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ACCUMULATION OF SELECTED ELEMENTS (AS, CU, HG, PB, SE, ZN) BY NORTHERN PIKE (*ESOX LUCIUS*) REARED IN SURFACE COAL MINE DECANT WATER

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Abstract --The average mercury concentration in northern pike (*Esox lucius*) reared in decant water from a surface coal mine at West Decker, Montana, increased from 0.00 to 0.13 µg Hg/g wet tissue from 5 May to 7 October, 1977. This rate of mercury uptake is only slightly faster than that experienced by northern pike in the Tongue River Reservoir. Pike reared in mine water did not accumulate arsenic, copper, lead, selenium, or zinc. We conclude that coal mining at West Decker is not currently causing the dissolution of harmful concentrations of these elements and that the high concentrations of mercury present in adult northern pike from the Tongue River Reservoir are not attributable to coal mining activity.

The Tongue River Reservoir, located in southeastern Montana, lies in that portion of the Northern Great Plains which is undergoing extensive and expanding surface mining for coal. Preliminary studies of the influences of coal mining at Decker, Montana, have shown that ground and groundwater disturbances associated with coal mining enhance mineralization processes and thereby increase the rates of dissolution of many ionic substances to natural waters [20]. Discharge waters from the West Decker mine have been shown to contain higher concentrations of sodium, chloride, fluoride, silicon, carbonate and bicarbonate than Tongue River or Tongue River Reservoir water [21]. In addition, one study suggests that mine water is enriched in mercury [5].

Older individuals of most gamefishes from the Tongue River Reservoir contain mercury concentration in edible portions that exceed the U.S. Food and Drug Administration recommendations (0.5 µg Hg/g) for safe human consumption [11]. However, the major source(s) of mercury to the reservoir have not been identified. This study was conducted to assess the impact of mining at West Decker on the dissolution of mercury and several other toxic elements to the Tongue River. To do this, we measured the accumulation of mercury, arsenic, copper, lead, selenium and zinc in northern pike (*Esox lucius*) reared in mine decant water. Measuring tissue residues in fish rather than monitoring concentrations of these elements in water has the advantage of representing the entire exposure history of the organisms; water

monitoring programs often fail to reflect periods of fluctuating conditions.

METHODS AND MATERIALS

Mine settling pond

Water discharged from the mining operation at West Decker, Montana, originates from surface runoff and from groundwater seeping into the mine pit. From the onset of mining in 1972 through April 1978, water collecting in the base of the mine was pumped to a settling pond for clarification and then discharged to the Tongue River flood plain just upriver from the Tongue River Reservoir. We stocked northern pike fry in the settling pond on 5 May 1977; pike were collected for subsequent tissue residue analyses on 9 June, 10 July and 7 October 1977. Fish weights were recorded at the time of capture.

Pike spawning marsh

As part of a U.S. Fish and Wildlife Service enhancement project, a northern pike spawning and rearing marsh was constructed adjacent to the upstream end of the Tongue River Reservoir in the fall of 1977. Beginning in the spring of 1978, water collecting in the bottom of a previously mined pit and water from a well located near the edge of the mine were pumped into the marsh. Northern pike fry were stocked in the marsh on 24 April; tissue concentrations of the various elements and fish weights were determined for the initial fry and for pike collected on 24 April, 28 May, 27 June, 10 July, 31 July, and 29 August 1978.

Heavy rains throughout May 1978 caused the Tongue River to exceed its 100-year flood stage. During the flood, river water spilled into the marsh resulting in an estimated ten-fold dilution of mine water. Thus, over most of the study period, the observations of metals uptake by pike in the marsh were conducted in water that originated primarily from the Tongue River.

Analytical

Mercury concentrations were measured in muscle tissue samples from all settling pond fish and from marsh fish collected during the second through fourth sampling periods. Mercury analyses were also performed on whole fish homogenates from marsh pike collected on the first, third and all remaining sampling dates. A comparison of whole fish mercury content vs. muscle mercury content of the same fish (from the marsh) confirmed that little difference existed between the two; for the seven fish analyzed, muscle mercury content was 109, 115, 79, 100, 102, 115 and 93% (mean=102%; SD=13%) of the mercury content of whole fish. Thus, it is reasonable to compare the mercury content of fish sampled at the various dates regardless of the type of sample analyzed. Other elements, including arsenic, selenium, lead, zinc and copper, were determined from whole fish

homogenates. Tissue homogenates were prepared in a high speed blender. Whole frozen fish were blended with a few grams of dry ice to form a frozen powder; samples were then warmed to room temperature resulting in a homogenous paste. Aliquots of the paste were analyzed for the respective elements.

