Biomonitoring in the mercury-contaminated Wabigoon—English—Winnipeg River (Canada) system: selecting the best available bioindicator

J W Parks,*† P J Craig,* B P Neary,‡ G Ozburn§ and D Romani

* Department of Chemistry, Leicester Polytechnic, Leicester, UK LE1 9BH. ‡ Ontario Ministry of the Environment, Dorset, Ontario, Canada POA 1EO, § Lakehead University, Oliver Road, Thunder Bay, Ontario, Canada P7B 5E1 and || Ontario Ministry of the Environment, 435 St James Street South, Thunder Bay, Ontario, Canada P7C SG6

Several organisms used for biomonitoring in the mercury-contaminated Wabigoon-English River System, Ontario, Canada (sport fish, forage fish, crayfish and others) were examined for their utility as bioindicators. Causes for spatial and temporal variability in mercury concentrations in biota are reviewed. The significance of intertrophic and intratrophic biotic relationships is evaluated on both a site-specific and intersite basis. Larger mature fish are the most effective integrators as these organisms are the most buffered from site-specific and seasonal variations in mercury concentrations and bioavailability. Where there are no physical barriers preventing movement of biota between contaminated and uncontaminated parts of the watercourse, younger, smaller organisms can better - ical zones of tamination because of their restricted range. Because many organisms can provide information on mercury contamination, the choice of the most suitable indicator depends upon the purpose of the study, the pharmacokinetics of mercury uptake by the organisms in question, and the chemodynamics of methyl and inorganic mercury species in the field.

Keywords: Bioindicator, sport fish, forage fish, mercury, biomonitoring

INTRODUCTION

The discovery of elevated mercury concentrations in aquatic biota frequently leads to restrictions being issued on the suitability of consuming such

† Prepared while on leave from the Ontario Ministry of the Environment, Thunder Bay, Ontario, Canada. Author to whom correspondence should be addressed.

biota by the public. In many cases biomonitoring programs are established to provide contamination information on which organisms can be safely consumed.

In this work we examine biomonitoring in one contaminated watercourse; however, we believe many of the conclusions drawn here can be applied to other systems. The Wabigoon-English-Winnipeg River System (Ontario, Canada) is one of the more intensively studied watercourses anywhere with respect to identifying and quantifying the bioaccumulation, cycling and fate of mercury introduced into the aquatic environment.

Over 12 000 biota have been sampled^{1,2} since 1970 when elevated mercury levels were first observed in fish downstream of a chlor-alkali plant in Dryden, Ontario, Canada (Fig. 1). The Wabigoon–English–Winnipeg River System continues to recover from the discharge of an estimated 10 metric tons of mercury from the plant between 1962 and 1969.³

From a synthesis of available data, we suggest several options for improving the efficiency of sampling programs on this system by providing a framework to evaluate the significance and precision of the biological results. Finally the characteristics of indigenous organisms are compared with the characteristics of a hypothetical ideal bioindicator.

ORGANISMS EXAMINED

Many organisms have been used in field studies on the bioaccumulation of mercury in the Wabigoon-English-Winnipeg river system, including walleye (Stizostedion vitreum), 1.2,4-7

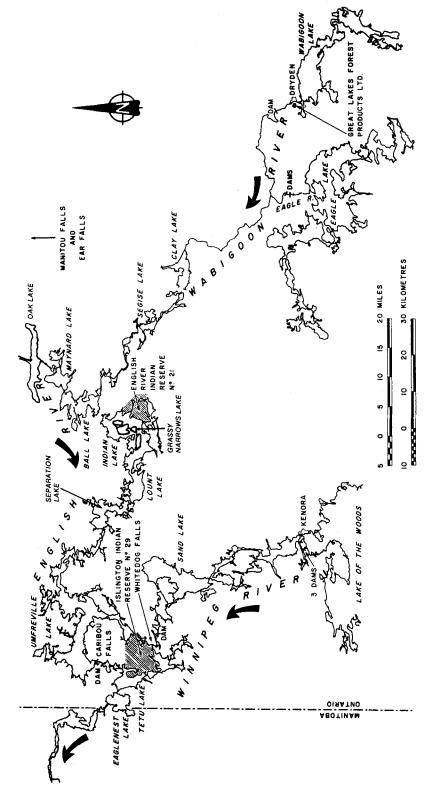


Figure 1. Sampling locations (lakes and rivers) on the Wabigoon-English-Winnipeg River System. Note that major influxes of 'clean' water occur at the Ball Lake junction of the English River and the Tetu Lake junction of the Winnipeg River System.

