Government of Canada
Gouvernement du Canada

Ontario

Mercury Pollution in the Wabigoon-English River System of Northwestern Ontario, and Possible Remedial Measures

A Progress Report for 1978-1979 Prepared by the Committee

80

Wabigoon-English River Mercury Study
Steering Committee

The Honourable John Roberts, M.P.,
Minister of the Environment,
OTTAWA

The Honourable Harry Parrott, M.L.A.
Ontario Minister of the Environment,
TORONTO

The Honourable James A.C. Auld, M.L.A.,
Ontario Minister of Natural Resources,
TORONTO

Gentlemen:

The Steering Committee of the Canada-Ontario Wabigoon-English River Mercury Study submits to you this interim progress report on Mercury Pollution in the Wabigoon-English River System of Northwestern Ontario, and Possible Remedial Measures.

Respectfully submitted,

CANADA

R. J. Allan
Dr. R. J. Allan
Co-chairman

Dr. R. D. Hamilton

Mr. K. Shikaze

ONTARIO

D. M. Jeffs
Mr. D. Jeffs
Co-chairman

T Brydges
Dr. T. Brydges

Douglas P. Dodge
Dr. D. Dodge

MERCURY POLLUTION IN THE
WABIGOON-ENGLISH RIVER SYSTEM
OF NORTHWESTERN ONTARIO,
AND POSSIBLE REMEDIAL MEASURES:
A PROGRESS REPORT

Edited by

Togwell A. Jackson

April, 1980

FOREWORD

The research treated in this report was financed equally by the governments of Canada and Ontario in accordance with a special agreement drawn up under the terms of the Canada Water Act. The work of Jackson and Woychuk, Wilkins and Irwin, and Curry and Suns was supported under regular programs of their respective agencies.

This interim report contains progress reports on individual components of the study. The overview of the investigations and results given in the introduction and discussion chapters provides a basis for review and consideration of the findings of the first year's work. The overall results of the investigations during 1978, 1979, and the winter and spring of 1980 will be given subsequently in a final report of the Wabigoon-English River Mercury Study Steering Committee.

TABLE OF CONTENTS

INTRODUCTION: THE PROBLEM OF MERCURY POLLUTION IN THE WABIGOON-ENGLISH RIVER SYSTEM

by

Togwell A. Jackson[1]

J. W. Parks[2]

J. W. M. Rudd[3]

[1] Department of the Environment
Freshwater Institute
501 University Crescent
Winnipeg, Manitoba, R3T 2N6

[2] Ontario Ministry of the Environment
(Northwestern Region)
Ontario Government Building
P. O. Box 5000
Thunder Bay, Ontario, P7C 5G6

[3] Department of Fisheries and Oceans
Freshwater Institute
501 University Crescent
Winnipeg, Manitoba, R3T 2N6

The Wabigoon-English-Winnipeg River system of Northwestern Ontario and eastern Manitoba has the dubious distinction of being one of the more severely polluted waterways of Canada (Armstrong and Hamilton, 1973). This report is primarily concerned with mercury pollution in the river system and its associated lakes, and with the evaluation of methods which might be employed to cope with it. In order to put the problem in perspective, it would be useful at this point to give a brief description of the river-lake system and its environs, as well as an historical sketch of the pollution problem and a review of the available literature on the subject.

Spilling out of Wabigoon Lake in Northwestern Ontario, the Wabigoon River flows through the town of Dryden, widening out about 53 miles further downstream to form Clay Lake, and finally enters Ball Lake, where it becomes one with the English River. The English River, in turn, flows through a chain of lakes and finally merges with the Winnipeg River, which empties into the south basin of Lake Winnipeg more than 100 miles west of Dryden. This vast river-lake system stretches across a sparsely populated land of boreal forest, low relief, and Precambrian granitic rock and greenstone belts overlain by patches of Pleistocene glacio-lacustrine clay and sandy till. Located on the banks of the English River downstream from Ball Lake, and at the confluence of the English and Winnipeg Rivers, are the Ojibway communities of Grassy Narrows and White Dog, respectively. The people of these bands used to fish the waters of the river-lake system for commercial gain as well as for their own dinner tables, and the lakes have been popular among visiting sport fishermen. The economy of the region as a whole depends heavily on tourism and the pulp-and-paper industry.

The principal sources of pollution in the river-lake system are a paper mill and chlor-alkali plant at Dryden (German, 1969; Armstrong and Hamilton, 1973; Fimreite and Reynolds, 1973; Troyer, 1977). This industrial complex is presently operated by the Dryden Mill Division of the Great Lakes Forest Products Company but was called Reed, Ltd., from 1970 to 1979, and was known as Dryden Paper, Ltd., before 1970.

The paper mill has been discharging organic wastes into the Wabigoon River since its construction in 1913 (German, 1969). Consequently, the riverbed between Dryden and the village of Quibell (near the inflow to Clay Lake) is largely covered with a blanket of putrefying wood fragments and scum, and floating masses of foam together with heavy loads of suspended debris may be seen in the water. Effluent from the municipal sewage treatment plant is also released into the river following primary and secondary treatment (German, 1969). The mercury pollution was mostly derived from the effluents of the chlor-alkali plant (Armstrong and Hamilton, 1973; Fimreite and Reynolds, 1973). From 1962 to 1970 unrestricted quantities of mercury amounting to approximately 9-11 metric tons (about 20,000 lbs.) were released into the river; but from 1970 to 1975, under pressure from the Ontario government, the mercury outputs were reduced by waste-treatment procedures, and in 1975 the use of mercury in the plant was discontinued (Bishop and Neary, 1976). The distribution of mercury in the sediments of the system has been studied by Armstrong and Hamilton (1973), Parks (1976), and Jackson (1979).

The mercury pollution has had pronounced and far-reaching ecological effects, causing fish populations throughout the river-lake system from Dryden at least as far downstream as the Manitoba border to have mercury levels well over 0.5 parts per million (ppm), the limit for edible fish marketed in Canada (as set forth in the Federal Food and Drug Directorate) (Kenney, 1972; Scott and Armstrong, 1972; Armstrong and Hamilton, 1973; Fimreite and Reynolds, 1973; Annett _et al._, 1975; Bishop and Neary, 1976). Mean mercury levels in pike were found to be consistently greater than 2.0 ppm from Clay Lake (the first lake downstream from Dryden) all the way to Tetu Lake (at the confluence of the English and Winnipeg Rivers), whereas pike in "off-system" lakes were invariably found to range from less than 0.5 to 2.0 ppm (Bishop and Neary, 1976). Other aquatic organisms too have been affected (Armstrong and Hamilton, 1973; Vermeer et al., 1973; Annett et al., 1975). Since controls were imposed on the mercury discharges, mercury levels in fish have declined somewhat (Armstrong and Scott, 1979), although they remain too high for human consumption. The effect of age, growth rate, and condition of Clay Lake fish on mercury concentrations in their flesh was investigated by Scott (1974).

The mercury pollution has had a serious impact on certain human populations in the region, especially the Ojibway Indians of the Grassy Narrows and White Dog bands. When it was learned that the fish in the river-lake system had mercury concentrations exceeding 0.5 ppm, all commercial fishing in the affected area was banned. This was a severe economic setback for the Ojibways. The mercury has also posed a more direct threat to the health of the Ojibway people owing to their customary reliance on locally caught fish as a source of protein. The band members have been urged to stop eating the contaminated fish, and the Ontario government has been providing the communities with uncontaminated frozen fish free of charge (Wheatley, 1979).

Medical surveys conducted between 1971 and 1978 (Health and Welfare Canada, 1973; Clarkson, 1976; Wheatley, 1979) showed that some individuals in both communities had blood mercury levels exceeding 100 parts per billion (ppb), even in the winter (when blood levels should be lowest owing to reduced consumption of fish). The highest levels were generally in the range 200-500 ppb, but the maximum value recorded was 660 ppb. At blood levels above 100 ppb, a human adult is considered to be "at risk," and symptoms of methyl mercury poisoning (Minamata disease) may first be seen in the most sensitive 5% of adults whose blood levels are in the range 200-500 ppb. Unborn children, however, are more sensitive than adults (Wheatley, 1979; Wheatley et al., 1979). Out of 40 "at risk" individuals in Northwestern Ontario who submitted to clinical examination, none were found to have unequivocal symptoms of mercury poisoning as of December 31, 1978, although 10 of them had neurological abnormalities which are possibly attributable to it. The uncertainty arises from the fact that symptoms of mild forms of Minamata disease are similar to those of various other conditions, thus making conclusive diagnosis difficult (Wheatley, 1979; Wheatley et al., 1979).

Although commercial fishing was banned, sport fishing continued to be permitted, the Ontario government providing information to the public on the danger of eating the contaminated fish. Ojibways employed as guides by owners of fishing lodges catering to sportsmen may be particularly vulnerable to chronic mercury poisoning owing to their practice of joining the customers in the consumption of "shore lunches" composed of freshly caught fish.

A layman's account of social, political, economic, and medical aspects of the mercury problem has been published by Troyer (1977).

Whereas different government-employed scientists had been studying the pollution of the river-lake system for several years, the Federal government and the government of Ontario decided in 1978 to undertake a coordinated joint investigation of the problem with the ultimate objective of finding a practical solution. Thus, on June 5, 1978, a one-year cost-sharing agreement was reached in accordance with the terms of the Canada Water Act.

Each of the two governments agreed to contribute $50,000 to the study, and a team of Federal and provincial scientists and technicians was selected for the task. The project was to cover the biogeochemistry and pathways of mercury, an assessment of the sources, distribution, and transport of methyl mercury and other forms of mercury in the system, and an evaluation of possible anti-pollution procedures. A year later the agreement was renewed for one additional year, and $100,000 was contributed by each government.

This interim report primarily covers the results of the first year's work. Upon completion of the second year's work, a comprehensive final report will be prepared.

REFERENCES

Annett, C. S., D'Itri, F. M., Ford, J. R., and Prince, H. H., 1975, Mercury in fish and waterfowl from Ball Lake, Ontario: Jour. Environmental Quality 4: 219-222.

Armstrong, F. A. J., and Hamilton, A. L., 1973, Pathways of mercury in a polluted Northwestern Ontario lake: In Singer, P. C. (ed.), Trace Metals and Metal-Organic Interactions in Natural Waters. Ann Arbor Science Publishers, Ann Arbor, Mich., p. 131-156.

Armstrong, F. A. J., and Scott, D. P., 1979, Decrease in mercury content of fishes in Ball Lake, Ontario, since imposition of controls on mercury discharges: Jour. Fisheries Research Board Canada 36: 670-672.

Bishop, J. N., and Neary, B. P., 1976, Mercury levels in fish from Northwestern Ontario, 1970-1975; Unpubl. report, Laboratory Services Branch, Ontario Ministry of the Environment.

Clarkson, T. W., 1976, Exposure to methyl mercury in Grassy Narrows and White Dog reserves: Interim Report, Canadian Dept. of Nat. Health and Welfare.

