

EXAMINATION OF BIOACCUMULATION AND BIOMAGNIFICATION OF METALS IN A PRECAMBRIAN SHIELD LAKE

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Abstract. This paper reports on a comprehensive examination of metal levels at various trophic levels within an undisturbed Precambrian shield lake ecosystem. Concentrations of 21 naturally occurring elements (Hg, Cu, Al, Ba, S, Ni, Cd, Ca, Be, Zn, P, Pb, Mg, Sr, Fe, V, Mo, Mn, Ti, B, Co) were measured in sediments, clams, fish, birds and mammals. Mercury was the only element to exhibit biomagnification in both aquatic and terrestrial food chains. The levels of several metals were elevated in fish-eating birds relative to concentrations observed in the fish. Mercury was the only metal which accumulated in muscle tissue with increased age and size of all fish species tested. The concentrations of a few other metals were correlated to fish length, but these relationships were not consistent between species.

1. Introduction

Fundamental to the purpose of this paper is growing evidence of increases in the concentrations of certain waterborne metals in lakes of the Precambrian Shield and other waters with similar bedrock geology (Beamish, 1976; Scheider *et al.*, 1979; Bengtsson, 1980). These phenomena are attributed to atmospheric deposition from anthropogenic sources (Jeffries and Synder, 1981) and increased mobilization of metals in soils, sediments and bedrock by lowered lake and precipitation pH (Malmer, 1976; Beamish and VanLoon, 1977; Schindler *et al.*, 1980) which may also enhance rate of metal uptake by resident fish (Brouzes *et al.*, 1977; Merlini and Pozzi, 1977; Hakanson, 1980; Suns *et al.*, 1980).

Although studies have attributed the loss of aquatic life from some lakes to the effect of acid rain (Beamish, 1976; Grahn, 1980) it is difficult to isolate the relative effects of lowered pH and increased metal levels in the aquatic environment. However, little information is recorded about the natural distribution and concentration of metals in the abiotic and biotic components of undisturbed Precambrian Shield lakes. This paper, therefore, reports on the distribution and relative concentrations of 21 naturally occurring elements at various trophic levels within the Tadenac Lake ecosystem and identifies those metals for which there is evidence of food chain accumulation (biomagnification) and increasing concentration with fish age or size (bioaccumulation).

2. Materials and Methods

2.1. STUDY AREA

Tadenac Lake (45°04' N, 79°57' W) is located some 50 km south of Parry Sound, Ontario, Muskoka County. The drainage area is underlain by metamorphic rocks of Precambrian age belonging to the Grenville Structural Province of the Canadian Shield. The Tadenac Lake watershed is undeveloped and protected from direct human impact by a peripheral forest of conifers and mixed hardwoods, and an absence of roads (Turner and MacCrimmon, 1970). The lake is also remote from any direct anthropogenic sources of metals.

Tadenac Lake has a surface area of 308 ha, maximum and mean depths of 32 and 8.2 m respectively, and a mid-summer thermocline formation at about 8 m below the surface. Principal limnological characteristics of the lake pertinent to the present study are a pH of 7.1, total hardness (CaCO₃) of 12 mg l⁻¹, a conductivity of 36 μS, and an alkalinity (CaCO₃) of 7 mg l⁻¹.

2.2. SAMPLE COLLECTION

Sediment surface samples were collected from 14 sites at different water depths in Tadenac Lake with an Ekman grab. Sediment material was placed in paper kraft sediment bags and allowed to air dry. The relative organic content of each sediment sample was determined by weighing a sample (± 0.00001 g) before and after ignition at 550 °C for 60 min. The relative organic content is expressed as percent weight loss on ignition (Coker and Nichol, 1975).

Freshwater clams (*Elliptio dilatata*) were collected by hand from a number of sites using SCUBA equipment. Clam shells were measured (± 1 mm) and the soft tissue was removed, patted dry, and frozen for metal analysis. Representative fish species, rainbow smelt (*Osmerus mordax*), smallmouth bass (*Micropterus dolomieu*), northern pike (*Esox lucius*) and lake charr (*Salvelinus namaycush*) were caught by monofilament gill net set in late afternoon and retrieved the following morning. Bluntnose minnows (*Pimephales notatus*) were collected with a standard beach seine. Fish were patted dry and measured for weight (± 1 g) and total length (± 1 mm). A 10 to 20 g section of dorso-lateral muscle was excised from the left side of larger fish, while whole skinless fillets were taken from smaller fish for metal analysis.

Herring gulls (*Larus argentatus*) were collected in 1979 under authority of a scientific kill permit from the Canadian Wildlife Service. A single common loon (*Gavia immer*) caught in the net of a local fisherman was donated to the study. An American coot (*Eulica americana*) was collected during the regular 1979 waterfowl hunting season. The birds were individually weighed (± 10 g) and tissue samples taken from the pectoral muscle for metal analysis. Liver samples were also analysed for Hg.