northern pike (Esox lucius), 1,2,4-6 yellow perch (Perca flavescens), 1,2,8-11 white sucker (Catostomus commersonii), 1,4,5 whitefish (Coregonus clupeaformis), 1,4,5 pearl dace (Margarita semotilus)⁸ and crayfish (Orconectes virilus). 2,3,10 Most of the mature northern pike walleye data and whitefish data for the 1980s originated from Ontario's Fish Contaminant Monitoring Program (e.g. Ref. 12). Data from all these studies provide the basis of the information used in this paper and from which the conclusions were derived.

FACTORS AFFECTING ACCUMULATION IN BIOINDICATORS

The accumulation of mercury in these aquatic organisms depends upon exposure as modified by organism- and species-specific factors such as growth, sex, breeding status, size, metabolism, life span, diet, and uptake and depuration rates. ^{13,14} Exposure is defined by both mercury concentrations and speciation in various abiotic and biotic components of the ecosystem. Methylmercury is particularly important as it is the form most prevalent in fish (approximately 85 %)¹³ and it is a potent neurotoxin. For the purposes of this work methylmercury in fish is taken to be synonymous with total mercury.

Mercury concentrations in abiotic compartments for this watercourse has been investigated for waters, 3,15-19 for sediments, 2,3,20,21 and for suspended sediments. Toncentrations in these compartments for much of the contaminated watercourse are governed directly or indirectly by mercury recycling from sediments contaminated by historical mercury loadings from a pulp and paper mill complex at Dryden. 18,19 At control sites total mercury concentrations are believed to be influenced by atmospheric loadings (e.g. Ref. 22).

Control sites are defined as main-stream waters 'upstream' of watercourses influenced by mill loadings. For the Wabigoon River System, Wabigoon and Eagle Lakes are considered to be control sites; for the English River, Maynard or Oak Lakes were considered to be control sites; and for the Winnipeg River System, Sand Lake was considered to be a control station.

Regardless of the source of mercury (sediments or atmosphere), methylmercury in water appears to be in a pseudo-equilibrium with the inorganic fraction.¹⁹ Methylmercury in water is also

believed to be the source of most mercury in top predatory sport fish, indirectly through the food web or through direct uptake across the gill. Mercury concentration data for many parts of various food webs are available from the biological studies mentioned above. Such data were used in this work.

DISCUSSION

Causes of variation in mercury concentrations in biota

For a given quantity of mercury cycling within an ecosystem, various biota accumulate very different levels of mercury. As an example, total mercury concentrations in biota in Clay Lake varied over four orders of magnitude (Fig. 2). In situations where changes in the net supply of mercury to the ecosystem are negligible, mercury accumulation in the biotic community forms a distinct pattern or 'structure' (i.e. Fig. 2) and average mercury concentrations for each population are stable on a year-to-year basis. For similar biological conditions and mercury loadings the measure of dispersion around this value is an indication of the variation in mercury bioavailability as mercury cycles through the water, suspended sediments, sediments and components of the food web.

At control sites, i.e. sites unaffected by anthropogenic point-source discharges, mercury concentrations in biota appear similar on a year-to-year basis, displaying no temporal trends. Total mercury concentrations for a standardized (60 cm northern pike) mature sport fish at any given control site were similar for various years sampled, fluctuating by less than $\pm 10\%$ from the mean values (Table 1). Fish were standardized for length to facilitate most accurate comparisons between samples.1 Temporal similarities in adult pike (60 cm) mercury concentrations are evident in sequential year samplings and when the sampling frequency exceeds the life spans of the organisms and results represent different generations. Overall the data suggest that mercury concentrations in the adult population of fish vary relatively little on a year-to-year basis. Yearling perch values tended to be somewhat more variable at some control sites (Table 2).