Fimreite, N., and Reynolds, L. M., 1973, Mercury contamination of fish in Northwestern Ontario: Jour. Wildlife Management 37: 62-68.

German, M. J., 1969, Water pollution survey of the Wabigoon River: Report of the Ontario Water Resources Commission.

Health and Welfare Canada, 1973, Final report of task force on organic mercury in the environment (Grassy Narrows & White Dog, Ontario: Report of Canadian Dept. of Nat. Health & Welfare (Health & Welfare Canada)).

Jackson, T. A., 1979, Sources of heavy metal contamination in a river-lake system: Environmental Pollution 18: 131-138.

Kenney, A. R., 1972, Total mercury and methyl mercury in fish organs: In Uthe, J. F. (ed.), Mercury in the aquatic environment: A summary of research carried out by the Freshwater Institute 1970-1971: Fisheries Research Board of Canada Manuscript Report Series no. 1167, p. 40-45.

Parks, J. W., 1976, Mercury in sediment and water in the Wabigoon-English River system: Report of Ontario Ministry of the Environment.

Scott, D. P., 1974, Mercury concentration of white muscle in relation to age, growth, and condition in four species of fishes from Clay Lake, Ontario: Jour. Fisheries Research Board Canada 31: 1723-1729.

Scott, D. P., and Armstrong, F. A. J., 1972, Mercury concentration in relation to size in several species of freshwater fishes from Manitoba and Northwestern Ontario: Jour. Fisheries Research Board Canada 29: 1685-1690.

Troyer, W., 1977, No Safe Place: Clarke & Irwin, Ltd., Toronto & Vancouver.

Vermeer, K., Armstrong, F. A. J. and Hatch, D. R. M., 1973, Mercury in aquatic birds at Clay Lake, Western Ontario: Jour. Wildlife Management 37: 58-61.

Wheatley, B., 1979, Methylmercury in Canada: Report of the Medical Services Branch, Department of National Health and Welfare (Ottawa, Canada).

Wheatley, B., Barbeau, A., Clarkson, T. W., and Lapham, L. W., 1979, Methylmercury poisoning in Canadian Indians--The elusive diagnosis: Canadian Jour. Neurological Sciences 6: 417-422.

DISCUSSION, WITH TENTATIVE CONCLUSIONS AND RECOMMENDATIONS, BASED ON RESULTS OF THE 1978-1979 STUDY OF MERCURY IN THE WABIGOON RIVER SYSTEM

by

T. A. Jackson[1]

J. W. Parks[2]

J. W. M. Rudd[3]

[1] Department of the Environment
Freshwater Institute
Winnipeg, Manitoba

[2] Ontario Ministry of the Environment (Northwestern Region)
Thunder Bay, Ontario

[3] Department of Fisheries and Oceans
Freshwater Institute
Winnipeg, Manitoba

SUMMARY OF TENTATIVE CONCLUSIONS

1) Concentrations of total and methyl mercury in the sediment, water, and biota are above background levels at all study sites between Dryden and Ball Lake. Elevated mercury levels are due principally to contamination of sediments by pre-1971 discharges and subsequent plant effluents from the pulp and paper industrial complex at Dryden.

2) The industrial complex continues to discharge appreciable quantities of mercury into the river. Although the present loading from this complex amounts to 1% of the previous uncontrolled discharges, it is still five times the natural mercury loading above Dryden. This loading, a cause for concern, is expected to be reduced by modernization at the Dryden mill and by the installation of improved wastewater treatment facilities scheduled for implementation by December, 1980, and December, 1983.

3) Mercury methylation occurs mainly in the surface sediment and water column. Mercury in the Wabigoon River between Dryden and Clay Lake is being actively methylated. Older mercury deposits buried in the sediments of Clay Lake are probably not a significant source of bio-available mercury at the present time. Mercury currently being transported into Clay Lake by the Wabigoon River contributes considerably to the present-day problem.

4) Mercury in fish in the watercourse will exceed the guidelines for human consumption for several decades. Remedial measures examined in this study show a potential for accelerating recovery; but from the standpoint of the rate, extent, and cost of restoration, even the more promising methods appear to have limitations which are not altogether predictable.

To facilitate use of the main text, the principal conclusions and interpretations (with reference to the appropriate reports), are described in more detail as follows:

(1) The Reed plant has been the major source of mercury contamination in the Wabigoon River system. Total- and methyl-mercury concentrations in water and fish are higher in the Wabigoon system downstream from Dryden than in unpolluted headwaters upstream from Dryden or in unpolluted tributaries (Parks _et_ _al_.; Curry and Suns).

(2) The effluents from the Great Lakes Forest Products (formerly Reed) plant still contain appreciable quantities of mercury (Parks _et_ _al_.; Wilkins), despite the fact that the use of mercury was discontinued in 1975. Although the present mercury loadings from this plant into the Wabigoon River amount to 1% of the uncontrolled loadings discharged in the past, they are five times the natural mercury loadings.

(3) Methylation is occurring in the largely organic surficial sediments of the riverbed, and possibly in the water column, of the river between Dryden and Clay Lake (Jackson and Woychuk; Parks _et_ _al_.; Rudd _et_ _al_.). Release of methyl mercury and other forms of mercury from these river sediments into the overlying water continues to cause mercury contamination in Clay Lake (Parks _et_ _al_.; Rudd _et_ _al_.; Jackson and Woychuk; Curry and Suns). Total and methyl mercury loadings to Clay Lake are intensified by erosion during the spring flood but are greatest during the summer, owing perhaps to accelerated microbial activity. Loading from newly sedimented material in Clay Lake and Ball Lake to the overlying hypolimnion water also appears to be important, particularly during the summer (Parks _et_ _al_.; Jackson and Woychuk). The autumn overturn in Clay Lake brings hypolimnion mercury accumulations

to the surface, whence they may be partially flushed downstream (Parks et al.). Nearly half of the annual load of mercury to Clay Lake from the Wabigoon river was retained in the lake; but there was no net retention of methyl mercury (Parks et al.). During the study period, the Wainwright Reservoir had no net effect on total mercury loadings in the river, and appears to have had no effect on methyl mercury loadings (Parks et al.). Nevertheless, preliminary calculations suggest that at least one metric ton of mercury has accumulated in the thick deposit of decomposing wood particles trapped between the paper mill and the dam (Jackson and Woychuk).

(4) Inorganic mercury introduced into Clay Lake water from the Wabigoon River is readily transformed, in part, into methylated forms which can be accumulated by fish (Rudd et al.). The reactions occur in the flocculated ooze at the sediment-water interface, and/or in the water column, and do not depend on the presence of the clay-silt mud underlying the ooze (Rudd et al.). Possibly the rate of mercury uptake by fish could be reduced by suppressing primary production, by adding dissolved selenium salts, or by increasing the concentration of suspended clay (Rudd et al.).

(5) Methyl mercury levels in surficial bottom sediments of the Wabigoon River system appear to depend primarily on environmental factors (pH, nutrients, sulfide, iron-manganese oxides, chloride, cation exchange sites, and microbial activities involving methionine biosynthesis) rather than total mercury supply (Jackson and Woychuk). Although total mercury concentrations in sediments decline sharply from Dryden to Ball Lake, methyl mercury levels remain relatively high throughout, and even increase from Clay Lake to Ball Lake. In general, chemical speciation of the sedimentary mercury varies systematically with distance downstream from the source of pollution,

reflecting a gradational transition from the deposits of rotten wood and slime near Dryden to the clay-silt mud and associated iron-manganese oxides and humic matter which predominate in Ball Lake. Methyl mercury from lake sediments is probably more available to bottom-feeding fish than to pelagic fish; pelagic species (e.g. walleye) may be more strongly affected by the mercury transported into the lakes by river water.

(6) According to Federal and Provincial studies, mercury levels in Clay Lake fish and crayfish have been declining exponentially since 1970, when the unregulated discharge of mercury into the river was halted. However, the rate of decline is now so gradual that fish in this lake are expected to continue to exceed the guidelines for human consumption for a long time -- probably for many decades -- unless effective remedial measures can be taken.

(7) About 5 metric tons of mercury, comprising 50% of the total quantity discharged, are estimated to have accumulated in sediments deposited between the plant at Dryden and the outflow of Clay Lake, and approximately 2 to 3 of these tons of mercury are in the riverbed upstream from Clay Lake (Jackson and Woychuk; Wilkins).

DISCUSSION OF POSSIBLE REMEDIES

From the work done thus far, it is clear that any measures taken to restore the lakes would be doomed to failure unless they included an effective procedure for preventing the release and downstream transport of methyl mercury and other forms of mercury from the contaminated organic sediments blanketing the riverbed between Dryden and Clay Lake and from the Great Lakes Forest Products effluent. However, this would not necessarily bring the mercury problem rapidly to an end; some degree of mercury pollution would continue to exist in the lakes of the system for an unknown period of time, inasmuch as the surface sediments of these lakes (and the intervening stretches of river) are themselves secondary sources of bio-available mercury. In addition, the plant at Dryden is still discharging some mercury to the system. At present we lack sufficient information to evaluate each amelioration technique in terms of the time it would take to lower the mercury concentrations of fish populations to safe, acceptable levels, partly because we still do not know to what extent the mercury in the water and biota of a given lake is derived from (1) the river-lake system upstream from it, (2) present mercury loadings from the plant at Dryden, and (3) the bottom sediments of the lake itself. Nevertheless, the available data on the distribution of mercury in water, sediments, and biota do suggest that river-borne mercury is of particular importance to pelagic fish, and that removal or immobilization of the mercury in the riverbed upstream from Clay Lake should accelerate reduction of the mercury levels in these fish.

Although further research is needed for a full evaluation of possible remedial measures, we are now in a position to discuss the different options in terms of their relative effectiveness and feasibility and narrow down the viable possibilities. The available choices, and their merits and disadvantages, may be summarized as follows:

(1) Dredging:

Wholesale removal of contaminated sediments would probably be the most effective way of dealing with the sources of mercury in the Wabigoon River between Dryden and Clay Lake. A conservative estimate of the cost is $40,000,000 at $10/cu. yd. (plus an extra $1,000,000 for access roads) (Wilkins and Irwin), but the cost could be as high as $200,000,000 at $50/cu. yd. (Wilkins). If Clay Lake were included, an extra $60,000,000 to $600,000,000 would be required (Wilkins). The project could take up to 35 years, would not be guaranteed to remove all of the contaminated sediment, and might temporarily aggravate the mercury problem by causing resuspension of fine-grained contaminated particles, which would then be swept downstream (Wilkins and Irwin). There also remains the important question of finding a suitable way to dispose of the dredge spoil.

In brief, dredging the river is worth considering, but it would not be a rapid, fully efficient, or low-cost solution.