Carcasses of beaver (*Castor canadensis*), raccoon (*Procyon lotor*) and otter (*Lutra canadensis*) trapped within the Tadenac Lake watershed were obtained from a local trapper. Muscle samples were removed from the left thigh of each animal. The tissue

TABLE I
Size and number of species analyzed for metals in this study

Species	Number of Specimens	Total length (cm)		Weight (g) ^a	
		Mean	Range	Mean	Range
Clam (<i>Elliptio dilatata</i>)	20 (12)	7.4	6.8–8.3	–	
Bluntnose minnows (<i>Pimephales notatus</i>)	20 (6)	7.4	5.8–8.4	–	
Rainbow smelt (<i>Osmerus mordax</i>)	20	17.3	15.5–18.6	–	
Smallmouth bass (<i>Micropterus dolomieu</i>)	20	26.6	17.2–44.6	270	63–1270
Northern pike (<i>Esox lucius</i>)	20	68.2	42.0–84.0	2536	400–5200
Lake charr (<i>Salvelinus namaycush</i>)	16	36.3	21.0–53.0	532	110–1330
Common loon (<i>Gavia immer</i>)	1	–		4750	
Herring gull (<i>Larus argentatus</i>)	5	–		1000	560–1200
American coot (<i>Fulica americana</i>)	1	–		810	
Beaver (<i>Castor canadensis</i>)	4	–		9960	7400–1200
Raccoon (<i>Procyon lotor</i>)	4	–		5000	4750–6250
Otter (<i>Lutra canadensis</i>)	4	–		7330	5100–9500

^a Weight of mammal species does not include weight of pelt.

distribution of Hg and the relative amounts of methylmercury in these animals has been reported previously (Wren *et al.*, 1980). Tissue samples from all sources (Table I) were taken immediately to the field laboratory for processing, packaged in sterile Whirl Pak® bags and frozen for subsequent metal analysis.

A linear correlation matrix of sediment characteristics was employed to examine the interrelationships of these factors. The relation of metal concentration with length of the fish was examined by plotting individual metal levels against length of a species and obtaining the corresponding correlation coefficients (*r*) from regression analysis of the data. This was conducted for each metal detected in northern pike, smallmouth bass, and lake charr.

2.3. METALS ANALYSIS

2.3.1. Sample Preparation

Clam tissue was ground prior to analysis because of the extreme inhomogeneity of the sample. Grinding of other tissues was avoided if possible in order to prevent contamina-

tion from the stainless steel blades which introduces extraneous Fe, Ni, Cr and Mn into the samples. The natural levels of Fe and Mn in clams are sufficiently high that the contamination introduced was insignificant.

An aliquot of tissue (~2.5 g) was weighed and placed in a calibrated 25 × 200 mm digestion tube. A typical run consisted of 2 reagent blanks, 2 control samples, 33 samples and 3 sample duplicates. Glass beads were added to prevent bumping. Nitric acid (conc. 7 ml) and perchloric acid (conc. 2 ml) were added to all tubes. The run was placed in a Technicon hot block and digested at 100 °C for 11/2 h followed by 170 °C until heavy white fumes were evolved and approximately 1/2 ml of clear, colourless to pale yellow solution remained, (normally 8 to 10 h).

Some samples with high lipid content darkened toward end of the digestion. Additional HNO₃ was added dropwise and heating continued until a clear digestate was obtained.

The tubes were allowed to cool, brought to 25 ml with distilled water, covered, mixed by repeated inversion and submitted for analysis.

2.3.2. Analysis

Sample digestates were analyzed using a Jobin Yvon J-Y-48 inductively coupled plasma atomic emission spectrometer. Parameters were optimized for this matrix; background and interelement corrections were applied using a DEC PDP 11 minicomputer and manufacturer supplied software.

Listed below are the lowest reliable concentrations for the dilute perchloric acid matrix and a 2.5 g sample aliquot.
All results in $\mu\text{g g}^{-1}$

S	2	Cd	0.1	Mg	1
Mo	0.1	Co	0.1	V	0.1
B	0.5	Ni	0.1	Al	1
Zn	0.1	Ba	0.4	Be	0.1
P	10	Fe	0.5	Ca	1
Pb	0.6	Me	0.1	Ti	0.4 ^a
Ca	1	Cu	0.1		
Sr	0.4				

^a Ti is partially volatilized by the digestion procedure and, therefore, not accurate.

In determinations of complex matrices there is always the possibility of systematic error above the stated detection limit. Thus, low level data should be viewed with caution.