In other cases variation in mercury concentration in biota can be due to changes in the *net* J W PARKS ET AL

supply of mercury cycling within the contaminated watercourse. For example, the empirical biotic-abiotic relationships for mercury in this watercourse in conjunction with temporal trends for biota (discussed later) clearly suggest a dramatic decrease in mercury concentrations in the ecosystem since the reduction in point-source mercury loadings at Dryden.⁹

In yet other cases variations in mercury concentrations in biota in the contaminated watercourse can be traced to differences in the bioavailability of mercury to which biota are exposed. The bioavailability to young northern pike decreased by at least 70% at the inflow to Clay Lake in 1980.9 During this time there were extremely low water flows: dilution and assimilation of organic wastes from a pulp and paper complex was reduced by a factor of 5 and most of the upstream river was anoxic. Despite the presence of higher-thannormal inorganic and methylmercury levels in water at this time, 18,19 mercury concentrations in young fish were dramatically lower than in previous years¹⁰ because of the availability factors. Much of the inorganic mercury and methylmercury in water was believed to be associated or complexed with reduced sulphur compounds and less available for uptake by fish at this time.

Geographical trends

In general, mercury concentrations in biota show similar geographical trends (decreasing away from the point source) regardless of whether they were in a top predator (northern pike), a secondary consumer (yellow perch) or an omnivore (crayfish). Total mercury concentrations in biota in the Wabigoon River System trended as follows: (Clay Lake)>English River System Separation, Lount Lakes) > Winnipeg River (Tetu, Eaglenest Lakes) System>control sites (Fig. 3) Mercury concentrations in biota within each river system were usually comparable, as exemplified by results for Ball, Separation and Lount Lakes on the English River System. The geographical trend for some young organisms changed during atypical low flows which, as previously mentioned, altered mercury bioavailability in waters receiving industrial wastes at Dryden. During very low flows in 1980 the lowest mercury concentrations in young pike in the contaminated Wabigoon River System observed at Clay Lake inflow, with much higher levels noted downstream. 10 There was relatively little variation in mercury concentrations in biota at various control sites, as exemplified by average

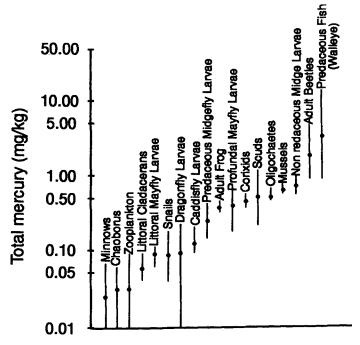


Figure 2. Comparative mercury concentrations in biota from Clay Lake. Lines and points refer to the range and geometric mean respectively. The data refer to 1970–1971. Modified from Ref. 3. Walleye data from Ref. 4.

Table 1. Mercury in standardized northern pike (*Esox lucius*) [60 cm] on system control lakes for multiple years collections Data standardized from log Hg vs log length regression, when P < .05 and $n \ge 10$. Data from Refs 1 and 2

Lake	Year	Mercury ($\mu g g^{-1}$)	Mean	
Wabigoon	1976	0.053	0.50	
U	1986	0.047		
Oak	1971	0.52	0.54	
	1975	0.56		
Sand	1974	0.60	0.59^{a}	
	1975	0.65		
	1976	0.53		
	1977	0.62		
	1978	0.62		
	1978	0.60		
	1979	0.57		
	1980	0.55		

^a Coefficient of variation = 6.9.

standardized pike (60 cm) values of 0.50, 0.54 and 0.59 mg g^{-1} for Wabigoon, Oak and Sand Lakes respectively.

