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Perspectives on the Favorability of the Tongue River Reservoir and other Freshwater Environments for Bacterial Methylation of Mercury

by

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INTRODUCTION

Methylmercury is the predominant mercurial present in fish tissue (Westöö 1973) and is the form responsible for neurological disorders in humans (Clarkson 1973). Bacteria present in natural waters can convert inorganic mercury to methylmercury (Jensen and Jernelöv 1969); thus, given suitable conditions, any mercurial can become hazardous.

Measurements of methylmercury in natural waters have been unattainable until very recently because of the very low concentrations present. Currently, we are aware of only one laboratory that is measuring methylmercury in natural waters and this in the highly contaminated Clay Lake-Wabigoon River System of southwestern Ontario (Park et al. 1980). Nonetheless, fish can concentrate methylmercury to measurable quantities and thus can be used as an index of how much methylmercury is present in water.

Fig. 1 near here

In this paper we report our observations on mercury uptake by fishes from the Tongue River and Tongue River Reservoir[2] (Fig. 1) in southeastern Montana relative to total mercury concentrations in the reservoir's sediments and water. Limnological characteristics of the reservoir are compared to conditions known to favor methylation of mercury and the potential for mercury methylation in this and other freshwater environments is discussed.

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[2]Although surface coal mining is occurring near the Tongue River Reservoir, mining is not affecting mercury dissolution to the reservoir and therefore further discussion of mining is not relevant to this report.

MATERIALS AND METHODS

Sampling and analytical

Fishes, including northern pike (*Esox lucius*) and white crappie (*Pomoxis annularis*), were collected using trap nets or gill nets. Shortly thereafter fish were weighed and measured; a portion of axial muscle tissue was removed, placed in a whirl-pak bag, and frozen. Sediment samples were collected with an Ekman dredge, frozen in whirl-pak bags, and stored. Sediments were prepared for analyses by thawing, drying at 45-60°C, and pulverizing with a mortor and pestle. Water was collected with a VanDorn sampler, transferred to 500 ml glass bottles, preserved with nitric acid and potassium dichromate, refrigerated, and analyzed for mercury within 21 days. Water samples were oxidized with potassium permanganate and potassium persulfate prior to analysis.

Total mercury concentrations in fish tissue, sediments, and water were determined with a Varian model AA-6 atomic absorption spectrophotometer equipped with a carbon rod atomizer. Fish tissue and sediment samples were burned in a combustion chamber and aqueous mercury was vaporized. The evolved mercury was collected on a porous gold-plated tube, the tube was heated in the atomizer, and the resulting absorption signal was measured (Siemer and Woodriff 1974). Accuracy of analyses were verified by known duplicates (2-5% of samples), blind duplicates (5-10% of samples), spike and recovery (5-10% of samples), U.S. Environmental Protection Agency certified water samples, and National Bureau of Standards albacore tuna. Using our methodology, over the range of concentrations encountered, precision was estimated at ±0.01 μg Hg/l for water and ±0.05 μg Hg/g for tissue and sediment.

Limnological parameters

Limnological parameters measured included dissolved oxygen, temperature, and pH. Parameters were measured at three reservoir stations (Fig. 1); however the deepest pool located near the downstream end of the reservoir will be the only station discussed in detail. All parameters were measured twice monthly and at 2 m intervals of depth. Measurements were made using a Hydrolab Model 8000 water quality analyzer (Hydrolab Corp., Austin, Texas) that was calibrated before and after each days use. Calibration was with a standard mercury thermometer for temperature, against standard buffer solutions for pH, and relative to oxygen in water-saturated air (corrected for altitude and temperature) for dissolved oxygen.

Statistics

Regressions of fish length vs. mercury concentration in tissue were derived after a log transformation of mercury content. Degree of difference between regression lines was determined by F-test (Neter and Wasserman 1974). Student's t-test was used to compare sample means (Steel and Torrie 1960).

RESULTS

Mercury in water and sediments

During the last year (April-October 1980) we collected water samples at two week intervals from several locations in the Tongue River Reservoir and determined total mercury concentrations. Locations sampled included the inflow, the outflow, and surface, midwater, and bottom depths at three locations on the reservoir including upstream, mid-reservoir, and downstream (Fig. 1). Mercury concentrations in water from all locations were consistently low (Table 1). The average concentration for all locations combined was 0.02 μg Hg/l; no significant differences were seen between sampling locations and mercury concentrations (Student's t-test).

Table 1. Total mercury concentrations in water from various locations in the Tongue River Reservoir.

Location	n	Total mercury (μg Hg/l) mean	±SD
Reservoir inflow	12	0.01	0.01
Station 1			
surface	12	0.02	0.01
midwater	8	0.02	0.01
bottom	9	0.03	0.03
Station 2			
surface	12	0.02	0.01
midwater	12	0.02	0.01
bottom	12	0.02	0.02
Station 3			
surface	12	0.02	0.01
midwater	12	0.02	0.01
bottom	12	0.02	0.01
Reservoir outflow	12	0.02	0.01

Similarly, 176 surficial sediment samples collected from throughout the reservoir during 1979 averaged only 0.04 μg Hg/g (dry basis). The highest concentrations were associated with finer sediment particles located near the downstream end of the reservoir and the lowest concentrations were found in coarser sediments collected along the shores (Fig. 2). A similar relationship was noted for Lake Erie sediments (Thomas and Jaquet 1976) and was attributed to the higher affinity of mercury for fine clay and silt-like particles over coarser sands and gravels.

