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Mercury and Selenium Concentrations in Fish, Sediments, and Water of Two Northwestern Quebec Lakes

M. R. Speyer

Process Technology Department, Noranda Research Centre, Pointe Claire, Quebec H9R 1G5 Canada

The findings presented in this paper are a portion of a more detailed study conducted in the Rouyn-Noranda region of Quebec on behalf of Noranda Mines Limited (Horne Division), Noranda. As a result of Noranda's desire to learn more about mercury in the aquatic ecosystem and ways to possibly moderate the toxicity of mercury accumulated by aquatic organisms, select samples of fish, sediment and water were analysed for both mercury and selenium.

While the mechanisms by which methylmercury is accumulated by fish are not yet fully understood, it is generally agreed that methylmercury is the predominant form of mercury found in fish (WESTOO 1973, HUCKABEE et al. 1974). Mercury is not an essential trace element as is selenium (GANTHER 1970) which has certain nutritional aspects. Selenium concentrations of >1 $\mu g\ g^{-1}$ have been observed in both lake sediments and fish (SANDHOLM et al. 1974).

The interaction between mercury and selenium in biological systems has been shown to be both antagonistic and synergistic. Studies demonstrating the antagonistic interactions of mercury and selenium have been discussed by GROTH et al. (1974) and GANTHER et al. (1972a, b). PARIZEK et al. (1973) working with a divalent form of mercury and a selenium compound, found a synergistic interaction between the two compounds that elicited a more toxic response in male rats than either of the two compounds administered individually. HUCKABEE and GRIFFITH (1974) studied the effects of Hg II and SeO_3^{-2} on the hatchability of carp (Cyprinus carpio) eggs by exposing them under controlled conditions to mercury and selenium mixtures. They found synergistic interactions between the two compounds, whereas selenium administered alone did not appear to exert any toxicity at concentrations up to 5 $\mu g\ L^{-1}$.

The scope of this study did not include an assessment of the role of selenium, or its interaction with mercury, in the aquatic environment. It was intended only to determine the

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levels of mercury and selenium in certain compartments of two Northwestern Québec lakes: Lake Dufault (48° 17'N, 79° 00'W) and Lake Duparquet (48° 27'N, 79° 15'W).

METHODS

Specimens of northern pike (Esox lucius) for mercury and selenium analysis were collected with experimental gill nets during the summer of 1977. Individuals were weighed, measured for total length, sexed and filleted on the site of capture. The subcutaneous muscle tissue samples were taken from the region just posterior of the pectoral girdle to the caudal peduncle and placed into sterile Whirl-Pak® bags. Samples were kept over ice for a maximum of 6 h prior to freezing. Homogenization of the muscle tissue was achieved with a Waring® blender under clean conditions at the Centre de Recherche Noranda. Portions of the frozen homogenate were then submitted for analysis to the Noranda Environmental Laboratory.

Lakebed sediments were collected with either a K.B.® type sediment corer equipped with Lexar® plastic liner tubes or an Ekman dredge. The sediments were sectioned horizontally noting the depth from the surface of each sub-sample. Prior to freezing, the samples were held in Whirl-Paks® over ice. Homogenization was achieved by thawing the sample in an acid washed Pyrex beaker, removing any organic and inorganic debris, and stirring the sediments with a glass rod until homogeneity was reached. Sub-samples were submitted to the above laboratory for mercury and selenium analyses.

Water samples were collected from just below the surface (0.5 m) with an acid-washed borosilicate glass BOD bottle taking the necessary precautions to avoid sampling the surface film; samples were also collected from measured depths with an Alpha-style vertical water sampler and transferred to a BOD bottle. A mixture of concentrated H_2SO_4 (analytical grade suitable for Hg analyses) and 5% potassium dichromate (Primary Standard Baker Analyses) was used as a preservative for samples analysed for mercury at a ratio of 1.0%. Concentrated nitric acid (1.0%) (Ultrex®) was used to preserve samples collected for selenium analyses.

Mercury and selenium analyses in fish, sediment, and water samples were conducted by cold vapour and flame atomic absorption methods respectively in accordance with Environment Canada (1975) procedures.

RESULTS

The results of mercury and selenium analyses conducted on northern pike (Esox lucius) muscle tissue indicate distinct and

significant differences between the mercury and selenium levels of fish from the two lakes (Table I). While fish samples from Lake Dufault had very low mercury concentrations, they appeared to have elevated amounts of selenium. Conversely, fish samples originating from Lake Duparquet had elevated mercury concentrations and low selenium levels. In both cases a comparison of means by the Student "t" test indicated significant ($P<0.01$) differences between the mercury and selenium concentrations of fish samples from the two lakes.