Temporal trends

Substantial declines in mercury concentrations in biota are evident at all sites in the contaminated watercourse over time. As an example, concentrations for standardized adult northern pike (60 cm) for several sites are presented in Fig. 4. For any given site (e.g. Clay Lake), mercury concentrations in various biota have declined in a similar fashion. Results indicate that limited consumption of smaller fish of certain species from the most contaminated part of the system (Wabigoon River and Clay Lake) can now be advised. In the contaminated English River System most sizes of fish tested have been found to be increasingly suitable for consumption. 12

Developing and utilizing biotic relationships

The similarities in geographical and temporal trends suggest that relationships may exist between mercury levels in various biota on both a

Table 2. Mercury concentrations ($\mu g g^{-1}$) in yearling yellow perch (*Perca flavescens*) in the Wabigoon–English–Winnipeg River System. Each result is usually the mean of at least five samples with at least five fish composited per sample. Data for 1978 from Ref. 8, for 1979–1981 from Ref. 10, and for 1982–1984 from the Water Resources Unit, Ministry of the Environment, Northwestern Region, Thunday Bay.

	Year								
Site	1978	1979	1980	1981	1982	1983	1984		
Wabigoon Lake ^a	0.03 ± 0.01	0.03 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.08 ± 0.01	0.02 ± 0.01	0.02 ± 0.01		
Eagle River ^a		0.03 ± 0.01	0.03 ± 0.01	0.02 ± 0.01	0.03 ± 0.005	0.03 ± 0.01	0.05 ± 0.01		
Wabigoon River at Rugy Cr							0.16 ± 0.04		
Wabigoon River at Hwy 105						0.77 ± 0.07	0.35 ± 0.04		
Clay Lake inflow	0.41 ± 0.04	0.30 ± 0.06	0.18 ± 0.05	0.55 ± 0.07	0.42 ± 0.04	0.32 ± 0.07	0.24 ± 0.02		
Clay Lake outflow	0.45 ± 0.10	0.38 ± 0.06	0.34 ± 0.05	0.49 ± 0.06	0.58 ± 0.05	0.30 ± 0.04	0.21 ± 0.03		
Wabigoon River at Ball Lake inflow									
(contaminated inflow)		0.37 ± 0.07	0.34 ± 0.06	0.33 ± 0.06	0.38 ± 0.01	0.15 ± 0.02	0.13 ± 0.02		
English River at Ball Lake inflow									
(Maynard Lake) ^a									
(clean inflow)		0.09 ± 0.01	0.02 ± 0.01	0.01 ± 0.0	0.04 ± 0.01	0.03 ± 0.01	0.04 ± 0.01		
Ball Lake outflow		0.09 ± 0.02	0.04 ± 0.01	0.14 ± 0.01	0.16 ± 0.02	0.07 ± 0.01	0.16 ± 0.04		
Lount Lake					0.16 ± 0.02	0.11 ± 0.01	0.08 ± 0.01		
Umferville Lake					0.08 ± 0.02	0.05 ± 0.02	0.06 ± 0.01		
Umferville Lake below dam,									
upstream of Winnipeg River					0.11 ± 0.01	0.04 ± 0.01	0.06 ± 0.01		
Eaglenest Lake					0.08 ± 0.01	0.05 ± 0.01	0.05 ± 0.01		
Sand Lake ^a					0.05 ± 0.01	0.04 ± 0.005	0.04 ± 0.01		

^a Control sites—not impacted by point-source discharges of mercury.

J W PARKS ET AL

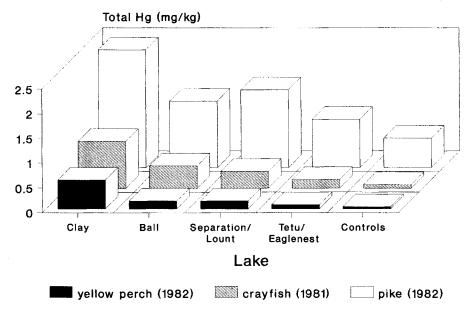


Figure 3. Geographical trends for adult northern pike (Esox lucius), 2 yearling yellow perch (Perca flavescens) (Table 2), and crayfish (Orconectes virilis) 10 for the Wabigoon River System (Clay Lake), English River System (Ball, Separation, Lount Lakes), and the Winnipeg River System (Tetu, Eaglenest Lakes).

site-specific and watercourse basis (see below). In previous publications, 9,10 relationships between certain organisms on a geographic basis were presented. Here we extend those observations by examining site-specific relationships developed by

pairing results from a single site for biota collected in different years as mercury concentrations in the ecosystem declined over time.