Fig. 2 near here

Mercury in fish

Notwithstanding, concentrations of mercury in some fish species from the reservoir are relatively high. Northern pike, in particular, contained up to 2.47 μg Hg/g (wet basis) in axial muscle. Data for males (Fig. 3) and females (Fig. 4) are shown separately because sex related growth differences resulted in different mercury uptake patterns. Mercury concentration in tissue increased with fish length. Data for northern pike, as well as other fish species in the reservoir, are best described by regressions of the form $\log_{10}$ Hg = a(length)-b. The logarithimic relationship probably results because older age classes cover increasingly shorter intervals of fish length. Plotting age vs. mercury concentration resulted in a linear fit (Phillips et al. 1980).

Figs. 3 and 4 near here

White crappie collected from the Tongue River immediately below the dam and from a location 52.3 river km downstream (near the town of Birney) accumulated mercury at significantly slower rates, (p = 0.002 and 0.001, respectively) relative to fish length, than white crappie from the reservoir (Fig. 5). Although age and growth information were not available for the river crappie, it is probably safe to assume that they grew slower than crappie from the reservoir and, thus, were not younger at a given size.

Fig. 5 near here

Reservoir limnology

Figs. 6 thru 8 near here

Seasonal isopleths (April thru October 1980) for several limnological parameters known to influence mercury methylation rates are shown in Figs. 6-8. In general, the Tongue River Reservoir is a well-mixed, eutrophic, warmwater impoundment. Primary productivity averages 1280 mg $C/m^2 \cdot day^{-1}$ (Leathe 1980). Deep water withdrawal, a relatively fast turnover rate (mean = 67 days), and wind generated mixing maintained a relatively isothermal temperature profile (Fig. 6). However, even in the absence of a thermocline, the oxygen profile (Fig. 7) was clinograde during the summer months due to heterotrophic activity in the bottom waters combined with high oxygen production by phytoplankton in the euphotic zone. Considering the trophic status of the reservoir, this is a relatively mild oxygen deficit and is attributable to the mixing that was discussed previously. Although oxygen concentrations approached zero, bottom waters were not anaerobic.

The pH profile (Fig. 8) was similar to that for dissolved oxygen and reflected respiratory and photosynthetic processes that govern the equilibrium between free carbon dioxide, carbonate, bicarbonate, and carbonic acid. The pH of Tongue River Reservoir water is generally high (8-9) due to the high buffering capacity (high alkalinity) of the water. However, the heterotrophic consumption of oxygen and accompanying release of carbon dioxide resulted in bottom waters having lower pH values (7.7) during the warm summer months.

DISCUSSION

In comparison with other lakes and reservoirs for which information is available on mercury concentrations in both fishes and sediments (Table 2), the relatively high mercury concentrations in fishes from the Tongue River Reservoir are an anomaly. Although the fish species and the extent of information on mercury in sediments varied between studies, clearly the ratio between the maximum mercury concentration in fish and the mercury content of sediments is greater for the Tongue River Reservoir than for most of the other lakes and reservoirs.

Langley (1973) has shown that the mercury-methylating capacities of mercury-contaminated river sediments were more dependent on the ability of the sediments to promote microbial activity than on mercury concentration. Our observations lead us to believe that the physical and chemical characteristics of the Tongue River Reservoir are highly favorable for methylation of mercury. This conclusion is supported by the fact that white crappie from the Tongue River downstream from the reservoir accumulate mercury at a slower rate than the same species in the reservoir (Fig. 5). A similar relationship exists for walleye from Cookson Reservoir, Saskatchewan and from the Poplar River downstream from that reservoir (unpublished data, 1980).

Many of the limnological characteristics of the Tongue River Reservoir coincide with conditions shown to promote methylation of mercury in the laboratory. Methylation of mercury is inhibited by anaerobic conditions because of the concomitant sulfer-reducing activity that results in mercury precipitation as a sulfide (Park _et al_. 1980). However, low dissolved oxygen concentrations and increased water temperatures favor methylation of mercury (Bisogni and Lawrence 1975), apparently owing to

Table 2. Reports from the literature of maximum mercury concentrations in fish muscle tissue relative to mercury concentrations found in sediments from the same environment.