The procedure for Hg analysis is identical to the metal preparation with the following exceptions:

- a 0.25 g tissue aliquot is used with 5 ml of a 4 : 1 sulphuric : nitric acid mixture;
- the samples are digested at 250 ° for at least 3 h.

The Hg samples were analyzed using a conventional automated cold vapor generation system and UV detection with a Pharmacia Mercury Monitor. The working detection limit is $0.01 \mu \text{g g}^{-1}$ of tissue.

Detailed descriptions of the methodologies used are available in the 'Handbook of Analytical Methods for Environmental Samples', Laboratory Branch, Ministry of the Environment 1982, Rexdale, Ontario.

3. Results

3.1. SEDIMENTS

Concentrations of all metals examined, except Zn and Mn, in Tadenac Lake sediments (Table II) are within normal background levels occurring in sediments in Ontario and other lakes (Fitchko and Hutchinson, 1975; OME, 1978; Forstner and Wittman, 1979). Mercury levels in the lake sediments ($0.14 \mu \text{g g}^{-1}$) are not highly correlated with organic content ($r = 0.46$) in the sediments, but do become highly correlated ($r = 0.90$) when sediment samples ($n = 41$) from the surrounding drainage basins are included. Mercury levels in the sediments are highly correlated with water depth at the sample location ($r = 0.89$), and with the concentrations of Pb ($r = 0.90$), Cu ($r = 0.84$), Zn ($r = 0.65$), % S ($r = 0.90$) and Mg ($r = -0.68$) (Table III). Organic content of the sediments is highly correlated with % Fe ($r = 0.64$), and with the concentrations of Ni ($r = 0.70$) and Zn ($r = 0.65$).

TABLE II

Description of Tadenac Lake sediments. Reported values are in ($\mu \text{g g}^{-1}$) unless otherwise stated.

Variable	Mean	Range	Variable	Mean	Range
% loss ^a	19.1	3.0–29.8	Cu	26	9–44
% Fe	4.6	2.6–14.0	Ni	31	17–47
% S	0.6	0.1–1.4	Hg	0.14	0–0.30
Al (mg g^{-1})	47.4	31.0–64.8	Se	2.5	1.0–4.3
Ca (mg g^{-1})	12.4	5.2–27.5	As	13	2–62
P	1440	950–2040	Be	1.7	1.3–2.1
Ti	2500	1230–3760	V	85	63–139
Mg	5875	2820–14200	Sr	141	61–254
Mn	4609	497–3800	Cd	<3	
Zn	262	133–484	Co	<7	
Pb	98	25–225	Mo	ND	

^a Percent weight loss on ignition.

3.2. BIOTA METAL LEVELS

Among those organisms representative of various aquatic trophic levels within the Tadenac Lake ecosystem, most metals with exception of Hg, Mg, B, and S, are most highly concentrated in clams (Table IV). The same general relationships in metal level

TABLE III
Correlation matrix of Tadénac Lake sediment characteristics

	Hg	% Fe	% S	Mg	Mn	Ni	Zn	% loss ^a	depth ^b	Pb	Cu
Hg	1.00										
% Fe	NS	1.00									
% S	0.90	NS	1.00								
Mg	-0.68	NS	-0.56	1.00							
Mn	NS	0.91	NS	NS	1.00						
Ni	0.57	0.64	NS	NS	0.55	1.00					
Zn	0.65	0.72	NS	NS	0.68	0.90	1.00				
% loss	NS	0.64	NS	NS	NS	0.70	0.65	1.00			
depth	0.89	NS	0.76	-0.78	NS	NS	NS	NS	1.00		
Pb	0.90	NS	0.76	NS	NS	0.73	0.81	NS	0.68	1.00	
Cu	0.84	NS	0.76	-0.62	NS	0.78	0.80	0.68	0.76	0.81	1.00

NS not significant at the 0.05 level.

^a Percent weight loss on ignition.

^b Depth of water at location of sediment sample collection.

distribution was observed in bluntnose minnows. Although concentrations are considerably lower than in the clams, bluntnose minnows contain much higher metal levels than the other fish species examined. Furthermore, measureable quantities of Cd, V, Ba, and Sr are present in the clams and bluntnose minnows, but levels of these metals are below detection limits in the other fish species.

Biomagnification of metals with trophic level of the fish species examined is most pronounced for Hg, ranging from a mean tissue concentration of $0.116 \mu\text{g g}^{-1}$ in bluntnose minnows to $1.01 \mu\text{g g}^{-1}$ in northern pike. While less pronounced there is evidence to suggest biomagnification of Ni and S in this aquatic trophic system.