Relationships between mercury concentrations in mature northern pike and walleye taken at the

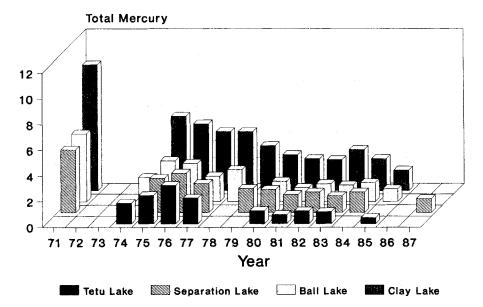


Figure 4. Temporal trends for total mercury for adult northern pike (*Esox lucius*) standardized to 60 cm, for four sites in the Wabigoon—English—Winnipeg River System, 1971–1987: Wabigoon River System, Clay Lake; English River System, Ball, Separation Lakes; Winnipeg River System, Tetu Lake. Data from Refs 1, 2 and 11.

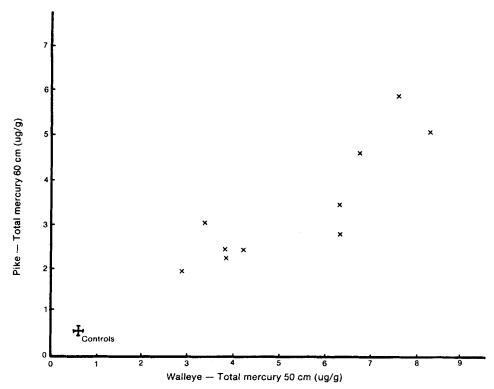


Figure 5. Mercury concentrations in northern pike (60 cm) and walleye (50 cm) sampled in different years, 1970–1986, from Clay Lake. Mean and range of three major streams on system control lakes are also included. Data from Refs 1, 2 and 11.

same time are presented for the Wabigoon River System (Clay Lake) in Fig. 5 and for the English River System (Separation Lake) in Fig. 6. Analogous data for other species (Ministry of the Environment, unpublished) suggests that significant relationships exist between mercury concentrations between all organisms examined for this

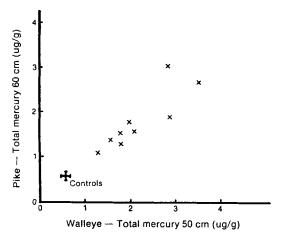


Figure 6

watercourse. These data suggest that there would be no major loss in information in this biomonitoring program if organism(s) and sites for collection were reduced, provided that the form of the relationship was known.

Thus, although differences in mercury concentrations in various organisms for a given lake can easily range over several orders of magnitude (Fig. 2), changes in the concentrations in one standardized organism could be used to predict the changes in many others by using plots such as those in Figs 5 and 6. These biological relationships can also have great utility in modelling, given the difficulties in quantifying cause and effect for mercury accumulation in any single species. These observations also suggest that many organisms have utility as bioindicators. Developing these relationships could provide a powerful approach to reducing costs associated with a biomonitoring programme.

Selecting the best available bioindicator

The characteristics of good bioindicators have been outlined, for example by Phillips.¹⁴

J W PARKS *ET AL*

Briefly, these characteristics include:

- (a) the organisms should accumulate the pollutant without mortality at the levels encountered in the environment;
- (b) the organisms should be representative of the study area;
- (c) the organisms should be abundant throughout the study area;
- (d) the organisms should be sufficiently longlived to allow the sampling of one or more years class if desired (i.e. fish of different ages);
- (e) the organisms should be of sufficient size to give adequate tissue for analysis;
- (f) the organisms should be easy to sample and hardy enough to survive in the laboratory.

Young of the year or yearling northern pike, yearling perch and crayfish meet many of these proposed criteria.¹⁰

We also believe that an indicator should provide data which are directly related to human health (i.e. they should be from fish which are consumed), show rapid response to environmental changes, and provide a high degree of confidence (robustness) that the effect was due to the environmental changes being investigated.