(2) Burying:

Burying the contaminated sediments with a layer of uncontaminated silt and clay, from either subaerial or subaqueous sources, is probably not a viable possibility (Wilkins; Wilkins and Irwin; Rudd *et al*.). It would not be effective in the river upstream from Clay Lake, because the layer of clean sediment would be subject to disruption by gas bubbles from the decomposing organic matter of the riverbed (as shown by Swedish workers) as well as erosion by current action. Burying the contaminated sediments of the lakes might be helpful if the mercury in the river upstream from Clay Lake were first dealt with by some other method and if present discharges from the plant were halted. There are not enough readily available subaerially exposed sources of clay and silt in the vicinity of the lakes, and the existing deposits are largely in use already for agricultural purposes; however, there might be adequate deposits of uncontaminated subsurface clay in Clay Lake itself.

(3) Ploughing

Ploughing the bottom sediments of lakes in order to dilute the contaminated surface material with underlying clean sediment can be ruled out, even as a secondary method to be used after cleaning up the river above Clay Lake. The method is hard to control in an irregular lake, and resuspension of mercury-contaminated sediment would be an especially severe problem (Wilkins). Other drawbacks are high cost and habitat modification.

(4) River Diversion:

From the standpoint of practicality, diversion of the Wabigoon River to bypass the most heavily contaminated part of the present riverbed (Wilkins and Irwin) could extend, at most, from Wabigoon Lake to Eagle Lake. A serious flaw in this plan is that it would ignore the contaminated sediments downstream from the confluence of the Wabigoon River and Eagle River (which drains Eagle Lake) and would create hardship for the people who live in the vicinity of Eagle Lake. The scheme is estimated to cost $20,000,000 not counting "hidden" costs owing to factors such as payment of compensation to the people of Eagle Lake and removal of polluted sediments from the old riverbed. This method does not appear to be a worthwhile alternative.

(5) Flushing and consolidation of contaminated sediments:

This method would consist of hydraulic excavation of the riverbed upstream from Clay Lake followed by accumulation of the sediments in settling ponds. This procedure would (a) reduce the area of the contaminated sediment-water interface, thereby decreasing the rate at which the river water is contaminated, (b) make dredging of the contaminated sediment easier and more economical, and (c) facilitate any chemical treatment that might be deemed necessary to suppress the methylation and release of the mercury (see section 7, below).

(6) Prevention of further discharges by the plant at Dryden:

The paper company should remove mercury from its effluent (Parks *et al.*), and, indeed, is presently taking steps which are expected to achieve this effect (Ontario Ministry of the Environment, personal communication). Although there has been no primary treatment of the effluent to date, the company is installing a primary clarifier together with retention lagoons for secondary treatment involving aeration and biological breakdown of organic refuse; these primary and secondary treatment facilities, which are required by an Ontario Ministry of the Environment Control Order, are scheduled to be in normal operation by December 31, 1980, and December 31, 1983, respectively. The clarifier, by removing about 70% of the suspended solids, should cause a substantial reduction in the total amount of mercury discharged into the river. Possibly secondary treatment will contribute to the overall removal of mercury. Anticipated modernization of the Dryden mill is also expected to reduce the quantity of mercury in the effluent, as it will involve replacement of old sewers and other facilities which are suspected of being sources of mercury.

(7) Chemical treatment *in situ*:

A possible alternative to dredging the Wabigoon River would be to create a chain of settling ponds similar to Wainwright Reservoir, including one just above the inflow to Clay Lake (Jackson and Woychuk; Parks et al.). The ponds would then be subjected to chemical treatments to promote the trapping and retention of mercury and to suppress methylation. Treatments might include addition of lime, sulfide (or sulfate, a sulfide precursor), and methyl mercury-adsorbing substances (Rudd et al.; Jackson and Woychuk).

This chemical approach would undoubtedly be, at best, a poor substitute for physical removal of the pollutants. It would probably not be fully effective; and even if it were less expensive than dredging in the short run, it might well be more expensive in the long run owing to the cumulative cost of the endless chemical treatments (and the likelihood of eventually being compelled to dredge out the settling ponds anyway).

Theoretically, the lakes themselves could be treated chemically too (assuming that the river upstream from Clay Lake was attended to first), but in practice this scheme would be neither feasible nor desirable (Wilkins and Irwin; Jackson and Woychuk). It would be too expensive as well as inefficient for so large a system, and the treatments would probably have harmful ecological effects of their own.

Reduction of primary productivity by restricting the input of nutrients such as phosphate is another possible method for inhibiting bio-accumulation of mercury (Rudd et al.). But even on the uncertain assumption that this scheme would be effective, it would be self-defeating because it would cause a decline in fish production. Moreover, Swedish investigators have reported that mercury levels in fish tend to be lower in eutrophic lakes than in oligotrophic lakes with a comparable degree of mercury contamination.

An altogether different sort of chemical treatment would be the addition of selenium to the river-lake system for the two-fold purpose of counteracting the toxic effects of mercury in fish muscle and inhibiting the uptake of mercury by fish (Rudd et al.). Experiments performed in Clay Lake have demonstrated that this approach could be successful. However, more research would be needed before selenium application could be considered, because selenium at excessively high concentrations is toxic to humans and animals.

In brief, the restoration techniques which deserve the most serious consideration would seem to be reduction of mercury discharges from the plant at Dryden, dredging of the river between Dryden and Clay Lake, immobilization of mercury in this stretch of the river by settling in a chain of ponds followed, perhaps, by chemical treatments or physical removal, and possibly selenium treatment (provided future research proves that it will be safe as well as efficacious). However, each of these approaches has ecological and/or economic drawbacks.

These options must be regarded as tentative pending collection of additional data. It is clear, however, that there is no simple, rapid, fully effective, inexpensive, trouble-free course of action for overcoming the mercury problem. At least one lesson can be learned from our study: The most satisfactory way to combat pollution is to prevent it.

ADDITIONAL RESEARCH

There remain many gaps in our understanding of the mercury problem in the Wabigoon-English-Winnipeg River system, and the results of the first year's research by the Federal-Provincial team are not altogether unambiguous. Thus, more information is needed to establish a firmer basis for recommending remedial action. The following additional investigations have been planned or initiated for the second year of the Federal-Provincial project:

(1) Mercury dynamics and sources of bio-available mercury

The year-round study of sources, concentrations, and loadings of total and methyl mercury in river and lake waters is being continued, and the field area has been extended to the Manitoba border. The research includes further study of the mobilization of methyl mercury and other forms of mercury from river sediments in the spring and summer, as well as the flushing of methyl and other mercury accumulations out of the deeper waters of lakes during the fall and spring overturns.

The ecological effects of the mercury moving through different regions of the river-lake system at different times is being monitored by means of caged crayfish or fish suspended in the water at control sites and contaminated sites.

(2) The geochemistry of mercury in sediments and water

Bottom sediments collected in 1978 are being analyzed for grain-size frequency and clay mineralogy. The distribution of mercury among different microscopic sediment components is being investigated by electron microprobe analysis. Characterization of humic-mercury complexes and other anionic complexes, and determination of cobalamin (a factor in methyl mercury biosynthesis), are also anticipated. A pilot project on the distribution of stable mercury isotopes in the sediments (as a possible aid in determining sources of mercury) is tentatively planned. The comparative study of different methods of wet-ashing for total mercury determination will be completed, and the effects of storage under frozen conditions and at 4°C. on the methyl mercury content of sediment samples are being studied.

Inasmuch as the loading of river-borne mercury to Clay Lake and beyond has been shown to be of importance, a project is being done on variations in the chemical speciation of mercury in the suspended solids and solution phase of the river water with distance from the Great Lakes Forest Products plant under different hydraulic regimes. The objective is to determine in what forms the mercury moves through the system, and what changes occur as a result of changes in aquatic environment and the nature of the sediment.

(3) Experiments on biological pathways and detoxification, and related studies

The first year's limnocorral experiments on the biological accumulation of mercury under different conditions are being confirmed and extended. An effort is being made to differentiate between the respective roles of primary productivity and suspended clay, and, if possible, to establish to what extent methylation occurs in the surface layer of the sediment as compared with the overlying water column. Additional data on the total mercury, methyl mercury, nutrient, and major ion budgets for Clay Lake are being collected, and the rates of mercury methylation in Clay Lake are being measured by means of bioassays.

Further investigation of the ecological effects of selenium is also underway. An attempt is being made to confirm the previously reported selenium effects, and additional experiments are being done to test the effects of lower selenium concentrations. The aquatic biota and sediments of the Wabigoon River are being analyzed for selenium as well. Finally, experiments are being performed to assess the toxicity (including sublethal toxicity) of selenium to fish and to obtain information on the mechanisms whereby selenium reduces the mercury concentrations of Clay Lake fish.

THE TRANSPORT AND DYNAMICS
OF TOTAL AND METHYL MERCURY
IN THE WABIGOON RIVER AND CLAY LAKE

J. W. Parks
J. D. Hollinger
P. M. Almost

Technical Support Section
Northwestern Region
Ontario Ministry of the Environment
Thunder Bay, Ontario

ACKNOWLEDGEMENTS

The Federal research team comprising of John Rudd, Michael Turner, Bruce Townsend, Allison Swick, Mark Gordon and Akira Furuntani provided generous assistance to this project which enabled us to begin our sampling program with a minimum of delay. We are also grateful to them for providing Clay Lake temperature and chemical data and for total mercury and methyl mercury data collected by the Federal team prior to August, 1978.

The authors are deeply indebted to Messrs. Andy Lutz and Chris Tam who developed more sensitive techniques for total and methyl mercury analysis, which were instrumental for defining the mercury flux in the river-lake system and, in particular, delineating internal lake dynamics. We are especially appreciative of Andy Lutz for providing analytical support during very intensive sampling periods and for his close rapport which added substantially to the study.

Water Survey of Canada and Reed Ltd. provided daily flow data for the Wabigoon River system, and North Star Camps at Clay Lake provided a lake-level monitoring site.

Thanks are extended to Mr. Jim Sutton and Mr. Eric Hansen for participation in field studies.

We also wish to thank T. Brydges, R. Allan, F. A. J. Armstrong, A. Hamilton, B. P. Neary, T. Jackson, W. A. Creighton and H. D. Griffin for helpful comments.

TABLE OF CONTENTS

Page

FIGURES

TABLES

REFERENCES

CONCLUSIONS

(1) The Wabigoon River exhibits elevated mercury and methyl mercury concentrations in the study area downstream of Dryden. In surface waters, total mercury and methyl mercury concentrations were controlled by dynamic processes and were generally at least three times greater than concentrations at Wabigoon Lake.

(2) In the Wabigoon River, the present effect of the Wainwright Dam on total mercury mobility or methyl mercury formation is negligible.

(3) The occurrences of high total and methyl mercury loadings from the Wabigoon River into Clay Lake strongly suggest that amelioration techniques applied to Clay Lake will be unsuccessful if the river influx is ignored.

(4) Clay Lake acts as a significant sink for total mercury entering via the Wabigoon River. Of the 35 kg (kilograms) of mercury transported by the river during the 1978-79 study year, 46 percent was retained in Clay Lake. Clay Lake was not a net sink for methyl mercury. Methyl mercury values at the outflow of Clay Lake, the last study site downstream of Dryden, were amongst the highest found anywhere on the system.

