Cu	22	13.6	18	15.0	16	9.98	18.37	
Hg ^d	21	38.3	44.5	40.6	7.3	37.2		
Mo	2.3	1.24	2.0	1.35	1.1	1.10		
Ni	3.4	1.94	2.5	2.23	6.6	1.73		
Pb	22	17.6	16	19.0	16	16.0	21.79	13.64
Rb	8.6	11	8.4	12	7.9	10		
Sb	6.4	20.5	4.8	22.7	4.5	18.8		
Se	9.9	5.13	7.5	5.71	7.0	4.72		
Sn	6.5	94.6	<8	104	<7	85.4		
V	7.8	3.7	6.4	4.24	6.8	3.16		
Zn	28	21.4	27	21.0	19	20.6	99.58	

^aSnails were a mixture of Campeloma crassula and Viviparus georgianus. Tabled values are means of 2 aliquots from the same sample.

^bAnderson, 1977: 348. Snails identified to genus Campeloma.

^cEnk and Mathis, 1977: 157. Snails identified to genus Physa.

^dppb.

Table 13 . Concentrations of pesticide residues found in sediment samples collected from the Keokuk Pool of the Mississippi River in Fall 1977 and Fall 1978. The symbol "nd" means "below the detection limits" (see Table 1 for detection limits). All concentrations are $\mu\text{g per kg}$ (ppb).

	Dallas		Station 4		Station 8		Station 9	
	City	Nauvoo						
	1978	1978	1977	1978	1977	1978	1977	1978
Aldrin	nd	nd	nd	nd	nd	nd	nd	nd
Dieldrin	4.2	18.4	0.4	6.0	0.2	1.5	3.2	5.4
Chlordane	nd	nd	nd	nd	nd	nd	nd	nd
DDT	nd	nd	nd	nd	0.1	nd	nd	nd
DDE	nd	nd	nd	nd	0.2	nd	nd	nd
Endrin	nd	nd	nd	nd	nd	nd	nd	nd
Lindane	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor Epoxide	6.4	4.3	4.8	2.4	0.4	1.2	2.7	2.4
BHC	nd	nd	nd	nd	nd	nd	nd	nd
PCBs	nd	nd	3.4	nd	1.7	nd	2.5	nd

Table 14 . Concentrations of pesticide residues found in plant samples collected from the Keokuk Pool of the Mississippi River in Fall 1977 and Fall 1978. The symbol "nd" means "below the detection limits" (see Table 1 for detection limits). All concentrations are in $\mu\text{g per kg}$ (ppb).

	Wild Celery				Coontail				Water Star Grass			
	Nauvoo		Station 9		Dallas City		Dallas City		Nauvoo		Station 9	
	1977	1978	1977	1978	1978	1978	1977	1978	1977	1978	1977	1978
Aldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dieldrin	1.9	0.14	1.8	0.9	nd	nd	3.4	1.3	0.5	1.2	1.1	2.0
Chlordane	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
DDT	nd	nd	nd	nd	nd	nd	nd	nd	0.8	nd	6.8	nd
DDE	nd	nd	nd	nd	nd	nd	6.6	nd	nd	nd	0.7	nd
Endrin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Lindane	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor Epoxide	2.0	nd	1.8	nd	nd	nd	14.0	0.8	1.2	1.0	1.1	1.3
BHC	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCBs	9.4	nd	9.3	nd	nd	nd	36.7	8.0	62.2	nd	23.0	10.0

Table 15. Concentration of pesticide residues in mollusks from the Keokuk Pool, Mississippi River. The symbol "nd" means "below the detection limits listed in Table 1". All concentrations are µg/kg (ppb).