Although young organisms are not directly related to human health (i.e. they are not eaten), it is clear that a relationship between mercury levels in young fish and older larger fish of the same species can be established.⁹

Young fish are more restricted in their movements in comparison with larger organisms. ¹⁰ Frequently, in this system, young pike and yearling perch are believed to spend essentially their entire life to that age in isolated nurseries that are perhaps no greater than 100 or 200 m in span. ¹⁰ This restriction in habitat greatly simplifies the sampling of other ecosystem variables (e.g. waters) in order to infer cause and effect. ⁹

Larger mature sport fish can range much further (up to many kilometers or more), 10 necessitating more work and expense to obtain exposure data, if such data can be obtained at all. In most monitoring cases the geographic habitat and seasonal movements for various mature sport fish stocks are unknown. This uncertainty causes difficulty when making decisions on where to sample other ecosystem variables. It can become extremely difficult in open systems where mature fish can move easily between habitats characterized by different mercury concentrations and/or bioavailability. Ball Lake on the English River

System is one such example. In this case young biota were particularly useful in measuring the importance of mercury in various inflows (Table 2), because they do not move so far.

With young fish, contaminant uptake is more rapid; consequently they are very responsive to environmental changes, which in this system can be large. For example, methylmercury concentrations in water typically fluctuated over an order of magnitude at many sites on a seasonal basis.¹⁹

Adult fish, because of their extended exposure periods, are better buffered from the effects of short-term environmental changes than young fish. This buffering is evident at control sites. The maximum fluctuation between years in mercury concentrations in 60 cm adult pike (approximately five years old) never changed by more than 23% (Table 1) while yearly fluctuations in 16 cm pike (a few months old) sometimes exceeded 300 %. 10

Thus, insofar as the accuracy of long-term temporal trends (years) are concerned, older larger adult fish appear to be the most robust indicators.

While adult fish are less responsive than young biota, they are clearly more relevant to human health, since movement of methylmercury into man is by way of consumption of contaminated adult fish.

When considering indicator organisms, other factors such as the collection of organisms must also be taken into account. Although widely distributed along the system, young pike are not as abundant as crayfish and perch, are more solitary in their habits, and generally inhabit weedy littoral areas that are difficult to sample effectively by seining. More time and effort are required to secure adequate samples of young pike than are required for crayfish and perch. Yellow perch is an abundant schooling species which shows less variation in growth rate and can be conveniently segregated into age groups. By pooling several fish of the same species to form one sample for analysis, estimates of average mercury levels are more robust. Collections of larger fish (e.g. walleye, pike, whitefish, suckers) did take more time and effort in most cases than did the young fish or crayfish collections).

CONCLUSION

Overall the data suggest different organisms do have different values as bioindicator organisms in terms of responsiveness, robustness and ease of collection.

In the Wabigoon/English/Winnipeg River System, standardized samples of adult walleye and pike probably provide the most precise data for temporal trends as well as information on appropriate consumption limits. The validity of the data generated is increased if sampling is designed to ensure that the same discrete population is sub-sampled regularly. Data for adult biota can also be used to determine geographical areas of mercury contamination, provided that the population range is suitably known. Younger organisms, because of their restricted habitat, are particularly useful in delineating local geographical effects and are very responsive to environmental changes. Young organisms can thus provide rapid feedback on the effectiveness of amelioration measures.

We suggest that there is no single ideal indicator, but rather the choice of indicator must be matched to the requirements of the investigator, bearing in mind the pharmacokinetics of mercury uptake in the organism and the chemodynamics of mercury and its species *in situ*.

Acknowledgements The leave for J W Parks was made possible by an IRAP (National Research Council Canada) contract with DAMSA for modelling mercury in aquatic systems. The concepts developed in this paper do not necessarily reflect either the views of or endorsement by the Ministry of the Environment. We thank K Suns for review comments.