Mean Hg concentrations in muscle of beaver ($0.01 \mu\text{g g}^{-1}$), raccoon ($0.22 \mu\text{g g}^{-1}$) and otter ($0.91 \mu\text{g g}^{-1}$), suggest that biomagnification of Hg is occurring within these mammal species (Table V). Levels of Cu, Ca, and S are also highest in the otter, while no appreciable differences between the mammals are observed for the other metals. Although most metal levels in the mammals are comparable to fish metal levels, concentrations of Cu, Fe, and Zn are much higher in the mammals, while Mn levels are lower.

Concentration of Hg in muscle tissue of the fish-eating loon ($1.5 \mu\text{g g}^{-1}$) and gulls ($1.7 \mu\text{g g}^{-1}$) examined, are higher than fish Hg levels. Concentrations of Hg in liver tissue of the loon and gulls (3.9 and $2.5 \mu\text{g g}^{-1}$, respectively) are higher than in muscle tissue. All birds accumulated high levels of Cu, Fe and Zn relative to the levels of these metals observed in the fish. Levels of Al were also slightly higher in the coot and gulls relative to fish Al levels.

Fish muscle Hg concentrations are highly correlated ($P \leq 0.01$) with length of pike ($r = 0.80$), smallmouth bass ($r = 0.76$) and lake charr ($r = 0.87$). Mean Hg concentrations in smallmouth bass and northern pike exceed the government recommended safe level of $0.5 \mu\text{g g}^{-1}$. Concentrations of Zn show a weaker but significant correlation ($r = 0.50$) with length of northern pike (Figure 1), but is not correlated with length of

TABLE IV
Metal concentrations ($\mu\text{g g}^{-1}$ wet weight) in fish muscle and whole clam soft tissue homogenate from Tadenac Lake.

Metal Clams	Bluntnose Minnow			Rainbow Smelt			Smallmouth Bass			Northern Pike			Lake Charr		
	Mean	Range		Mean	Range		Mean	Range		Mean	Range		Mean	Range	
Ca	11406	3540-17200	6811	5190-7870	488	312-793	442	150-1430	581	174-1710	587	143-2160			
P	8443	3950-12700	6770	5660-7590	2326	1910-2680	5126	3480-5520	4313	2940-5520	3658	3000-4420			
Mn	2446	970-3630	20.6	5.7-38.9	1.2	0.5-4.1	0.7	0.3-1.1	1.0	0.4-2.4	1.2	0.1-2.1			
Fe	1751	243-3370	109.6	45.7-226.0	7.7	4.4-13.5	6.4	3.2-10.1	5.6	2.5-10.0	8.1	5.4-14.5			
S	1530	702-2340	2445	2240-2950	2540	2065-2760	3450	3020-3630	3453	2950-3620	2505	2330-2720			
Mg	407	312-545	570	502-680	398	312-494	795	552-1080	650	501-752	464	374-540			
Ba	108	9-446	8.0	4.4-9.8		ND		ND		ND		ND			
Zn	78.5	48.0-120.4	60.2	51.1-68.5	29.0	17.1-53.9	10.9	6.7-16.1	11.0	7.9-17.5	6.7	2.4-9.4			
Sr	63.8	22.0-101.0	9.1	6.5-10.4		ND		ND		ND		ND			
Cd	5.8	3.1-9.2	0.22	0.16-0.29		ND		ND		ND		ND			
Pb	4.5	2.3-10.6	1.9	1.7-2.0	1.0	0.7-1.2		ND		ND		ND			
B	2.6	1.4-5.0	1.9	1.6-2.2	2.1	1.9-2.5	2.4	1.9-4.4	2.9	2.0-3.5	1.8	1.3-2.1			
Co	2.5	1.1-5.4	0.53	0.45-0.64	0.37	0.30-0.39	0.36	0.31-0.44	0.33	0.28-0.38	0.37	0.30-0.57			
Cu	2.0	1.3-2.8	1.9	1.8-2.2	1.1	0.7-2.4	1.1	0.6-1.6	0.8	0.4-2.1	1.0	0.8-1.3			
Ni	1.2	0.6-2.1	0.5	0.3-0.5	0.8	0.5-1.4	1.1	0.7-1.7	1.2	0.8-2.1	0.9	0.6-1.1			
Mo	0.73	0.46-1.31	0.55	0.50-0.61	0.50	0.40-0.59	0.63	0.49-1.27	0.52	0.46-0.63	0.41	0.32-0.51			
V	0.70	0.42-1.26	0.33	0.20-0.50		ND		ND		ND		ND			
Be	0.19	0.10-0.28		ND		ND		ND		ND		ND			
Hg	0.17	0.08-0.31	0.12	0.05-0.26	0.32	0.15-0.67	0.58	0.26-1.40	1.01	0.26-1.90	0.40	0.05-1.10			
Ti		ND	2.55	0.21-5.49		ND		ND		ND		ND			
Al		NA		NA	2.8	2.1-5.9		NA	1.7	0.5-3.7	2.8	1.9-4.4			

ND not detected.