Mercury was determined by atomic absorption spectrophotometry using a carbon rod atomizer [16]. Arsenic and selenium concentrations were determined by hydride generation from a ternary acid (nitric, perchloric and sulfuric) digest [14, 15]. Samples to be analyzed for copper, zinc and lead were digested in concentrated nitric acid; the resulting solutions were analyzed for copper and zinc by flame atomic absorption spectrophotometry and for lead using the carbon rod atomizer.

RESULTS AND DISCUSSION

The total quantity of mercury present in northern pike reared in the mine settling pond increased throughout the exposure period (Figure 1). Pike averaged 0.13 µg Hg/g and 310 mm total length after five months residence. According to the regressions of mercury concentration in muscle tissue vs. total length, derived for northern pike from the Tongue River Reservoir [12], male and female pike in the reservoir attained 0.13 µg Hg/g at 409 and 362 mm total length respectively. Thus, pike in the reservoir must grow to a larger size before they attain the same mercury concentration as pike in the settling pond.

The total quantity of mercury present in fish reared in the spawning marsh also increased with time; but the concentration of mercury in the tissue increased for one month then decreased (Figure 2). This decrease in mercury concentration is probably due to the dilution of mine water that occurred during the May flood. A comparison of the mercury uptake patterns of pike in the settling pond (pure mine water) and spawning marsh (diluted mine water) is instructive; the dilution that occurred in the marsh during the flood was enough to curtail mercury uptake by the fish.

The concentrations of selenium, arsenic, lead, zinc and copper in pike reared in both the mine settling pond and spawning marsh (Table 1) were relatively low; further, the concentrations of these metals tended to decrease with time. The selenium concentrations were similar to or lower than the average concentrations of selenium found in freshwater fishes during surveys in New York state [8], Canada [2], and Finland [13]. The mean arsenic concentrations were lower than those found in surveys of fishes from New York lakes [10, 18] and the southeastern United States [4]. The lead concentrations found were similar to those of fish collected from uncontaminated areas [1, 7, 9, 17] and zinc levels fell within the range of concentrations observed during a number of surveys of freshwater fishes [3, 6, 17, 19]; copper concentrations were also low relative to those reported elsewhere [3, 6, 17].

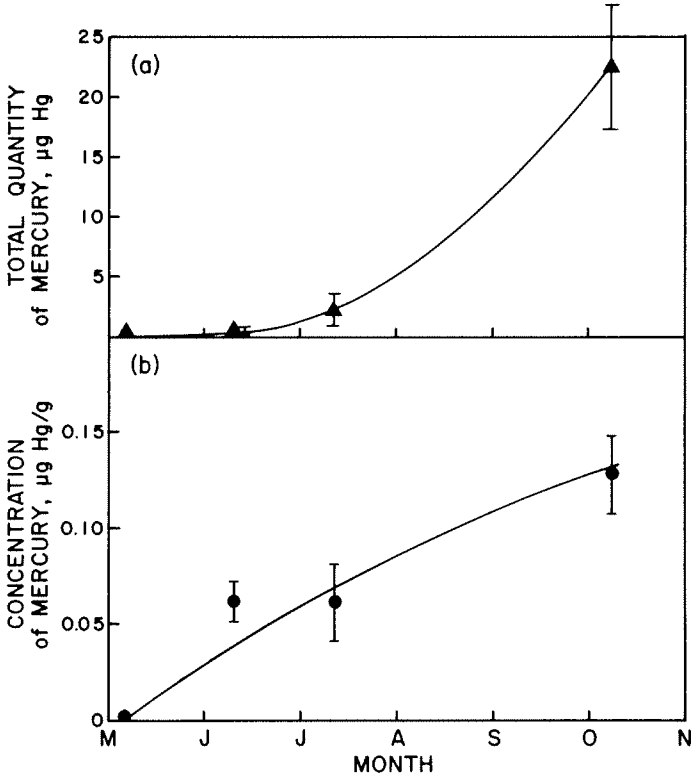

Figure 1. The relationship between the amount of time northern pike were held in Decker mine settling pond water and: (a) the total quantity of mercury they accumulated (estimated by multiplying their body weight by the mercury concentration present in their muscle tissue) (b) the mercury concentration in their muscle tissue. Curves fitted by inspection; intervals are 95% confidence limits ($\bar{x} \pm t_{0.025}\frac{s}{\sqrt{n}}$).