(5) Hypolimnetic waters in Clay Lake have substantially higher mercury and methyl mercury concentrations than those observed in the epilimnion.

(6) The current mercury loading from Reed Ltd. is one percent of pre-1970 rates; present discharges, however, are five times the natural loadings at Dryden.

(7) Historical biological data demonstrate that decades may be required to substantially improve the present situation.

SPECULATION ON THE IMPACT OF POSSIBLE REMEDIAL MEASURES

With one complete year of data and the historical perspective given in Figure 34, we believe a preliminary discussion of potential remedial measures would be useful in future planning.

It appears that the system at present is not functioning as many previously suspected in that significant mercury loadings are emanating from Dryden. It also must be emphasized that the removal of mercury from the contaminated river above Clay Lake and the point source in Dryden is a prerequisite for substantial improvements in Clay Lake biota. Unquestionably, physical amelioration techniques applied only to Clay Lake sediments, such as ploughing or covering of sediments, would be largely unsuccessful due to the river influx of total and methyl mercury.

Because the strong adsorbtion of mercury to some particles, the retention of 50 to 90 percent of the suspended solids in the company's wastes by improved waste treatment systems may substantially reduce mercury emissions to the river. Care must be taken, however, to ensure that significant quantities of methyl mercury are not generated in the waste treatment process. At present, it is not possible to quantitatively predict the effects of various waste treatment processes on mercury loadings. With current waste treatment technology, though, reduced mercury loadings are predicted and a preliminary investigation into the effects of primary and secondary treatment on mercury loadings in raw effluent from Reed Ltd. is underway.

To speed up the recovery of the river system and the lowering of mercury levels in fish and other biota, mercury deposits within the river must be removed or consolidated eliminating the vast mercury-enriched sediment-water interface. Methods other than dredging may be feasible and warrant further consideration. For example, if mercury-contaminated sediments were flushed down the river into selected natural or artificial settling basins either by releasing large flows from Wabigoon Lake or by flushing using pumps as for a placer mining operation, significant improvements might be obtained. The Wainwright Dam offers an ideal example of how large quantities of mercury can be effectively removed from further adverse interactions, but to ensure that the mercury is not released at some future date by extreme flood or other cause, further measures may be necessary. Prior to implementation of these or other procedures, a clear understanding of the environmental impact is required and pilot projects may be necessary. An optimum program would involve the translocation of mercury-laden bed sediments to a settling basin at a selected site with a minimum of methyl mercury entering the water column. Such conditions occurred during the spring runoff at the inflow to Clay Lake when water temperatures were near $0^{o}C$. Flushing during higher temperature regimes would, perhaps, be less desirable as more methyl mercury might be present or generated.

Once mercury contaminated sediments were localized, methods of permanently immobilizing these particles might be feasible. These measures might include burial, removal or settling and isolation in off-stream lagoons. Such methods should be evaluated as part of any investigation of the feasibility of localizing mercury-contaminated sediments.

If the point source for mercury in Dryden and river sediments above Clay Lake were purged of mercury, recovery of Clay Lake could be swift with most biota probably returning to normal levels within a decade.

INVESTIGATIONS DURING THE SECOND YEAR OF THE AGREEMENT

The extension to the Agreement between Canada and Ontario provided for a second year of study which ends on June 30, 1980. Studies which are underway or planned for completion during this second year of study are outlined below and will be reported in a report scheduled for completion in December, 1980.

(1) Having identified that the Wabigoon River loadings to Clay Lake are highly significant, further fluvial studies defining mercury transport and transformation mechanisms are planned. Field studies are in operation to elucidate transport mechanics using a field centrifuge unit which is capable of separating soluble and suspended mercury fractions. Samples of suspended material will be subjected to a progression of selective extractions in aid of understanding the binding characteristics of mercury.

(2) Data from this report indicate that waters immediately downstream of Clay Lake are probably contaminated with mercury. We, therefore, propose to monitor total and methyl mercury in Ball Lake. Additional sites farther downstream may also be included if mercury concentrations above the present detection limit are found.

(3) Observations have shown that rapid increases in flow mobilize and flush large quantities of mercury down the Wabigoon River. Further investigation of this process is planned for the spring of 1980.

(4) At present, a preliminary investigation into the effects of primary and secondary treatment on mercury loadings in raw effluent from Reed Ltd. is underway.

INTRODUCTION

Since the outbreak of mercury poisoning in Minamata, Japan, by the consumption of contaminated fish, many facets of the biogeochemical cycling of mercury have been studied. The discovery by Jensen and Jernelov (1) in 1969 that relatively innocuous inorganic forms of mercury could be transformed in the aquatic environment into methyl mercury, a very potent neurotoxin, spurred further studies in receiving streams where known mercury discharges occurred. One of these studies on waters downstream from a chlor-alkali plant indicated that fish from Clay Lake, on the Wabigoon River system in Northwestern Ontario, contained mercury concentrations of 10-20 ppm, higher than reported for any other freshwater fish in the world (2). A review of subsequent investigations (3, 4, 5) revealed severe mercury contamination in the Wabigoon River system downstream from Dryden. Lower but still excessive mercury levels were reported in the sediment and biota of the lower English River, no doubt stemming from mercury contributions from the Wabigoon River. In total, over 250 kilometres of the Wabigoon/English/Winnipeg River system were adversely affected by the release of an estimated 10 tons of mercury between 1962 and 1969 by a chlor-alkali operation in Dryden.

The mercury was derived primarily from a chlorine production process which used mercury cells. In 1970, abatement measures sharply curtailed mercury losses and in October, 1975, the mercury cells were dismantled. Despite a 99 percent reduction in the amount of mercury lost from the mill complex, biota in contaminated waters continued to exhibit very high mercury concentrations. In an effort to find methods to alleviate a long-term problem, a joint Federal/Provincial study began in June, 1978. Federal responsibilities lay primarily with investigating possible amelioration techniques, while the Provincial agency was charged principally with:

(a) Examining mercury dynamics in the Wabigoon/English River system between Dryden and the outlet of Clay Lake.

(b) Studying clay availability for possible burial of contaminated sediments in Clay Lake.

Prior to the signing of the joint agreement, the Federal research team initiated a mercury dynamics study on Clay Lake, which subsequently became a joint venture. One of the chief objectives of this study is to assess the significance of the Wabigoon River on mercury uptake by Clay Lake biota, particularly fish, since certain lake restoration techniques presupposed a "clean" inflow. The task is not simple; mercury-cycling in aquatic ecosystems is extremely complex and many quantitative aspects are presently not well understood, but by combining ongoing research with historical data, definitive conclusions on the future health of this watercourse are expected.

Mercury uptake by crayfish and young yellow perch was also examined. The minnow study was conducted outside the Federal/ Provincial Agreement, but due to its pertinence, the results are presented from the work of the Limnology and Toxicity Section of the Ministry of the Environment.

Due to the existence of several publications which review this topic (2, 6, 7, 8, 9, 10, 11), a detailed description of all known aspects of the natural interconversions of the various chemical forms of mercury has not been attempted, but a brief overview will be presented to serve as a basis for subsequent discussions.

The problem of excessively elevated mercury concentrations in fish flesh has been definitively linked with man's discharge of the element into aquatic systems. Because mercury is ubiquitous in nature, the problem is essentially one of kinetics. Most bodies of water in Ontario contain some fish with mercury concentrations greater than 0.5 ppm (4), the criterion established by the Canadian Food and Drug Directorate for unrestricted consumption. Despite extensive research, a complete quantitative description of how anthropogenic mercury releases affect fish and other aquatic biota remains unresolved.

In studying mercury dynamics in the Wabigoon River/Clay Lake system, an understanding of the significant physical, chemical and biological processes on a temporal and spatial basis is required.

Certain aspects of the present global problem are fairly well documented:

(1) High mercury levels in fish can remain long after point sources are stopped.

(2) Methyl mercury usually accounts for over 90 percent of the total mercury in predator fish species.

(3) In waters methyl mercury is a minor component of the total mercury present.

(4) Mercury is uptaken by fish from both food and water.

(5) Biota show preferential retention of methyl mercury. Methyl mercury concentrations in water have a significant influence on mercury body burdens in fish.

(6) Methyl mercury levels in water are a function of environmental conditions, i.e. pH, Eh, temperature, etc. and, consequently, will be dynamic in nature.

Despite the fact that a knowledge of concentrations of total and methyl mercury in water are critical to an understanding of food chain mechanics, a problem exists because little is known about mercury dynamics. Much of this study addresses this very problem.

METHODS

DESCRIPTION OF STUDY AREA

Hydrology

The Wabigoon River watershed is located approximately 300 km (kilometres) northwest of Thunder Bay. The study area of 9,700 km^2 encompasses the watershed upstream of Clay Lake outflow (Figure 1).

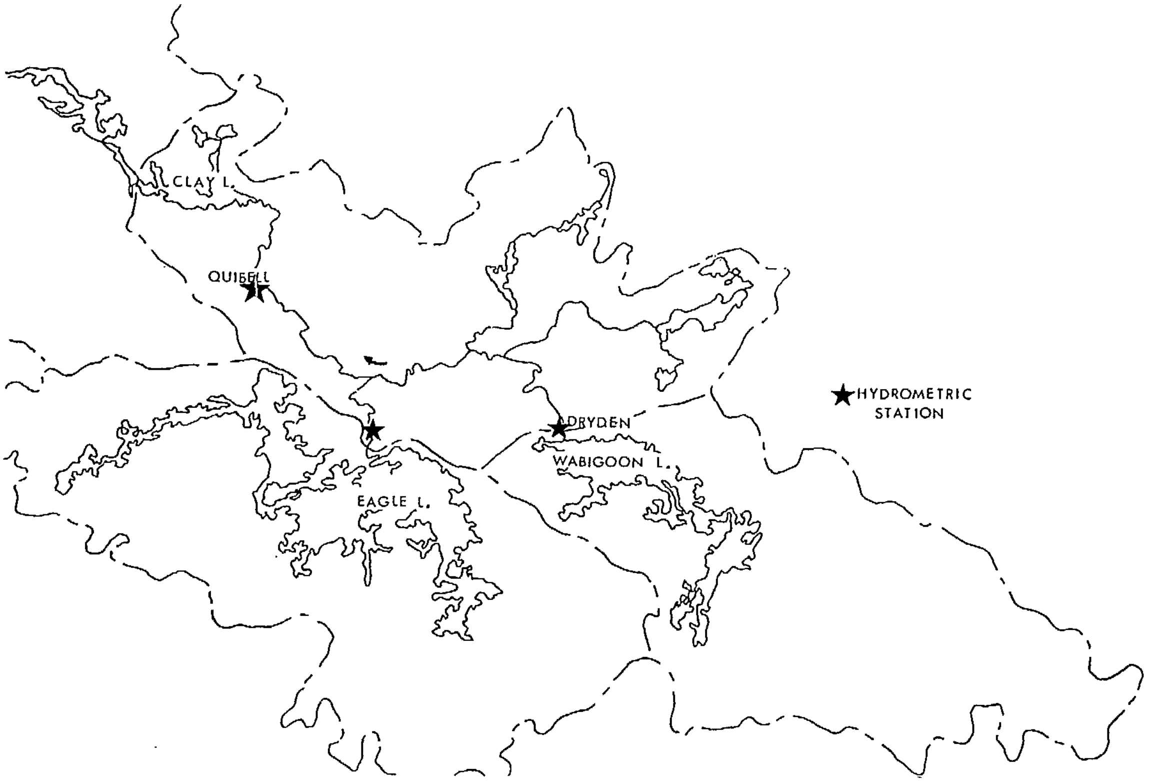


FIGURE 1. Upper Wabigoon River watershed.