NA not analyzed.

TABLE V
Muscle tissue metal concentrations ($\mu\text{g g}^{-1}$ wet weight) in birds and mammals from the Tadenac Lake area

Metal	Common Loon	American Coot	Herring Gull		Beaver		Raccoon		Otter	
			Mean	Range	Mean	Range	Mean	Range	Mean	Range
Ca	44	41	56	45-77	60	46-72	54	34-73	72	51-118
P	3440	4330	3986	3240-4440	2785	2470-2990	2312	1860-2730	2678	2320-3080
Mn	0.7	0.9	1.0	0.6-1.4	0.4	0.2-0.5	0.4	0.2-0.5	0.5	0.4-0.7
Fe	141	175	100	69-144	100	69-121	63	50-79	158	111-217
S	2290	2290	2295	2265-2330	1825	1280-2090	2145	1980-2280	2249	2190-2300
Mg	397	503	476	385-531	353	340-370	294	249-354	331	291-386
Ba	0.6	0.6	0.4	0.3-0.6	0.5	0.4-0.7	0.3	0.2-0.4	0.7	0.5-0.9
Zn	22.9	17.5	27.7	24.2-33.0	54.9	43.9-68.0	63.6	54.9-80.8	50.5	40.6-63.8
Sr	ND	ND		ND		ND		ND		ND
Cd	ND	ND		ND		ND		ND		ND
Pb	ND	0.8	0.7	0.6-1.0		ND		ND		ND
B	3.7	2.5	2.6	2.2-3.7	2.9	2.8-3.1	2.9	2.8-3.2	2.9	2.7-3.0
Co	0.56	0.56	0.52	0.48-0.57	0.48	0.44-0.50	0.42	0.41-0.44	0.59	0.39-0.75
Cu	10.6	9.2	6.8	4.6-9.3	2.5	1.9-3.3	2.5	2.0-2.9	4.2	4.0-4.4
Ni	1.1	1.5	1.0	0.6-1.3	0.9	0.6-1.3	1.0	0.9-1.3	0.8	0.6-1.0
Mo	0.59	0.58	0.58	0.56-0.64	0.46	0.35-0.51	0.56	0.52-0.61	0.54	0.46-0.60
V	0.14	0.12	0.1	0.1-0.1		ND		ND		ND
Be	ND	ND		ND		ND		ND		ND
Hg	1.5	0.34	1.7	0.66-4.0	0.01	0.01-0.01	0.22	0.10-0.31	0.91	0.67-1.35
Ti	ND	ND		ND		ND		ND		ND
Al	2.5	5.9	5.2	3.5-7.0	4.6	3.0-8.1	3.2	2.1-3.5	4.2	2.0-5.8

ND not detected.