Considering that the discharge at West Decker is diluted on the average 2000-fold when it enters the Tongue River [21], it appears unlikely that mining at West Decker is contributing to the high levels of mercury observed in some Tongue River Reservoir fishes [11]. Moreover, selenium, arsenic, lead, zinc and copper did not concentrate in whole fish reared in mine water. We conclude that the mining operation at West Decker, Montana, is not currently causing the dissolution of harmful concentrations of these elements.

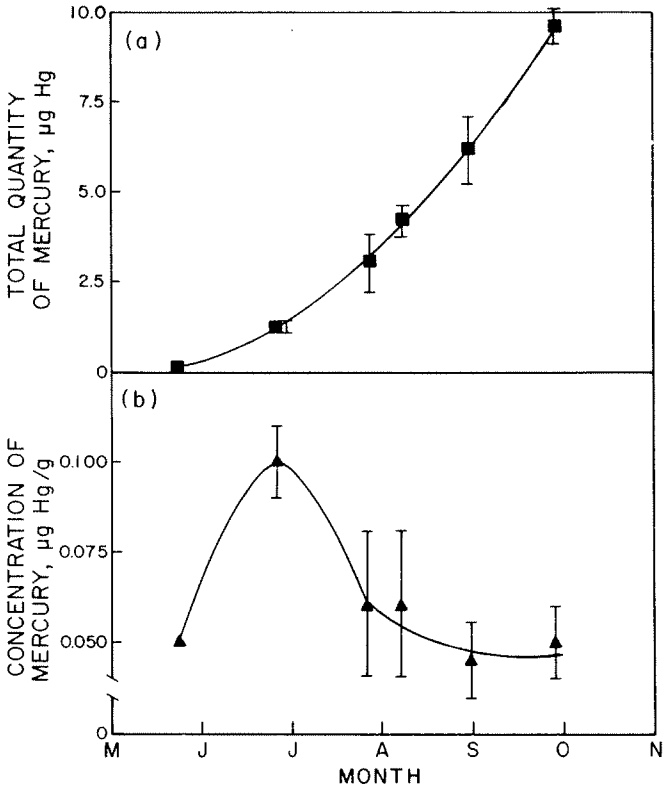

Figure 2. The relationship between the amount of time northern pike were held in Decker mine spawning marsh water and: (a) the total quantity of mercury they accumulated (estimated by multiplying their body weight by the mercury concentration present in their muscle tissue) (b) the mercury concentration in their muscle tissue. Curves fitted by inspection; intervals are 95% confidence limits ($\bar{x} \pm t_{0.025}\frac{s}{\sqrt{n}}$).

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Table 1. Concentrations of selected metals in whole northern pike collected from the Decker mine settling pond or northern pike spawning marsh. Fish were planted in the pond on 5 May 1977 and in the marsh on 23 May 1978. Values are means ± SD; ranges in parentheses.

Location	Exposure interval (d)	Sample size	Metal concentration (µg/g wet fish)				
			As	Se	Pb	Cu	Zn
Pond	35	5	0.17±0.04 (0.11-0.22)	0.42±0.06 (0.37-0.52)	0.29±0.14 (0.17-0.50)	2.5±0.4 (1.9-3.0)	32.9±7.5 (24.8-44.9)
	155	5	0.05±0.00 (0.04-0.05)	0.30±0.01 (0.28-0.31)	0.09±0.02 (0.07-0.11)	1.0±0.2 (0.7-1.2)	29.5±2.5 (26.5-33.1)
Marsh	34	5	0.08±0.02 (0.05-0.10)	0.63±0.08 (0.54-0.73)	0.92±0.64 (0.24-1.86)	-	47.6±7.6 (39.7-60.1)
	77	3	-	-	-	1.2±0.8 (0.7-2.2)	-
	127	15	0.04±0.01 (0.01-0.05)	0.55±0.05 (0.48-0.64)	0.22±0.10 (0.09-0.43)	1.0±0.2 (0.7-1.6)	36.1±4.2 (25.1-43.9)

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