Location	Mercury in sediment (μg Hg/g)	Max. Hg in fish (μg Hg/g)[e]	Fish species	Reference(s)
Antelope Reservoir (Oregon)	17.1[a]	1.79	rainbow trout	Phillips and Buhler (1979); Hill *et al.* (1975)
Unspecified river (eastern Canada)	0.01-109.0[b]	7.0	not specified	Langley (1973)
Lake Mývatn (Iceland)	0.01-0.04[b]	0.016	arctic char	Ólafsson (1979)
Hemlock Lake (Michigan)	0.02-1.25[b]	0.42	rainbow trout	D'Itrie *et al.* (1971)
American Falls Reservoir (Idaho)	0.21-0.95[b,c]	1.20	rainbow trout	Kent and Johnson (1979)
Lake Powell Reservoir (Arizona)	0.30[d]	0.76	walleye	Potter *et al* (1975)
Lohontan Reservoir (Nevada)	0.12-1.35[b]	2.72	white bass	Richins and Risser (1975)
Clay Lake (Ontario)	0.14-7.83[b]	16.0	northern pike	Armstrong *et al.* (1972); Bligh (1970)
Section Four Lake (Michigan)	0.03-0.12[b]	0.45	rainbow trout	D'Itrie *et al.* (1971)
Lake Sangchris Reservoir (Illinois)	0.05[d]	0.30	green sunfish	Anderson and Smith (1977)
Southern Indian Lake Reservoir (Manitoba)	0.01[d]	0.51	walleye	Bodaly and Hecky (1979)
Tongue River Reservoir (Montana)	0.04[d]	2.5	northern pike	This Study
Lake Jocasse Reservoir (South Carolina)	0.04[a]	4.49[f]	largemouth bass	Abernathy and Cumbie (1977)

[a]Only one sample taken.

[b]Range.

[c]Wet basis.

[d]Mean.

[e]Reported for axial muscle on wet weight basis.

[f]Mean of largest size group.

increased microbial activity. The high temperatures and low oxygen concentrations that occur at the sediment-water interface in the Tongue River Reservoir during the summer, combined with the high level of biological productivity of overlying waters (thus settling of organics) appear to provide ideal conditions for bacterial methylation of mercury. The sediment-water interface was the major site of methylmercury production in Clay Lake, Ontario (Park et al. 1980). Further, the mildly oxidizing conditions near the bottom and concomitant lowering of pH further favor monomethylmercury formation over volatile dimethylmercury (Fagerström and Jernelöv 1972).

The river influence may also contribute to the accumulation of mercury by fishes in the Tongue River Reservoir. The Tongue River rises in the spring and early summer due to snowmelt in the high country. Methylmercury produced in river sediments may be transported to the reservoir at this time. Park et al. (1980) have shown that scowering of Wabigoon River sediments during high flow events mobilized methylmercury and increased the loading of that compound into Clay Lake. High flow also imparts considerable turbidity on the upstream end of the reservoir. Organic particulates suspended in the water column may create additional substrates for bacterial growth, thereby enhancing methylation of mercury.

We submit that some bodies of water may develop considerable mercury problems, owing to their physical and chemical characteristics, even in the absence of an anthropogenic source of mercury. Although little information is available on methylmercury concentrations in natural waters, insight into the relative capacities of different environments for methylation of mercury can be gained by comparing mercury concentrations in fishes (an index of methylmercury concentrations in water) to mercury concentrations in sediments (an index of the total amount of mercury present).