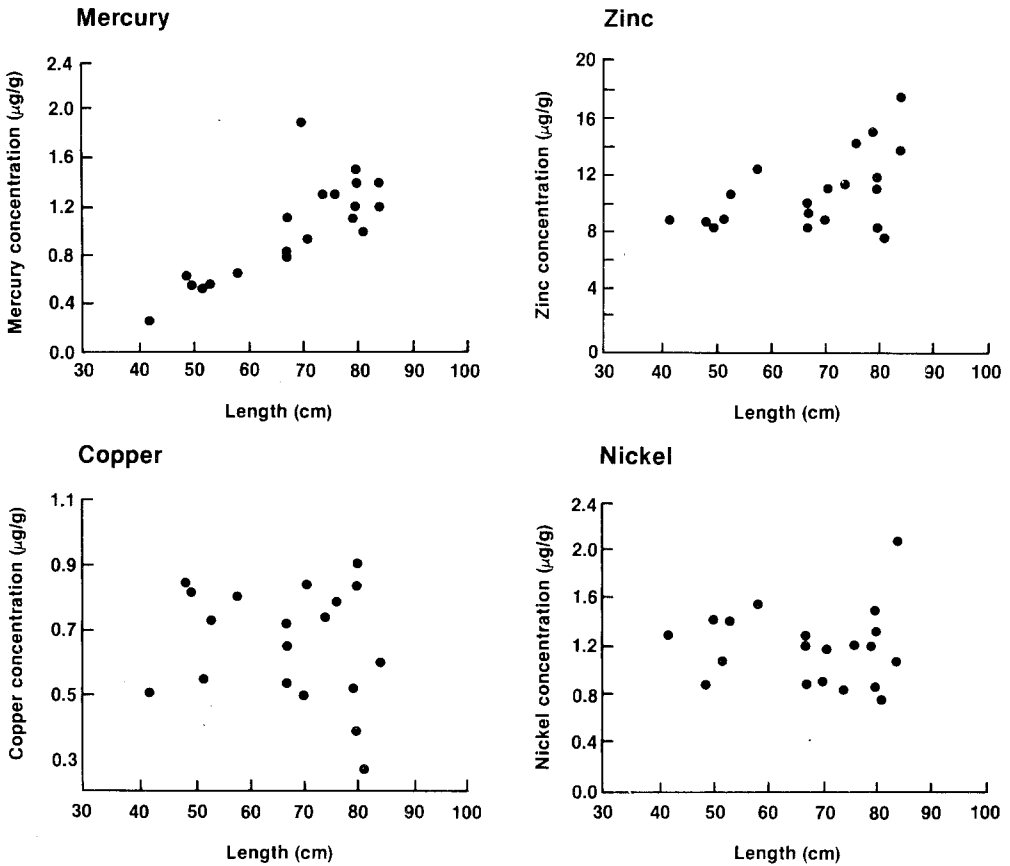


Fig. 1. Relationship of Hg, Zn, Cu, and Ni concentrations to total length of northern pike

the other fish species examined. No other metal concentrations are correlated to length of northern pike (Figure 1). Length of smallmouth bass was significantly ($P \leq 0.05$) correlated with concentrations of S ($r = -0.57$) and Mo ($r = 0.47$), while length of lake charr is significantly correlated with the concentration of Fe ($r = 0.52$) and Ca ($r = 0.62$). However, only the correlation of S concentration with length of smallmouth bass remains significant at the 99% confidence level.

4. Discussion

4.1. SEDIMENTS

The mean concentration of Hg in Tadenac Lake sediments is $0.14 \mu\text{g g}^{-1}$. Allan *et al.* (1974) report that background Hg levels in Precambrian shield lakes seldom exceed $0.20 \mu\text{g g}^{-1}$, even near areas of mineralization. Syers *et al.* (1973), in a study of Wisconsin lakes found Hg sediment background levels varied between 0.01 and

$0.24 \mu\text{g g}^{-1}$. In an extensive survey of Lake Huron sediments, Thomas (1973) reported a mean Hg concentration of $0.222 \mu\text{g g}^{-1}$ (range: 0.054 to $0.805 \mu\text{g g}^{-1}$). Examination of sediments of Lake Ontario revealed Hg concentrations related to industrial contamination as high as $2.0 \mu\text{g g}^{-1}$, with background levels estimated to be $0.33 \mu\text{g g}^{-1}$ (Thomas 1972). It is therefore apparent that sediment Hg concentrations in Tadenac Lake can be considered as normal background levels for an uncontaminated area.

Accumulation of organic material is one factor which can produce enhanced sediment Hg levels relative to surrounding bedrock (Allen *et al.*, 1974). Sediment Hg levels are greatly dependent on a number of physiochemical factors such as organic content, particle size, and mineral content (Thomas, 1972; Rust and Waslenchuk, 1976). In this study, Hg is highly correlated ($r = 0.89$) to depth of the water, indicating a probable association with the finer sediments in deep-water basins (Coker and Nichol, 1975). Mercury is also highly correlated with the % S. The binding of metals by sulphide and organic content is a well established process and may lead to accumulation and immobilization of the metals in bottom sediments (Jackson, 1978). Mercury is highly correlated to Zn, Pb and Cu, which according to Forstner and Wittmann (1979) indicates association with cultural activities. Anthropogenic input of metals to Tadenac Lake would have to be from long range atmospheric deposition as the lake is remote from any direct sources of contamination. Jeffries and Synder (1981) however report that atmospheric deposition of metals in the Muskoka-Haliburton region is as low or lower than median values reported in the literature from rural areas in North America.

While concentrations of most elements measured in Tadenac Lake sediments are within ranges generally regarded as background levels from uncontaminated areas (Forstner and Wittmann, 1979), the levels of Mn and Zn were elevated relative to normal background concentrations. While there are no known natural bedrock sources of metals in the Tadenac watershed, Fitchko and Hutchinson (1975) report elevated levels of Cd, Zn, Mn, and Hg in the sediments of a river draining an undeveloped watershed immediately north of the present study area. The source of these metals was unknown. As many areas of the Canadian Precambrian Shield are known to be rich in mineral deposits (Coker and Nichol, 1975), local zones of mineralization within the study lake drainage basin might possibly be contributing to metal levels observed in this study.

4.2. BIOMAGNIFICATION

The complex interrelationships of species within a natural ecosystem preclude description of a trophic system in terms of a simple linear model. It is important, however, to identify those components of an ecosystem which have naturally elevated metal concentrations relative to other species, and recognize those organisms or tissues which could be adversely affected by increased metal loading to the ecosystem.