The Wabigoon River drainage comprises runoff from two major subbasins which are dammed and a number of much smaller unregulated watersheds. Flow characteristics of the Wabigoon River major subbasins upstream of Clay Lake are given in Table 1. The river gradient is estimated at less than 0.3 m/km (metres/kilometre), excluding the falls. Waters collected by the Wabigoon River discharge into the English River system at Ball Lake and eventually discharge into the Winnipeg River near the Ontario/ Manitoba border. Because both the Eagle and Wabigoon Lake watersheds, which comprise the bulk of the Wabigoon River discharge, are regulated, downstream flows are atypical. The discharges from Wabigoon and Eagle Lakes are relatively stable throughout the year and high and low flow events in the Wabigoon River are usually moderated. For example, in 1978, the spring runoff in early May was retained in both the aforementioned basins (Figure 2).

Geology

Discontinuous Pleistocene deposits of glaciolacustrine material cover most of the watershed with limited outcrops of bare Precambrian bedrock in some areas. Deposits are predominantly clay and silt. Sandy till is also present. Morainic sand ridges and outwash sand plains occur in the Eagle Lake watershed (22). Bedrock consists of acid, igneous and metamorphic rocks with metavolcanics and some metasediments forming significant portions of the Eagle and Wabigoon Lake basins.

Limnology

Despite the proximity of the Wabigoon River watershed to the Experimental Lakes Area (some ELA lakes are in the Eagle Lake watershed), most waters in the Wabigoon basin are chemically dissimilar to values reported by Armstrong and Schindler for that area (13). This difference is presumably due to the weathering of lacustrine deposits which are more extensive in the Wabigoon River watershed.

TABLE 1. Drainage characteristics of the Wabigoon River watershed, upstream of Clay Lake, 1972-1976.

Watershed	Mean Daily Flow (m^3/s)	% of Total Flow	Flow Range (m^3/s)
Wabigoon Lake	13.6	30	0-121
Eagle Lake	17.0	37	0-90
Other	14.9	33	2-275[a]
Total	45.5	100	

[a] Wabigoon River at Quibell.

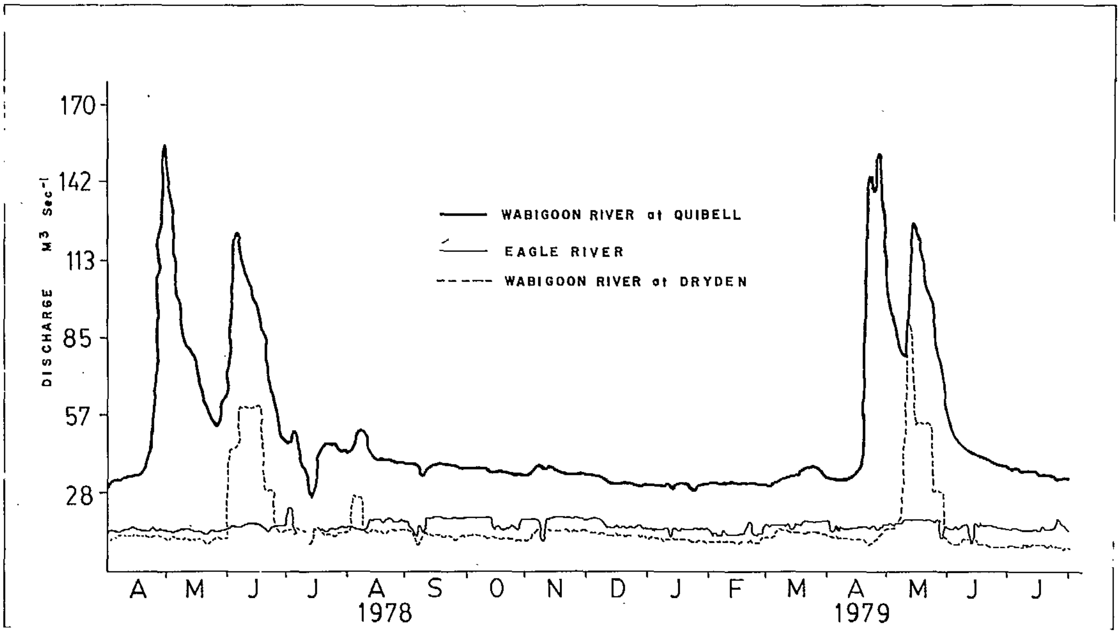


FIGURE 2. Hydrographs for selected sites within the study area 1978-1979.

Clay Lake (Figure 3) encompasses 3,000 ha (hectares), has a volume of 2.4 x $10^8 m^3$ (cubic metres) and a mean depth of 8 m. The theoretical residence time calculated from prorated Quibell flow records is 57 days at an annual mean flow of 49 m^3/s (1953-1976) and approximately 31 days using mean May flows. The lake is dimictic and considered mesotrophic. There are two distinct basins, a western basin which stratifies and an eastern basin which does not.

Effluent discharged from the Reed Ltd. pulp and paper mill complex in Dryden has substantially altered the physical, chemical and biological characteristics of the receiving waters (14, 15). During 90 percent of the study period, the raw effluent comprised 10 to 15 percent of the Wabigoon River flow immediately downstream of the mill. The deterioration of water quality is most evident at Dryden; however, chemical changes in the water column have been detected as far downstream as Ball Lake and severe algae blooms in Clay Lake have been attributed mainly to loadings from Reed Ltd. Perhaps, the most significant adverse effect is the loss of 40 km of the Wabigoon River downstream of Dryden as game fish habitat.

The natural substrate of the upper half of the Wabigoon River is blanketed by mercury-enriched wood wastes and more than 80 percent of the basin formed by the Wainwright Dam is filled with such waste. Anaerobic decomposition of the organic material results in notable gas production. Natural sediments in the Wabigoon River consist primarily of clay and silt. Wabigoon, Eagle and Clay Lake sediments are predominantly clay and silt overlain by several millimetres of loosely compacted organic material.

Selection of the Study Sites

For the first year of the study, sampling sites were selected (Figure 4) to examine mercury dynamics on the Wabigoon River system between Dryden and the outflow of Clay Lake; a watercourse found by many researchers (3, 4, 5) to exhibit much higher mercury levels in the sediment and the biota than any other section of the

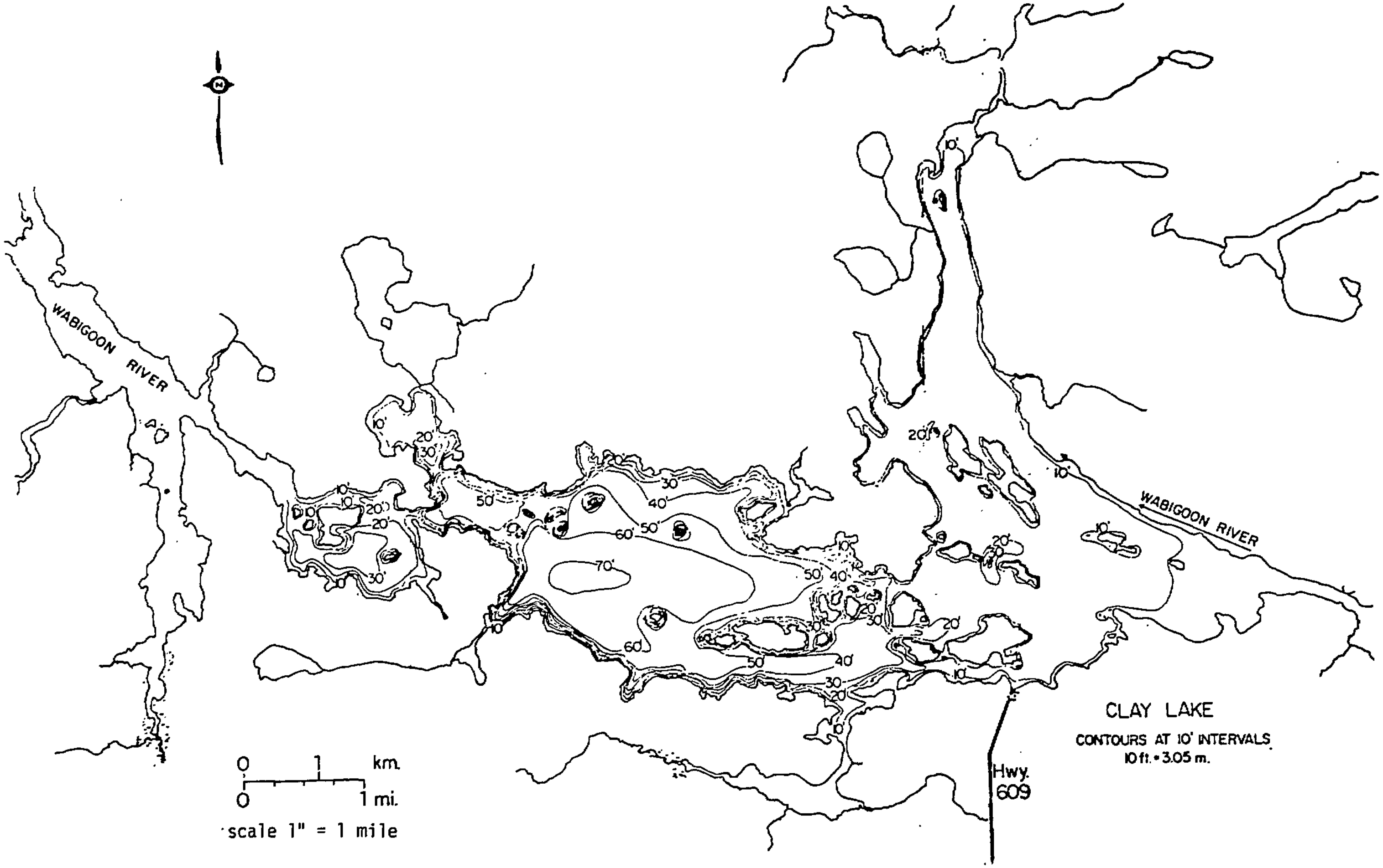


FIGURE 3. Bathymetric map of Clay Lake (courtesy of the Ontario Ministry of Natural Resources).