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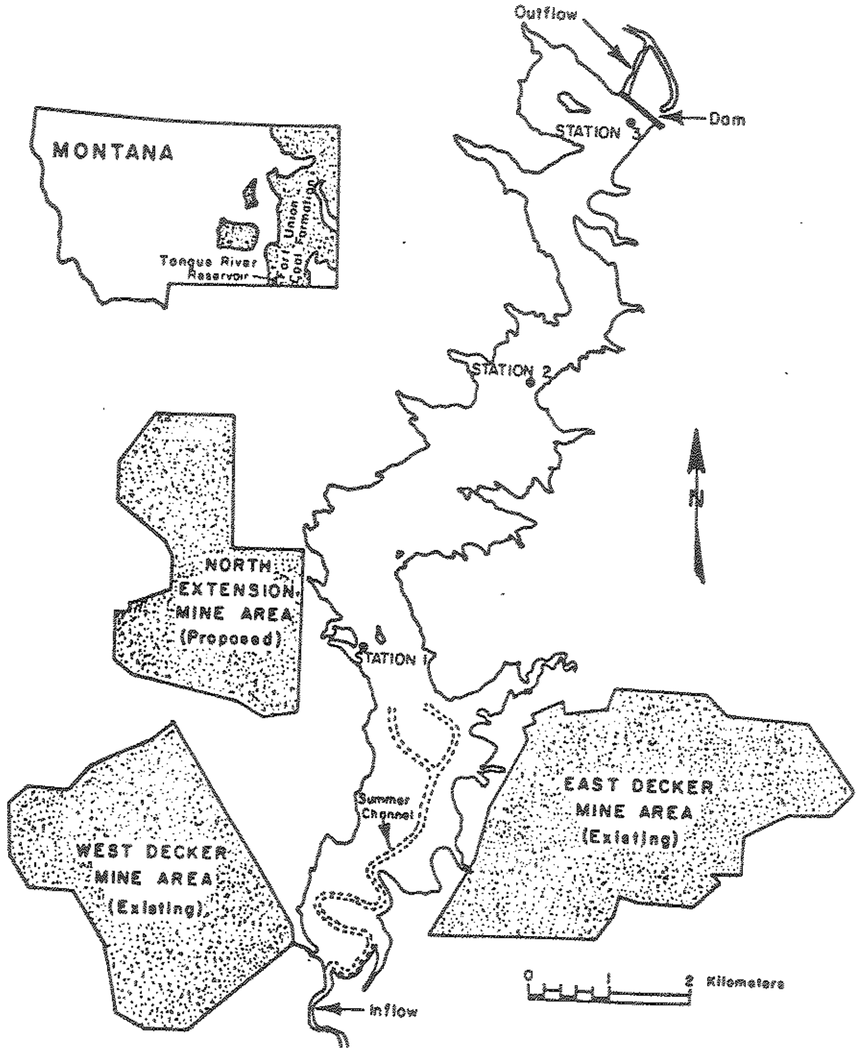
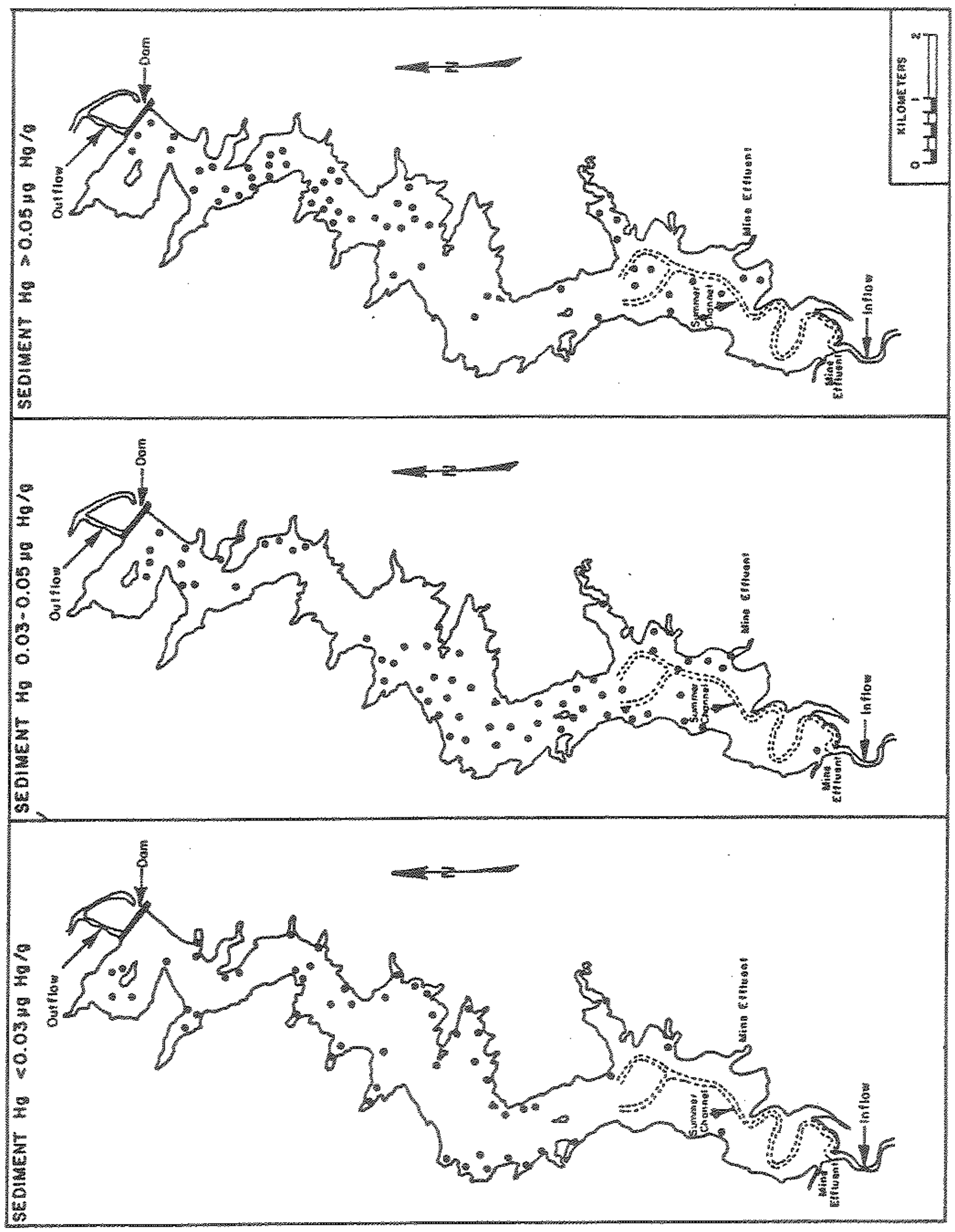