A prominent pattern which emerged as a result of this investigation was the significant accumulation of most metals, by clams and, to a lesser degree, by bluntnose minnows. The clams examined are primarily filter feeders, while bluntnose minnows are generally benthic detrital feeders (Scott and Crossmann, 1973). Levels of Mn, Fe, Co, Zn, Ca,

and P, in particular, were greatly elevated in clams relative to the species of pelagic fish. Several metals, measured in the clams and bluntnose minnows but below detection limits in the other species examined, emphasize the ability of these bottom dwelling organisms to accumulate substantial levels of metals. Many of the elements highly concentrated in the clams and bluntnose minnows also have high sediment concentrations, but are not accumulated in these organisms proportional to their sediment abundance.

The findings of high metal levels in organisms directly associated with the sediments inhabiting an uncontaminated site in this investigation agree with other studies. Mathis and Cumming (1973) measured the concentration of Cd, Cr, Co, Cu, Pb, Li, and Zn in various components of the Illinois River. They report highest metal concentration in sediments and in animals living in or on the sediments. Friant (1979) established that benthic molluscs and rooted plants accumulated metals in greater concentrations than either sediments or fish. Prosi (1979) also found that sediment dwelling organisms (Tubificidae) had greater metal concentrations of Cd, Pb, Zn, and Cu than other biota, including fish. Geisy and Weiner (1977) report no apparent biomagnification of Zn, Cu, Cr, Cd, and Fe between five species of freshwater fish from an uncontaminated reservoir in South Carolina. Windom *et al.* (1973) found that Cd, Cu and Zn levels in a number of marine fish species were inversely related to position in the food chain, while there was no apparent relationship with Hg.

The tissue concentration of most metals, therefore, appears to be more greatly influenced by association with bottom sediments rather than position in the food chain in aquatic organisms. Interpretation of previous biomagnification studies may have been masked by the fact that many organisms considered low on the food chain such as herbivores and detrital feeders are largely benthic dwellers, and so subject to sediment influence. Previously unrecognized analytical constraints of early multi-element analysis of biological samples should also be considered when comparing these data.

Mercury is the only element to exhibit clear biomagnification within the aquatic and terrestrial food chains. The species examined represent different feeding strategies and trophic levels. Bluntnose minnows are largely benthic detrital feeders, while smelt are pelagic planktonic feeding fish, and northern pike are top level predators. The concentration of Hg in tissues of fish eating birds was higher than Hg levels in the fish. These birds would generally feed on small fish which contain relatively low Hg levels. The Hg burdens found in these birds, therefore, represent substantial accumulation of Hg, especially in the liver, relative to food items. Food sources represent the only possible route of contaminant input to these organisms, unlike fish which can accumulate metals directly from the water (Rodgers and Beamish, 1981).

The concentration of Hg in the muscle tissue of the three mammal species examined indicates biomagnification of Hg in the terrestrial compartment of the ecosystem. Again, dietary intake represents the only possible source of metal uptake to these animals. The animals represent three different feeding types; herbivores, omnivores and carnivores. It has also been shown that Hg preferentially accumulates in the liver of raccoon and otter, and that these organisms may possess a detoxifying mechanism to deal with the

metal build-up (Wren *et al.*, 1980). A study by Smith and Rongstad (1981) reports levels of Cu ($12.0 \mu\text{g g}^{-1}$), Cd ($0.98 \mu\text{g g}^{-1}$), Ni ($42.0 \mu\text{g g}^{-1}$) and Hg ($9.4 \mu\text{g g}^{-1}$) in otter in Wisconsin which greatly exceed the concentration of these metals in otters from the Tadenac Lake area. In contrast, Zn levels in otter from Tadenac Lake were greater than Zn concentration ($14 \mu\text{g g}^{-1}$) in otter reported by Smith and Rongstad (1981). It must be pointed out that the latter study analyzed whole body homogenates, where our data represent muscle tissue metal levels only. Animals from the latter study were also collected from a mineralized area where metal levels are naturally elevated.

None of the other metals display a consistent pattern of biomagnification relative to trophic position in the food chain, although levels of Ni and S are elevated in the predatory fish species relative to other fish. In contrast, there is an apparent decrease in Zn concentration with increased trophic position among the aquatic species analyzed with freshwater clams containing the highest Zn concentration ($78 \mu\text{g g}^{-1}$), while bluntnose minnows, smelt and pike contain 60.2, 29.0, and $11.4 \mu\text{g g}^{-1}$ respectively. Levels of Cu in the piscivorous otter are approximately twice as high as Cu levels in muscle of beaver and raccoon. Copper concentrations are also much higher in the birds examined relative to fish Cu levels. It is difficult to attribute Cu accumulation in these species solely to biomagnification as they may represent normal tissue concentrations. Similarly, concentrations of Fe and Zn are uniformly elevated in the birds and mammals relative to Fe and Zn levels in fish. Since levels of these metals in the herbivorous beaver are comparable to levels in otter, the observed concentrations probably represent normal tissue levels. Comparison with other studies (Smith and Rongstad, 1981), however, suggests that metal levels in mammals can vary considerably between locations.