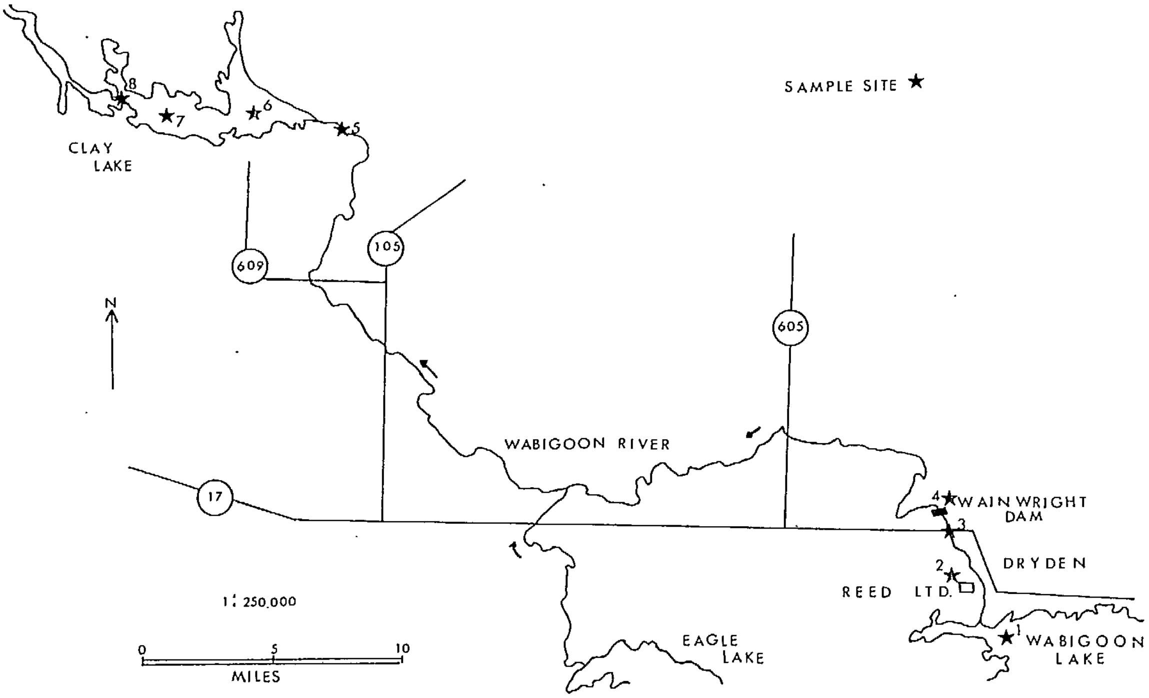


FIGURE 4. Map of the Wabigoon River system showing the location of sampling sites.

Wabigoon/English/Winnipeg River system. The control site (site 1) is located at the outflow of Wabigoon Lake upstream of any known industrial discharges. The Reed Ltd. effluent (site 2) was incorporated into the sampling program in order to obtain a mass balance for the system. Sites 3 and 4 were established to:

(a) Monitor mercury loadings downstream of Dryden.

(b) Monitor mercury loadings for comparative purposes with the inflow to Clay Lake.

(c) Determine the effect of the Wainwright Dam on mercury mobility and form.

Sites 5 to 8 were established to determine the dynamics and fate of mercury within the eastern and western basins of Clay Lake.

TOTAL MERCURY

Sampling Schedule

During the ice-free season, weekly duplicate water samples for total mercury were taken using either an acrylic "Van Dorn" or "Kemmerer" sampler. Winter sampling was conducted on a monthly basis. With the exception of site 7, all water samples were collected at a depth of one metre. At site 7, monthly profiles were collected at 1, 4, 7, 10, 13, 16 and 19 metres. In addition, duplicate weekly composite samples were taken from the epiliminion, metalimnion and hypolimnion which were determined prior to sampling with the aid of weekly temperature profiles taken with a "YSI" telethermometer. Each composite sample was composed of three samples taken at the top, middle and bottom of each limnetic zone. After preliminary investigations (discussion following), river sites were sampled midstream.

In early August, 1978, an intensive investigation at site 3, the first station downstream of Dryden, was undertaken to formulate river sampling strategy. Horizontal cross-sectional sampling at 10 percent increments was employed using a U.S.H.D. 49 depth-integrating, suspended-sediment sampler. Flow velocities were obtained using an Ott Universal Current Meter C-31. Duplicate filtrates of raw samples passed through a 0.45 μm Millipore filter using standard Millipore equipment were also obtained. Vertical fixed-depth sampling was conducted at midstream.

Cross-sectional sampling indicated that mercury concentrations did not appear to be related to water velocity (Figure 5). Although this finding suggests mercury is in solution, filtrate results (Table 2) indicate that 48 percent of the mercury is associated with particulate. Because of the inverse relationship between particle size and mercury concentration (3, 16) much of the mercury may be bound to sub-sieve particulate which tends not to be depth-dependent (17). Evidence supporting this conclusion was obtained from samples at fixed-point, vertical depths (Table 3) which revealed that mercury concentrations were not related to depth below the surface. Thus, for typical flows more than 90 percent of the year, mercury concentrations were relatively uniform throughout the water column. Another conclusion that may be drawn from these data is that any mercury loadings from Reed Ltd. are well mixed by the time they reach site 3.

Bed transport studies of mercury were not conducted after consideration of the morphology of the river channel and drainage basin. Bed sediment translocation which probably occurs to some degree during high flow periods (i.e. spring melt) is expected to have little or no immediate impact on uptake by biota, but could be a long-term factor where sediment settles. Midstream subsurface sampling was deemed adequate for survey purposes but may underestimate loadings at some monitoring sites during high flows.

Samples from the Reed Ltd. total effluent were collected jointly by Ministry of the Environment and Reed Ltd. staff using an "Isco" composite sampler. Aliquots from the total pulp and paper mill effluent were collected every twenty minutes in a 10-litre plastic container which was emptied daily. A possible short-coming recognized in this method was that some of the samples were twenty-four hours old before acidification. Another "Isco" was installed whereby the effluent was immediately preserved

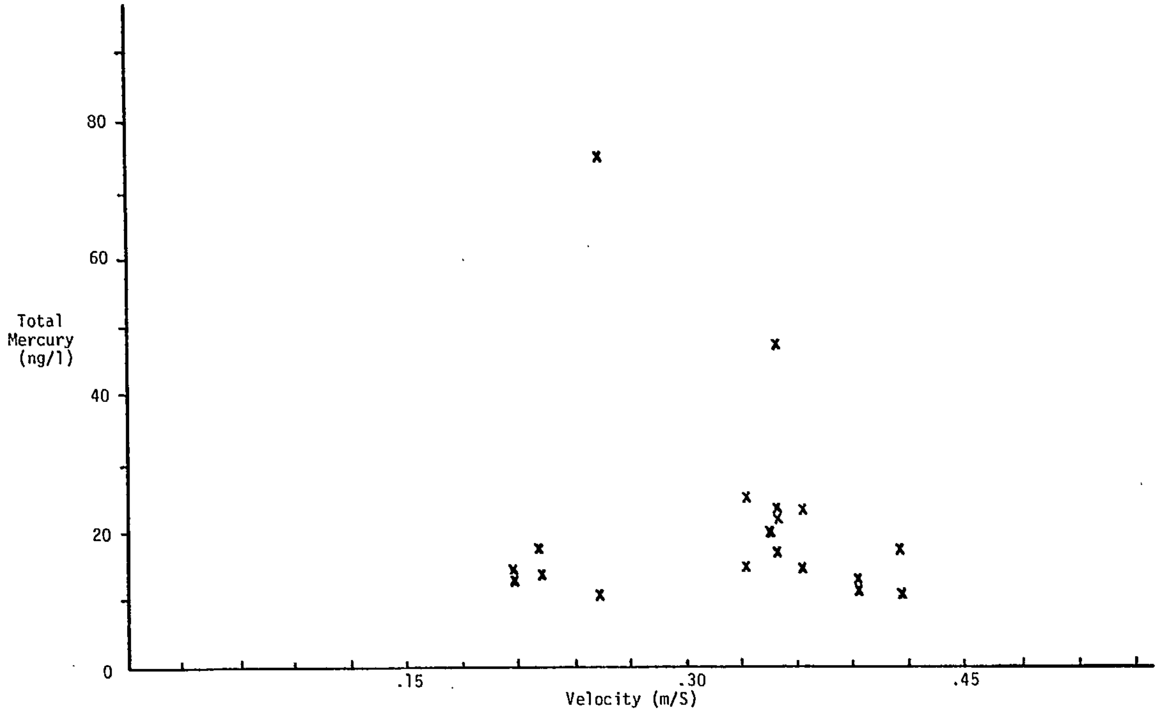


FIGURE 5. Mercury concentration plotted against velocity: Data obtained by intensive sampling of the Wabigoon River at Highway 17 (station 3) on August 23, 1978.

TABLE 2. Mean depth-integrated mercury concentrations in the Wabigoon River at Highway 17 (station 3), August 23, 1978.

Cross Section[a] Depth (m)	Total Mercury (ng/l)	Filtrate Mercury (ng/l)	Percent Mercury[b] on Particulate
.7	40	14	65
1.8	38	22	42
2.4	24	20	16
3.0	28	16	42
3.0	58	18	69
1.4	44	13	70
1.9	40	14	65
1.1	86	46	46
.5	26	23	12
.6	30		
Average	41	21	47

[a] In ten percent increments across the river facing upstream.

[b] By difference.

TABLE 3. Vertical profile of mercury concentrations in the Wabigoon River at Highway 17 (station 3), August 23, 1978.

Midstream Depth (m)	Mercury Concentration (ng/l)
.3	20
	23
1	21
	20
1.6	31
	17
2.3	25
	17
3	17
	28

and parallel samples from each unit were procured on a 24-hour composite basis. For twenty results per sampler, there was no significant difference between methodologies and the latter method was dropped. From the first effluent sample, duplicate results of 84 and 13 ng/l from the top, 114 and 121 from the middle and 410 and 270 from the bottom clearly indicate mercury concentrations were a function of sample location; consequently, one sample from the top and one from the bottom of the well-mixed contents of the container were obtained for analysis.

Although the usual effluent sampling frequency was weekly, daily samples were also collected for a 10-day period to ensure that these results were consistent with values obtained weekly.

The Eagle River was sampled 26 times. Four other uncontaminated tributaries of the Wabigoon River, namely, Buller, Rugby, Hutchison and Aubrey Creeks were sampled three times during the study period to get an approximation of the natural loadings to the Wabigoon River and Clay Lake. Five spot samples from the Dryden sewage treatment plant which utilizes secondary treatment were also obtained.

During the unregulated and regulated flow periods, sampling frequency at the river sites was increased in proportion to flow. Samples were often taken twice a day during the rising limb of the hydrograph. Mean annual concentrations were derived from monthly values. With the exception of spring flood episodes at river sites, monthly averages were obtained by averaging all data obtained. Daily values were used for the spring runoff period and, where necessary, data interpolations were incorporated.