Outflow
Dam
STATION 3
MONTANA
Fort Union Coal Formation
Tongue River Reservoir
STATION 2
N
NORTH EXTENSION MINE AREA (Proposed)
STATION 1
Summer Channel
EAST DECKER MINE AREA (Existing)
WEST DECKER MINE AREA (Existing)
0
1
2 Kilometers
Inflow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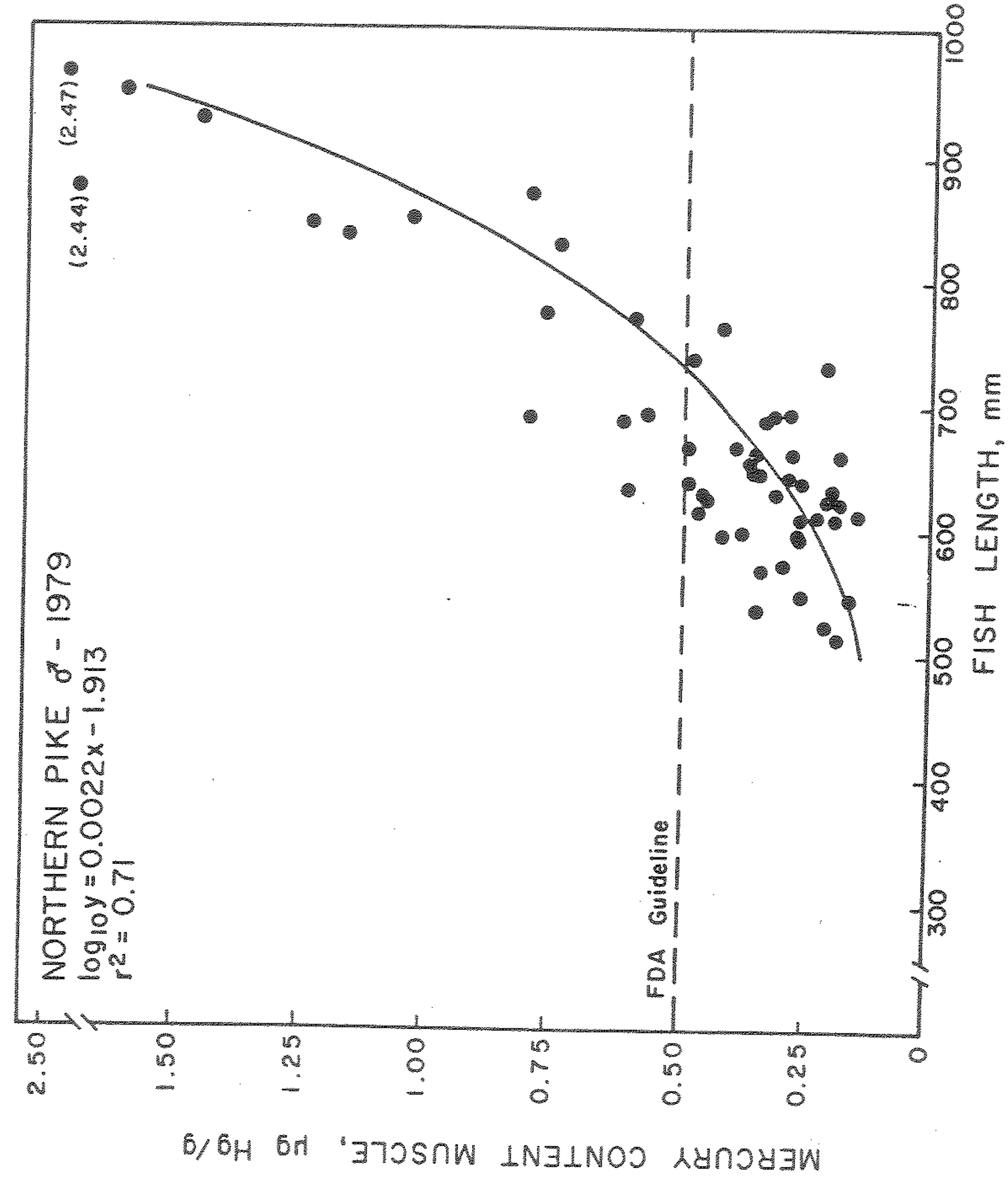
Outflow
Dam
N
Summer Channel
Mine Effluent
Mine Effluent
Inflow
SEDIMENT Hg 0.03-0.05 µg Hg/g
Outflow
Dam
N
Summer Channel
Mine Effluent
Mine Effluent
Inflow
SEDIMENT Hg >0.05 µg Hg/g
Outflow
Dam
N
Summer Channel
Mine Effluent
Mine Effluent
Inflow