TABLE I

Mercury and Selenium Concentrations (Wet Weight) in Northern Pike Muscle Tissue

LAKE DUFAULT				LAKE DUPARQUET			
Total Length cm	Weight g	Hg mg kg^{-1}	Se	Total Length cm	Weight g	Hg mg kg^{-1}	Se
52.0	750	0.02	2.2	40.0	215	0.58	0.50
54.3	960	0.02	2.3	39.5	270	0.57	<0.20
68.7	1025	0.02	2.6	36.9	280	0.35	0.30
60.2	1200	0.02	2.2	38.2	336	0.67	0.54
58.8	1250	0.01	1.1	38.1	337	0.24	0.32
60.0	1350	0.01	1.2	40.8	345	0.35	0.46
57.3	1380	0.01	2.3	43.4	499	0.46	0.26
58.0	1410	0.01	2.3	47.1	650	0.17	0.62
63.7	1550	0.01	1.7	47.7	650	0.47	0.35
65.2	1560	0.02	1.6	49.0	675	0.39	0.30
67.2	1565	0.03	2.4	50.3	740	0.56	0.40
64.0	1630	0.02	2.2	52.4	775	0.46	<0.20
65.6	1810	0.02	3.0	51.3	820	0.93	0.20
61.5	1830	0.02	2.5	48.6	840	0.63	0.38
66.4	1950	0.01	2.1	57.1	1000	1.37	0.36
73.5	2125	0.03	2.6	63.5	1890	0.25	<0.20
75.5	2320	0.01	2.0	68.5	2000	1.33	0.30
80.9	2505	0.02	1.5	81.5	3350	1.38	0.30
81.2	2840	0.03	1.1				

Analyses of superficial sediment samples indicated elevated mercury levels in both lakes, and higher than background selenium concentrations in Lake Dufault which were significantly higher ($P<0.01$) than those observed in Lake Duparquet. A summary of the analytical data is presented in Table II. While both Lakes Dufault and Duparquet have approximately the same surface area (50 km^2) and mean depth ($\simeq$4.0 m), and have been influenced by

mining activities, they have distinctly different types of bottoms. In Lake Dufault a heavy metal-enriched sludge-type of sediment has over the years covered a glacial grey clay, while in Lake Duparquet, a fine silty ooze (several cm thick) overlies the glacial clay. In Lake Duparquet, near the site of the mine tailings disposal, the sediments have been infiltrated by eroded tailings and have mercury concentrations ranging between 1-2 mg kg^{-1}, yet selenium levels remain <0.8 mg kg^{-1}.

TABLE II

Range of Superficial Sediment
Mercury and Selenium Concentrations

	Lake Dufault	Lake Duparquet
Mercury		
Range (µg kg^{-1} dry weight)	71-140	185-303
Standard Deviation (µg kg^{-1} dry weight)	168	50
Mean (µg kg^{-1} dry weight)	261	234
Selenium		
Range (mg kg^{-1} dry weight)	1.4-14.5	0.2-0.8
Standard Deviation (mg kg^{-1} dry weight)	3.7	0.2
Mean (mg kg^{-1} dry weight)	7.2	0.5

Analyses conducted on water samples from both lakes indicated mercury and selenium concentrations at or below analytical detection limits (0.02 µg L^{-1} and 0.1 µg L^{-1} respectively). The physical characteristics (Table III) of Lakes Dufault and Duparquet were somewhat similar, however Lake Dufault water had higher conductivity and hardness, and less alkalinity than Lake Duparquet.

DISCUSSION

Although an explanation of the observed mercury-selenium relationships was not within the scope of this study, the results may assist other researchers in such studies. Pike from Lake Duparquet were observed to have flesh mercury concentrations comparable to those reported by other authors (DELISLE and DEMERS 1976, B.E.S.T. 1979, and PENN 1978), and their mercury concentrations were also directly related to size as also noted by SCOTT and ARMSTRONG (1972) and SMITH and BERKES (1975).

TABLE III

Range of Physico/Chemical Water Characteristics

	Lake Dufault	Lake Duparquet
Conductivity (μmhos cm^{-1})	130-180	68-75
pH	7.0-7.6	6.7-7.6
Dissolved Oxygen (mg L^{-1})	8.0-9.6	6.9-9.0
Hardness (mg L^{-1} as $CaCO_3$)[1.]	68-120	51-68
Acidity (mg L^{-1} as $CaCO_3$)[1.]	0	0
Alkalinity (mg L^{-1} as $CaCO_3$)[1.]	14-41	34-49

Results of analyses conducted on water samples from both lakes indicate mercury and selenium concentrations at or below detection limits (0.02 μg L^{-1} and 0.1 μg L^{-1} respectively).

[1.] Readings by Hach Kit

Selenium concentrations were seen to range randomly regardless of size between <0.2-0.62 mg kg^{-1}. This agrees with observations made by NISHIGAKI et al. (1974) that mercury concentrations increased with size of fish, while selenium concentrations were unrelated to size in marine species. PENN (1978) reported the same observations for freshwater fish collected in Northwestern Quebec.

In contrast, pike from Lake Dufault were observed to have low mercury concentrations that were not related to size. Levels of mercury remained almost constant regardless of fish size. This is contrary to what other workers have found and does not agree with results of analyses conducted on individuals collected from other lakes during this study. While selenium levels were observed to be higher than any others noted in this study, there did not appear to be any relationship between size and concentration which agrees with the findings of NISHIGAKI et al. (1974). Selenium levels reported by the above were generally <1.0 mg kg^{-1} and lower than those reported in this study.

Researchers (GROTH et al. 1972, GANTHER et al. 1972a, b) have shown selenium to protect organisms from methylmercury intoxication, but there appears to be no information on the role of selenium in the bioaccumulation and clearance of mercury from aquatic organisms. The high selenium levels encountered in the flesh of pike from Lake Dufault may be related to the unexpectedly low levels of mercury in these fish, and their non-correlation with fish size.

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