All samples were collected in duplicate in 250-ml reagent bottles which were premuffled at 450°C and preserved with 3 ml concentrated nitric acid and 1 ml of five percent $K_2Cr_2O_7$. Tops were cleaned with 1:1 nitric acid and protected from dust in six-ounce plastic "Whirlpacks". Initially bi-weekly samples were collected at all sites to determine mercury levels in the soluble and particulate phase. Filtration through 0.45 μm Millipore filters using standard Millipore equipment produced filtrate and filters which were analyzed for mercury. Unfortunately, mass balancing the system proved impossible because of the background variation in mercury concentrations in "clean" filters. Use of a field centrifuge unit in 1979 studies should help to delineate soluble and particulate-bound mercury fractions.

Analytical

The organo mercury compounds in the water are oxidized to inorganic mercury compounds by heating with sulphuric acid, potassium permanganate and potassium persulphate. After oxidation, the mercuric compounds are then reduced with stannous sulphate in a hydroxylamine sulphate-sodium chloride solution. The mercury is sparged from the solution with a stream of nitrogen and trapped on silver which is heated and the released mercury flushed with nitrogen through an absorption cell which is situated in the light path of a mercury lamp. The absorption is read at 253.7 nm (nanometres). Sensitivity of the method is 5 ng/l on a 150-ml sample (18).

METHYL MERCURY

Sampling Schedule

Monthly sampling for methyl mercury analysis of water at all sites except stations 2 and 7 followed that outlined for total mercury. At station 7, methyl mercury samples were not collected at 3 m increments. Initially composite samples were obtained from the epi, meta and hypolimnia. In the fall of 1978, however, sampling strategy was modified to sampling one metre from the surface, one metre off bottom and a lake volume weighted composite was obtained from the water column. These changes were made to reflect increased budget considerations for Clay Lake at the expense of the dynamics portion. Spot samples were obtained from Reed effluent and the Dryden sewage treatment plant. Routine sampling was synchronized with total mercury and monthly water chemistry runs. Duplicate results were obtained for 90 percent of the samples.

Weekly samples were also collected at sites 4 and 7, during the ice-free season. Sampling was also increased during the spring melt at site 5.

Analytical

Methyl mercury complex is solubilized by sulphuric acid and then continuously extracted by an upward flow of condensed benzene in a liquid-liquid extractor for at least six hours and preferably overnight. The benzene layer is separated, extracted with aqueous thiosulphate and potassium iodide added. The resulting methyl mercury iodide is re-extracted into benzene and analyzed by gas chromatography using an electron capture detector (18). Sensitivity of the method is 0.2 ng/l on an 8-litre sample.

CALCULATIONS

Loadings

Mercury budgets were derived from sample results in conjunction with daily flow data supplied by Water Survey of Canada and Reed Ltd. for three hydrometric stations in the Wabigoon River watershed (Figure 2). Since the Reed Ltd. effluent was not incorporated into the given flows for the Wabigoon River at Dryden, effluent flow of 1.6 m^3/s was added to discharges at stations 3 and 4.

To determine the inflow to Clay Lake, discharges at Quibell were pro-rated. Since most of the flows in the watershed are dam controlled, unregulated runoff was used to estimate flow increments between Quibell and Clay Lake.

$$Q_{QCL} = .12\ Q_U$$

$$Q_U = Q_Q - (Q_{WD} + Q_{ER})$$

where:

Q_{QCL} = discharge to Wabigoon River between Quibell and Clay Lake

Q_U = unregulated discharge

Q_Q = Wabigoon River discharge at Quibell

Q_{WD} = Wabigoon River discharge at Dryden (regulated flow from Wabigoon Lake)

Q_{ER} = Eagle River discharge (regulated flow from Eagle Lake

The outflow of Clay Lake was assumed to equal the inflow.

Preliminary calculations suggest that errors in this assumption for the worst case situation (i.e. spring flows) are 10 percent or less and 5 percent or less at other periods. The two key factors that justify our equating the inflow and outflow, are the low theoretical residence time of two months (based on the mean annual flow) and the small runoff from the Clay Lake drainage basin itself.

RESULTS

STREAMFLOWS - 1978-1979

Daily flow readings at the three hydrometric stations are presented in Figure 2. Since the Reed Ltd. effluent was not incorporated into the flows for the Wabigoon River at Dryden, 1.6 m^3/s (cubic metres/second) was added to discharges at stations 3 and 4. Hydrographs for the hydrometric stations clearly demonstrate the influence of regulated flows in the Wabigoon River. Most striking are the twin peaks at Quibell for flows observed during the spring freshet in both years. Runoff from the unregulated watersheds was solely responsible for the first flood episode as both Eagle and Wabigoon Lake outflows were maintained at winter discharge values in order to store water for future power generation. It is evident that the storage capacity in Eagle Lake was sufficient to eliminate any spring flush as flows at the hydrometric station remained fairly constant throughout the study period. With spring rains, however, the storage capacity for Wabigoon Lake was exceeded and the resultant spill subsequently was reflected in the second peak at Quibell. As previously mentioned, the regulation of discharges from the Eagle and Wabigoon Lake watersheds significantly stabilizes flow regimes for the

Wabigoon River. Excluding spring runoff, flows at Quibell averaged 35 m^3/s during the 1978 study year, never deviating more than ±25 percent from this value.

TOTAL MERCURY

Concentrations

Results presented in Figures 6 to 13 are summarized in Table 4. Profile data for site 7 appear in Figure 14. All undetectable results were given a value of one-half the detection limit and a summary of the frequency of those results is given for each station in Table 5.

Loadings

Monthly loadings for relevant sites presented in Figure 15 are summarized in Table 6. Daily loadings during the spring runoff period are presented in Figures 16 and 17.

METHYL MERCURY

Concentrations

Methyl mercury concentrations at the study sites (Figures 18 to 24) are summarized in Table 7. Results of samples procured 1 m off the bottom in the western basin are presented with concomitant temperature, dissolved oxygen and total mercury values (Figure 25).

Loadings

Calculated loadings presented in Figure 26 are summarized in Table 8.

DISCUSSION

TOTAL MERCURY

Concentrations

Because of industrial loadings and river drainage form, limnological characteristics at each monitoring site are, in

TABLE 4. Mean concentrations of total mercury at study sites, August 2, 1978 to August 1, 1979.

Study Site	Concentration (ng/l)	Monthly Range (ng/l)	Number of Samples
Site 1	8.6	2.5 - 18	80
Site 2	294	N/A	78
Site 3	27	15.0 - 48	98
Site 4	23	2.5 - 42	98
Site 5	25	9.0 - 45	94
Site 6	22	2.5 - 49	67
Site 7 - Epilimnion	17	4.0 - 39	65
Site 8	14	4.0 - 23	66

TABLE 5. Summary of analytical values within analytical scope for total and methyl mercury.

Study Site	Number of Total Mercury Samples	% Below Detection	Number of Methyl Mercury Samples	% Below Detection
Site 1	80	50	25	48
Site 3	98	7	25	32
Site 4	98	7	25	32
Site 5	94	4	61	3
Site 6	67	3	26	4
Site 7 - Epilimnion	65	6	25	4
Site 8	66	6	50	4

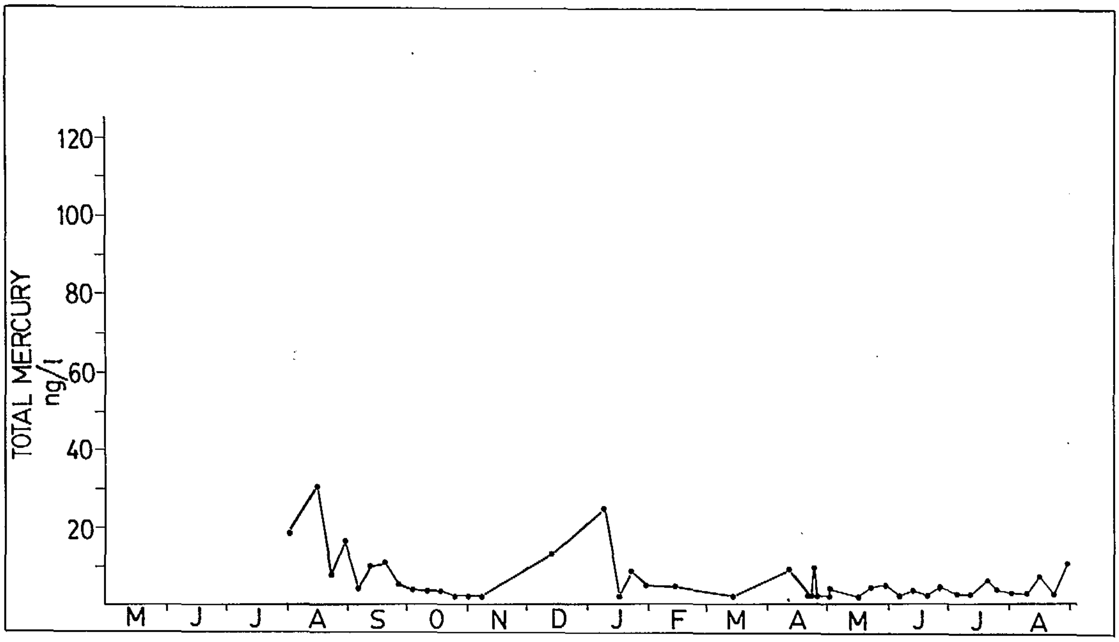


FIGURE 6. Monthly variation in mercury concentration at the Wabigoon Lake outflow (Station 1).

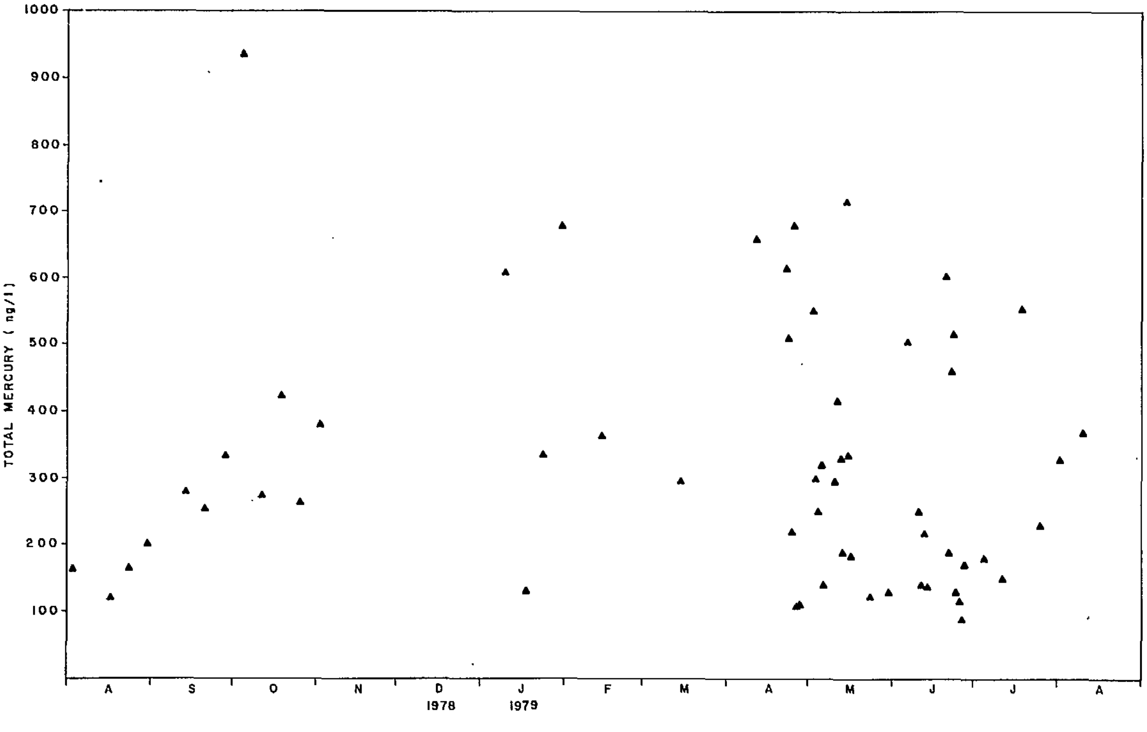


FIGURE 7. Monthly variation in the mercury level of the Reed Ltd. effluent (Station 2) during 1978-1979.