KILOMETERS
0
1
2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r² = 0.71
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(2.47)
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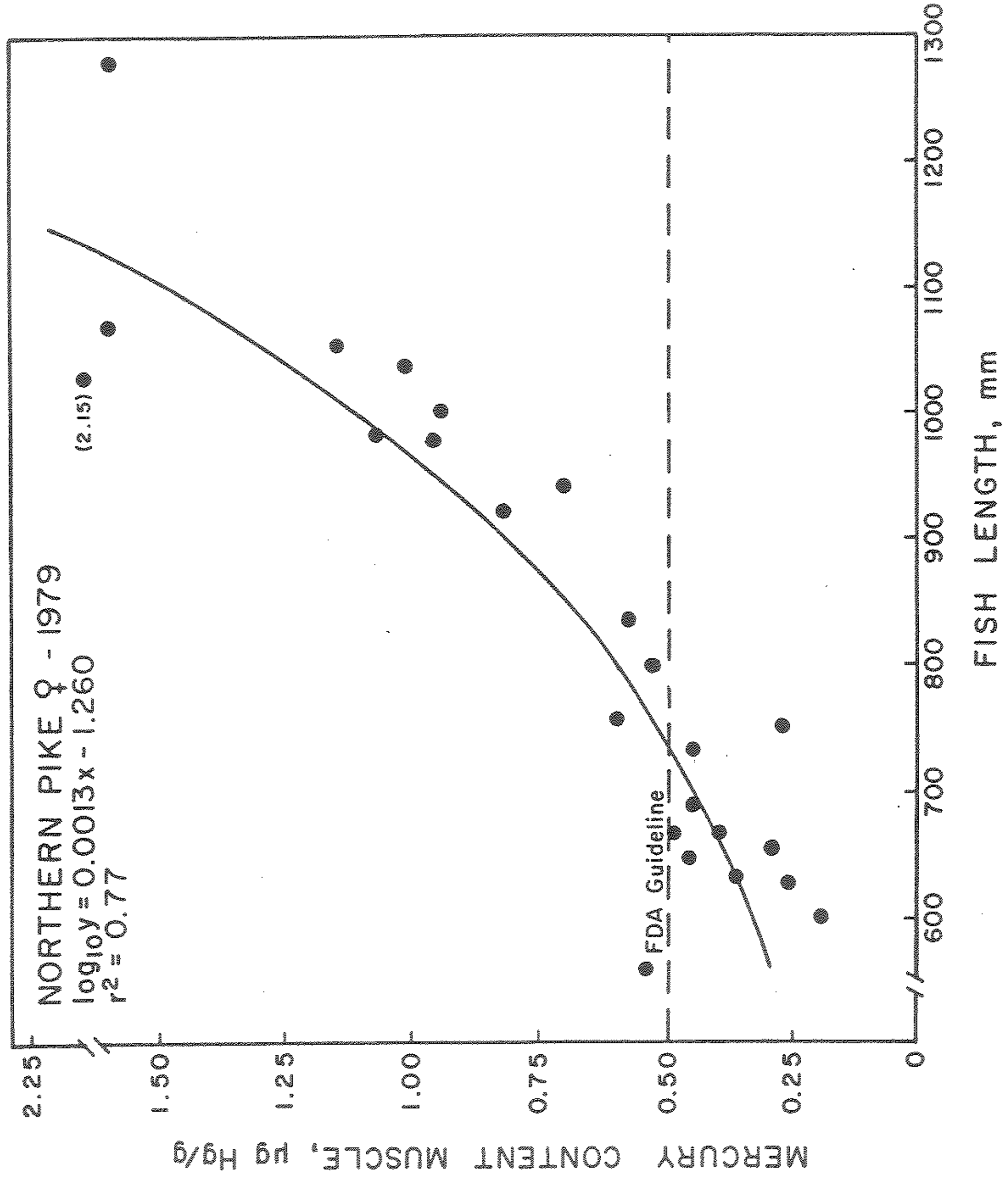
1.25
1.00
0.75
0.50
0.25
0
300
400
500
600
700
800
900
1000
FISH LENGTH, mm
MERCURY CONTENT MUSCLE, µg Hg/g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(2.15)
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700
800
900
1000
1100
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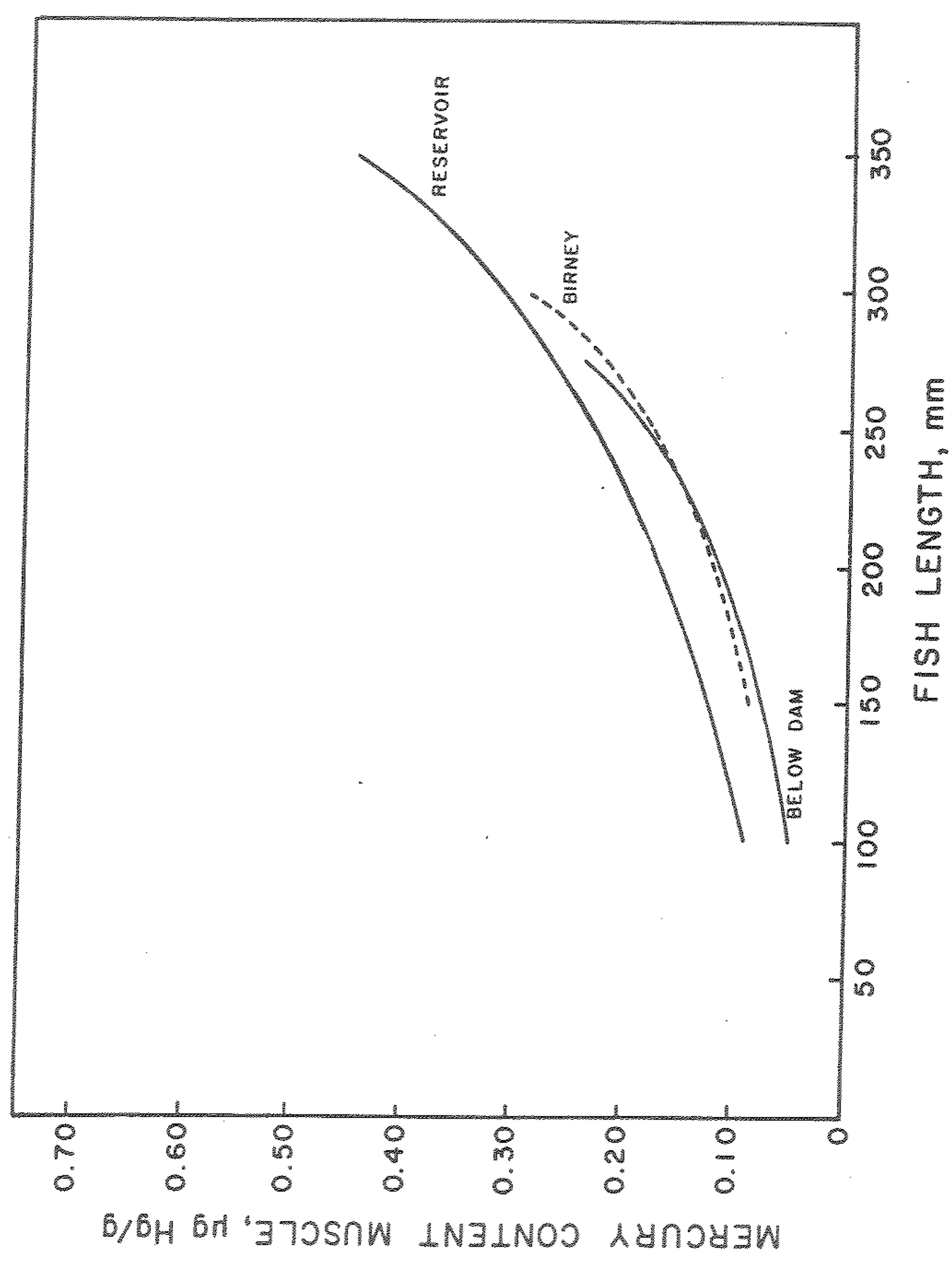
1.00
1.25
1.50
2.25