	Snails, <i>Helisoma trivolvis</i>			Snails, Mixture of <i>Cameloma crassula</i> and <i>Viviparus georgianus</i>			Fingernail Clams, <i>Musculium transversum</i>										
	Dallas City		Station 9	Station 4		Station 4	Station 8		Station 4	Station 8							
	1977	1978	1977	1978	1977	1978	1977	1978	1977	1978	1977	1978					
Aldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd					
Dieldrin	2.8	0.6	0.54	1.3	1.9	0.6	1.1	2.4	2.7	3.4	0.5	2.3	0.4	8.7	0.7	8.8	0.3
Chlordane	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
DDT	nd	nd	nd	nd	5.8	nd	1.3	nd	3.0	nd	nd	nd	nd	nd	nd	nd	nd
DDE	nd	0.6	nd	nd	30.3	nd	9.1	nd	5.8	nd	2.9	nd	nd	nd	nd	nd	11.9
Endrin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Lindane	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor Epoxide	2.4	0.95	0.56	2.9	nd	2.0	0.55	5.1	1.4	4.2	5.0	3.0	0.4	15.5	0.5	12.2	0.8
BHC	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB's	17.5	nd	24.7	25.6	nd	248	2.6	167	nd	185	50.7	52.0	27.5	316	27.9	927	14.5

in snails and fingernail clams were 1 hundredfold to several hundredfold greater than in the sediments. In most laboratory studies of bioaccumulation, the organisms are exposed to PCBs in water, rather than in sediment. Lowe et al. (1972) report, for example, that the American oyster, Crassostrea virginica, concentrates PCBs from water by a factor of 101,000. Munson et al. (1976: 223) report that "shellfish" (authors did not identify the organisms) concentrated PCBs by a factor of 4,000 above what was found on suspended sediment (including phytoplankton) in the water column. Almost 1 part per million PCBs was found in fingernail clams at station 9 in 1977. The PCB concentrations in 1977 in clams at upstream stations 8 and 4 were lower. A level of nearly 1 ppm is extremely high for a short-lived organism such as the fingernail clam, which has only one year in which to accumulate contaminants. PCB levels were also quite high in snails in 1977. Munson et al. (1976: 222) reported that the total PCB concentration in unidentified shellfish from Chesapeake Bay was .052 ppm (wet weight-- authors did not specify whether shells were removed). McDermott et al. (1976: 215) in a study of PCB contamination of southern California marine organisms, found concentrations of .4 ppm (wet weight, without shells) in intertidal mussels, Mytilus californianus, purposely exposed to a sewage outfall for 13 weeks, and .8 to 1.3 ppm PCBs (wet weight, without shells) in harbor mussels (Mytilus edulis) near commercial docks. Both these species live many years and were either living in water or placed in water known to be contaminated with 1 to 4 parts per trillion PCBs. The high PCB levels in the fingernail clams in Keokuk Pool may have interacted with the relatively higher body burdens of toxic metals in 1977 to make the clams more sensitive to other stresses such as ammonia.

In summary, concentrations of toxic metals and organics in the sediments of Keokuk Pool are generally low. The metals in the sediments of the Pool, in particular, are lower than in polluted streams, such as the Illinois River, and even lower than in non-industrialized streams and in the surficial sediments of Lake Michigan. In general, concentrations of metals and organics decreased between 1977 and 1978 in plants, snails, and fingernail clams in the Pool. This decline occurred at the same time as a drought and record low flows ended in the upper Mississippi during 1978. Without further evidence or studies, it is difficult to determine whether the return to normal flows and the reduction in body burdens of toxics was coincidental or causal. Except fo PCBs, which generally increased in fingernail clams and snails in the downstream direction in 1977, there did not seem to be a pronounced upstream-downstream trend in contaminant concentrations within the study reach of Keokuk Pool. The high levels of PCBs (almost 1 part per million) in fingernail clams in 1977 and the surprisingly high levels of silver and tin in both clams and snails seem worthy of additional investigation with both laboratory and field studies. The amount of silver in snails and clams should be verified by another laboratory. Laboratory studies should examine the effects of body burdens of PCBs and metals in sensitizing mollusks to other stresses, such as increased ammonia or lowered dissolved oxygen levels. Laboratory studies could also determine whether fingernail clams and snails acquire contaminants from water, sediment, food particles, or from all three sources.

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