REFERENCES

- Bishop, J N and Neary, B P Mercury levels in fish from Northwestern Ontario, 1970–1975. In: Report of Laboratory Services Branch, Ontario Ministry of the Environment, Toronto, Ontario, 1976, p 84
- Parks, J W, Sutton, J A and Hollinger, J D 1984. Mercury contamination of the Wabigoon/English Winnipeg River System—causes, effects and possible remedial measures, pp 1-352. In Mercury pollution in the Wabigoon/English River system of northwestern Ontario and possible remedial measures. Final Rep. of the Steering Committee. Vol. 1 and 2. Published by Government of Canada (Dep. of Environment) and Government of Ontario (Ministry of the Environment). 570 pp.
- Armstrong, F A J and Hamilton, A L Pathways of mercury in a polluted Northwestern Ontario Lake. In: Trace Metals and Metal-Organic Interactions in Natural Waters, Singer, P C (ed). Ann Arbor Science Publishers, Ann Arbor, MI, 1973, pp 131-156

- Scott, D P and Armstrong, F A J J. Fish. Res. Board Can, 1972, 29: 1685.
- 5. Scott, D P J. Fish. Res. Board Can, 1974, 31: 1723
- Armstrong, F A J and Scott, D P J. Fish. Res. Board Can., 1979, 36: 670
- 7. Parks, J W and Hamilton, A L *Hydrobiologia*, 1987, 149: 159
- Curry, C and Suns, K A young fish survey of the Wabigoon River/Clay Lake System, 1978. In: Mercury Pollution in the Wabigoon/English River System of Northwestern Ontario and Possible Remedial Measures: A Progress Report, Jackson, T A (ed), Government of Canada (Dept of Environment) and Government of Ontario (Min. of Environment), 1980, p 4
- 9. Parks, J W Water, Air and Soil Pollution, 1988, 42: 267
- Parks, J W, Curry, C, Romani, D and Russell, D D Environmental Monitoring and Assessment, in press
- Water Resources Unit, Ontario Ministry of the Environment, Northwestern Region, Thunder Bay, Ontario unpublished data
- OMOE/OMNR Guide to Eating Ontario Sportfish, Water Resources Branch, Ontario Min. of Environ., Toronto, 1988
- 13. Huckabee, J W, Elwood, J W and Hildebrand, S G Accumulation of mercury in freshwater biota. In: The Biogeochemistry of Mercury in the Environment, Nriagu, J O (ed), Elsevier/North-Holland Biomedical Press, New York, 1979, pp 277-301
- 14. Phillips, D J H Quantitative Aquatic Biological Indicators: Their Use to Monitor Trace Metal and Organochlorine Pollution, Applied Science Publishers, London, 1980, p 487
- Jackson, T A, Parks, J W, Jones, P D, Woychuk, R N, Sutton, J A and Hollinger, J D Hydrobiologia, 1982, 92: 473
- Rudd, J W M, Turner, M A, Townsend, B E, Sick, A and Furitani, A Can. J. Fish Aquat. Sci., 1980 37: 848
- Rudd, J W M and Turner, M A Can. J. Fish Aquat. Sci., 1983, 40: 2218
- Parks, J W, Sutton, J A and Lutz, A Can. J. Fish. Aquat, Sci., 1986, 43: 1426
- Parks, J W, Lutz, A, Sutton, J A and Townsend, B E Can. J. Fish Aquat. Sci., 1989, 46: 2184
- 20. Parks, J W Mercury in Sediment and Water in the Wabigoon/English River System, 1970-75, Ontario Ministry of the Environment Tech. Rept, 1976, available from Chief, Water Resources Assessment, Ontario Ministry of the Environment, Thunder Bay, Ontario
- 21. Jackson, T A and Woychuk, R N The biogeochemistry and distribution of mercury in the Wabigoon River System. In: Mercury Pollution in the Wabigoon/English River System of Northwestern Ontario and Possible Remedial Measures: A Progress Report, Jackson T A (ed), Government of Canada (Dept of Environment) and Government of Ontario (Min. of Environment), 1980, p 28
- 22. Johnson, M G Can. J. Fish Aquat. Sci., 1987, 44: 3