RESERVOIR
BIRNEY
BELOW DAM
FISH LENGTH, mm
50
100
150
200
250
300
350
MERCURY CONTENT MUSCLE, μg Hg/g
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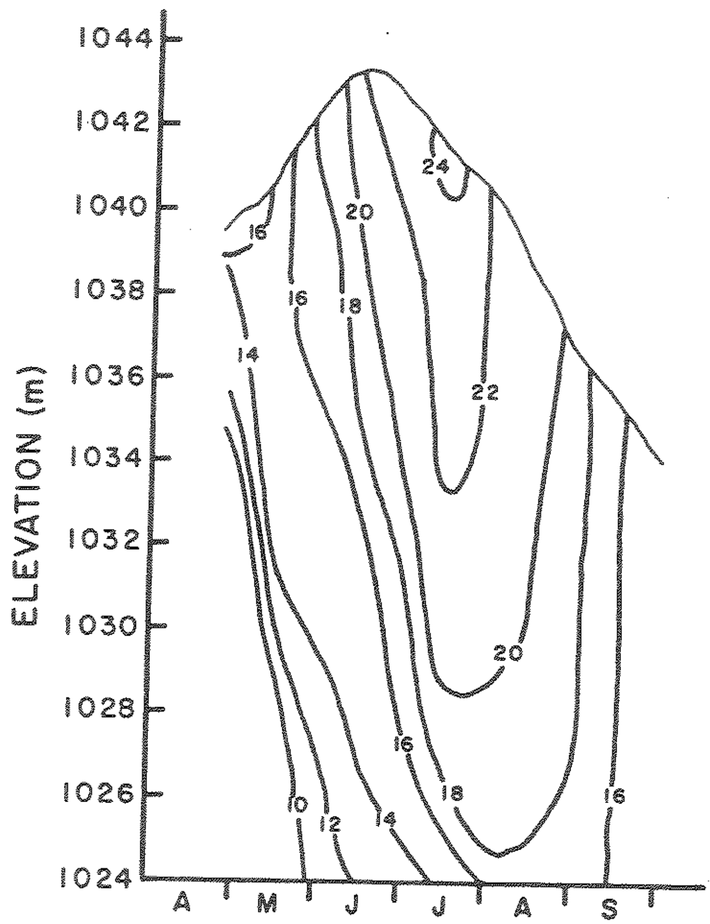
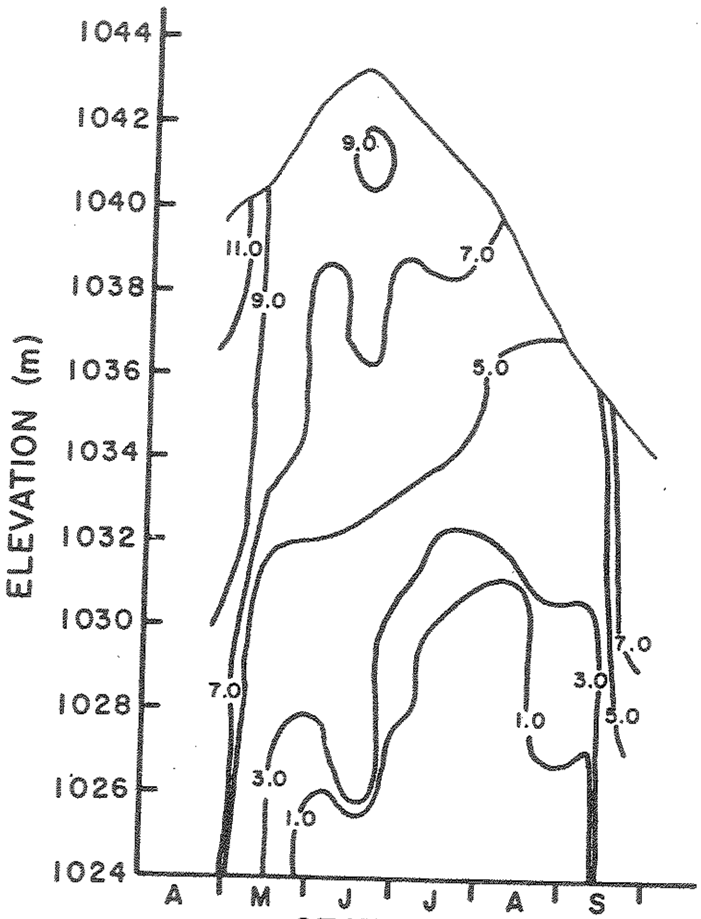
0.40
0.50
0.60
0.70