Despite recent widespread concern over Al levels in aquatic ecosystems (Grahm, 1980; Baker and Schofield, 1980; Nyholm, 1981) biomagnification of Al does not appear to occur in the aquatic food chain. Lake charr contained approximately the same level of Al as smelt, which constitute a major food item to charr in Tadenac Lake. Levels of Al in northern pike are also low. Aluminium levels are elevated in the coot and gulls examined relative to fish Al levels, but the Al level measured in the loon was low.

4.3. BIOACCUMULATION

Examination of the extent of bioaccumulation of the various metals in the white muscle of fish reveals a strong positive correlation of Hg concentration with age and size of the fish tested. These findings are consistent with other studies (Scott and Armstrong, 1972; Olsson, 1976). Although there is correlation of fish length with concentration of some other metals, namely Zn, Fe, S, and Mo, the correlations are weaker than for Hg and not consistent between species. Discrepancies between metal concentration relationships and fish size are also reported in the literature. Although we found a positive correlation ($r = 0.50$) between Zn levels and the length of northern pike, Geisy and Weiner (1977) report a negative correlation ($r = -0.52$) between Zn concentration and length of chain pickerel, and no correlation between length and concentration of Cd, Cr, Cu, or Fe. In a study of metal contaminated lakes in Manitoba, McFarlane and Franzin (1980) found increased concentrations of Cd, Cu, and Hg in pike liver related

to fish age and size, while only Cd levels increased with age and size of white suckers.

Bohn and McElroy (1976) report a negative correlation between Cu and Fe and length of cod. Cross *et al.* (1973), however, found no size dependent relation between the concentration of Cu, Fe, Mn, and Zn and length of two marine fish species. In a study of 36 metals in lake trout in Lake Cayuga, N.Y., Tong *et al.* (1974) found positive and negative correlations with fish age for Cr and Mo respectively. No other age dependent trends were reported, although Hg was not included in the study. Our data showed that Mo levels are generally consistent over the size range of pike sampled, and did not display the variability found with other metals. It has been proposed that small within species variation may occur in certain essential elements (Goodyear and Boyd, 1972) such as Co, Cu, and Zn, whose concentrations may be homeostatically regulated (Lucas *et al.*, 1970). Weiner and Geisy (1979) list Cu, Mn and Zn as essential trace metals whose fish levels are homeostatically controlled. They suggest that use of fish may not be appropriate as biological indicators of metal levels in ecosystems for certain elements such as Zn and Cu which are homeostatically controlled (Geisy and Weiner, 1977).

It is apparent that metal accumulation in fish tissue does not occur with increased age and size of a fish for most metals. Individual species may accumulate certain metals but these relationships cannot be generalized. Although Hg does regularly bioaccumulate in fish tissue exceptions to this have been reported (McFarlane and Franzin, 1980).

5. Summary

Geochemical sediment analysis showed that metal concentrations in Tadènac Lake are within the range generally accepted as background levels. Elevated sediment concentrations of Mn and Zn may be due to the presence of local sources of mineralization. It was established that aquatic organisms in contact with sediments can accumulate very high levels of certain metals relative to other species. The metal levels measured in benthic organisms may reflect natural sediment characteristics which should be taken into account when using such animals as biological indicators of contamination.

Our findings indicate that only Hg bioaccumulated in the fish species examined. Concentrations of Zn, S, Fe, and Mo, correlated with the length of some fish species, but not with others. Comparison of our data with the literature suggests that most metals do not accumulate with increased fish age or size. Some metal concentrations displayed considerable within species variation.

Mercury accumulated in higher trophic levels within the aquatic food chain, and also displayed biomagnification between three mammal species. Mercury concentrations in smallmouth bass, pike and lake charr, exceeded the government recommended safe level in this isolated lake. Fish-eating birds contained high levels of Hg, Cu, Fe, Zn, and to a lesser extent Al, relative to the fish examined. Dietary uptake represents the only source of metal uptake to both birds and mammals in comparison to fish which can accumulate metals directly from the water. The observed higher levels of some trace metals in birds and mammals relative to fish may represent normal biological retention of certain essential elements, rather than contaminant biomagnification. Further

research should be directed at examining metal levels in birds and mammals living in or around lakes which may be affected by increased metal loading.

In view of widespread concern regarding increasing metal loading to natural surface waters, this study represents a detailed examination of a single ecosystem which provides valuable data for comparison and application to further ecological studies.

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