STATION 3
TEMPERATURE



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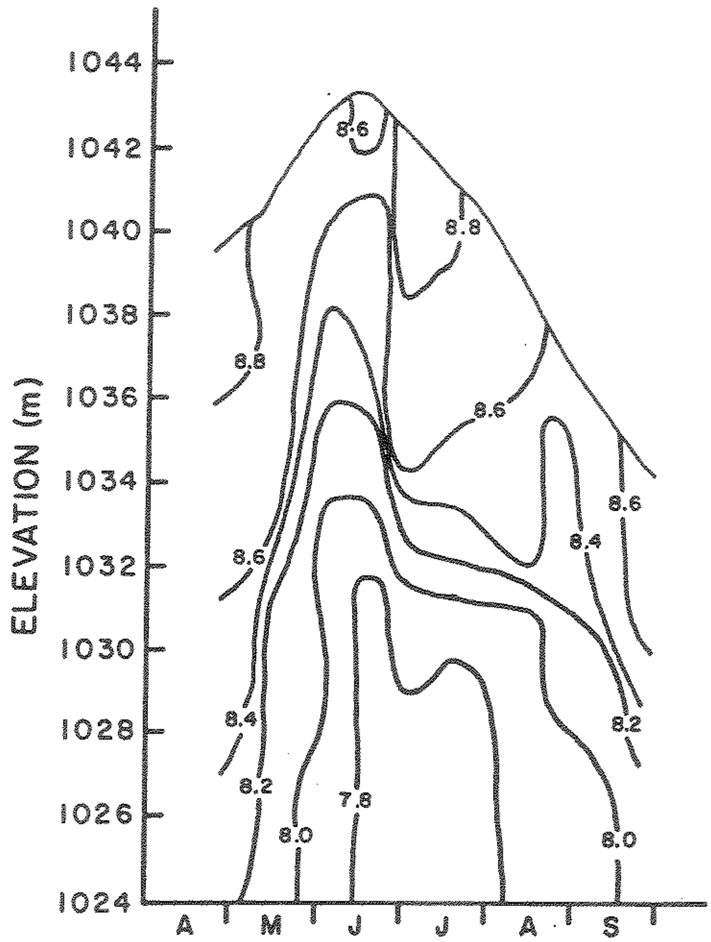
DISSOLVED OXYGEN



1044
1042
1040
1038
1036
1034
1032
1030
1028
1026
1024
ELEVATION (m)
8.6
8.8
8.8
8.6
8.6
8.6
8.4
8.6
8.4
8.2
8.2
8.0
7.8
8.0
A
M
J
J
A
S

STATION 3 - pH

FIGURE CAPTIONS

Figure 1. Map of the Tongue River Reservoir showing sampling lo for limnological measurements and mercury monitoring.

Figure 2. Map showing the distribution of mercury in the surfic ments of the Tongue River Reservoir.

Figure 3. Relation between total fish length and mercury concen in axial muscle tissue for male northern pike taken f: Tongue River Reservoir during spring and summer 1979.

Figure 4. Relation between total fish length and mercury in axia tissue for female northern pike taken from the Tongue Reservoir during spring and summer 1979.

Figure 5. Comparison of the relationships between total fish len mercury concentration in axial muscle tissue of white collected from the Tongue River Reservoir ($\log_{10}$ Hg = length -1.47; r^2 = 0.67; n = 35), from the Tongue Rive the dam ($\log_{10}$ Hg = 0.0038 length -1.66; r^2 = 0.50; n : and from the Tongue River near Birney ($\log_{10}$ Hg = 0.00 -1.73; r^2 = 0.64; n = 14) during 1978.

Figure 6. Temperature isopleths for the Tongue River Reservoir be April and October 1980.

Figure 7. Dissolved oxygen isopleths for of the Tongue River Rese between April and October 1980.

Figure 8. Isopleths for pH at the Tongue River Reservoir between and October 1980.

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