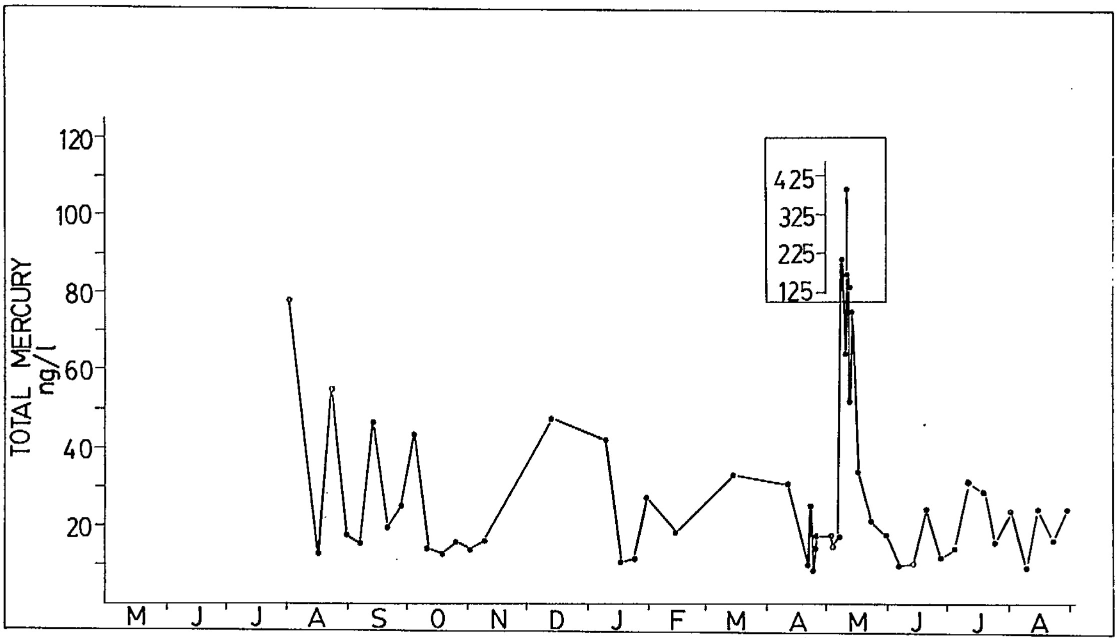


FIGURE 8. Monthly variation in the mercury concentration of the Wabigoon River at Highway 17 (Station 3).

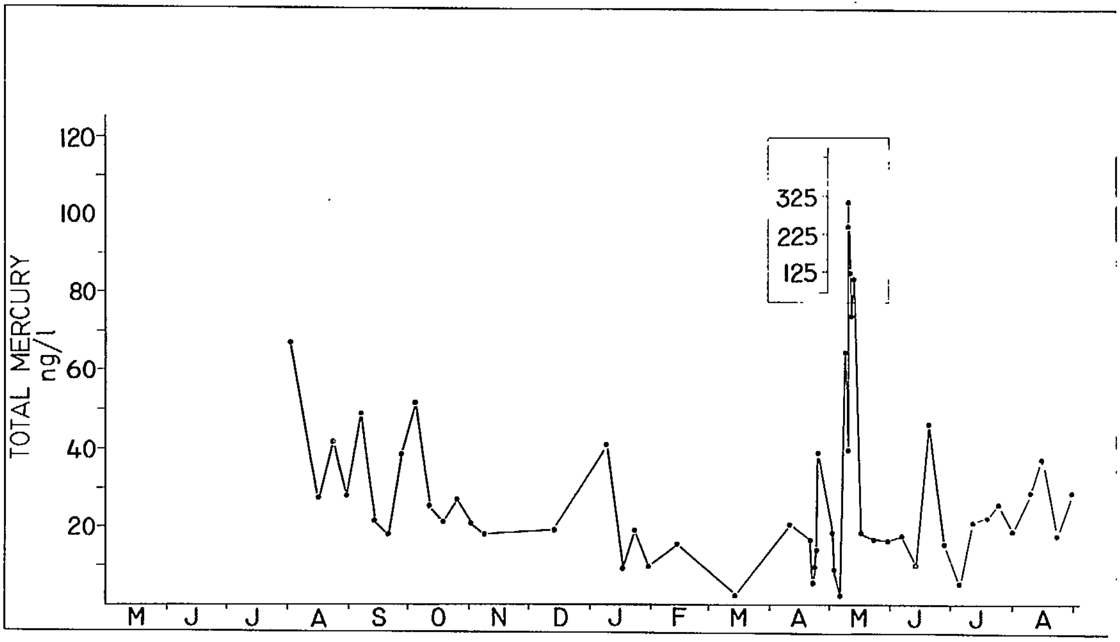


FIGURE 9. Monthly variation in the mercury concentration of the Wabigoon River at Wainwright Dam (Station 4).

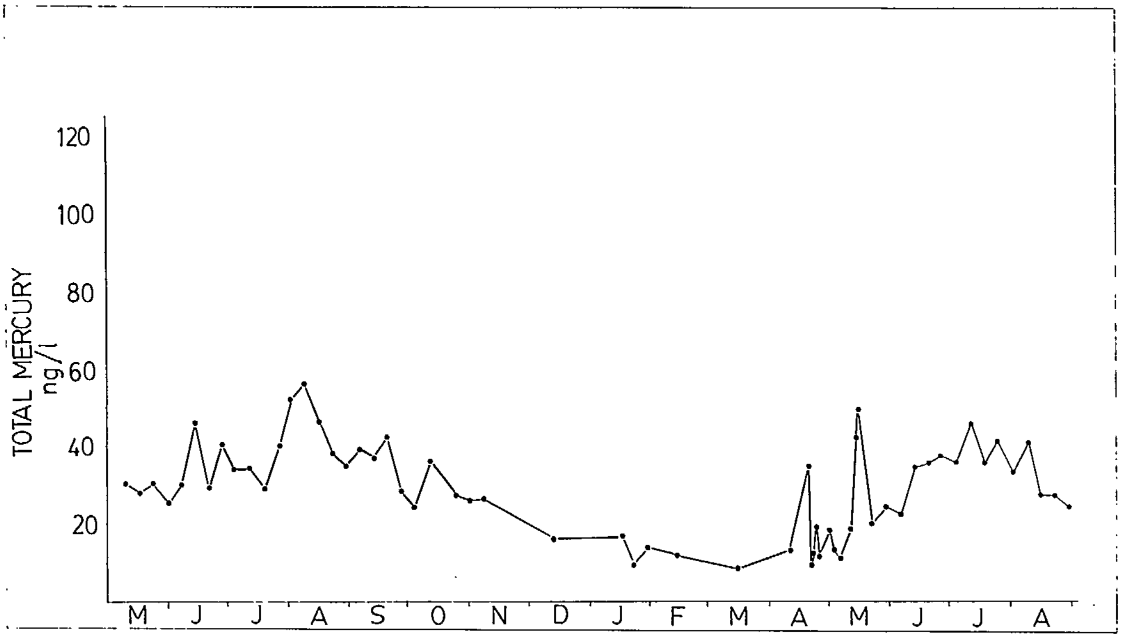


FIGURE 10. Monthly variation in mercury concentration at the inflow to Clay Lake (Station 5).

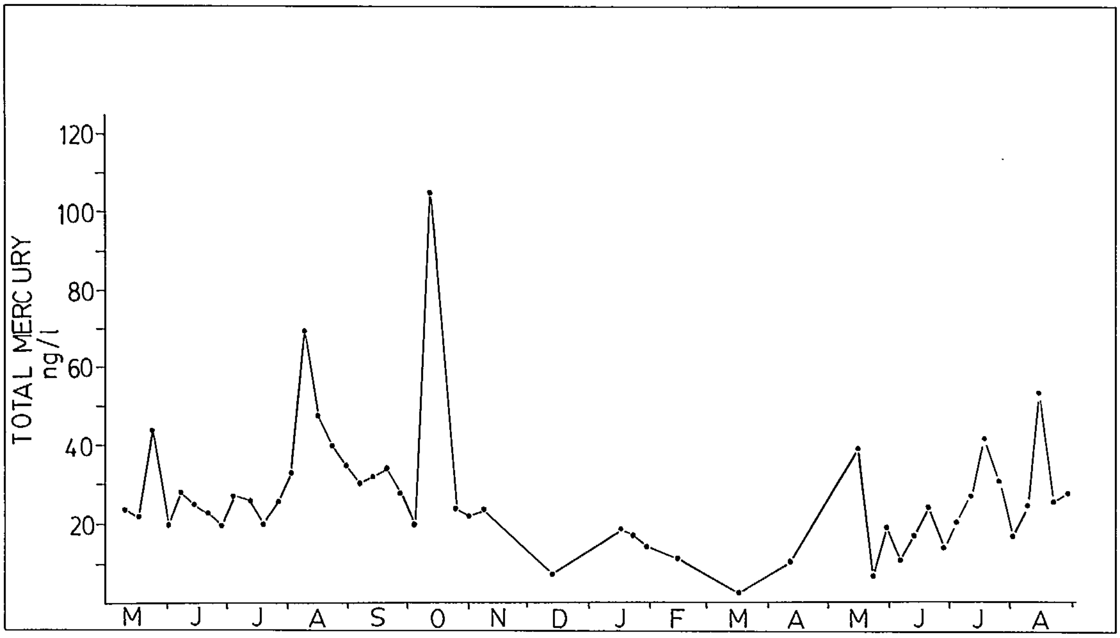


FIGURE 11. Monthly variation in mercury concentration in the eastern basin of Clay Lake (Station 6).

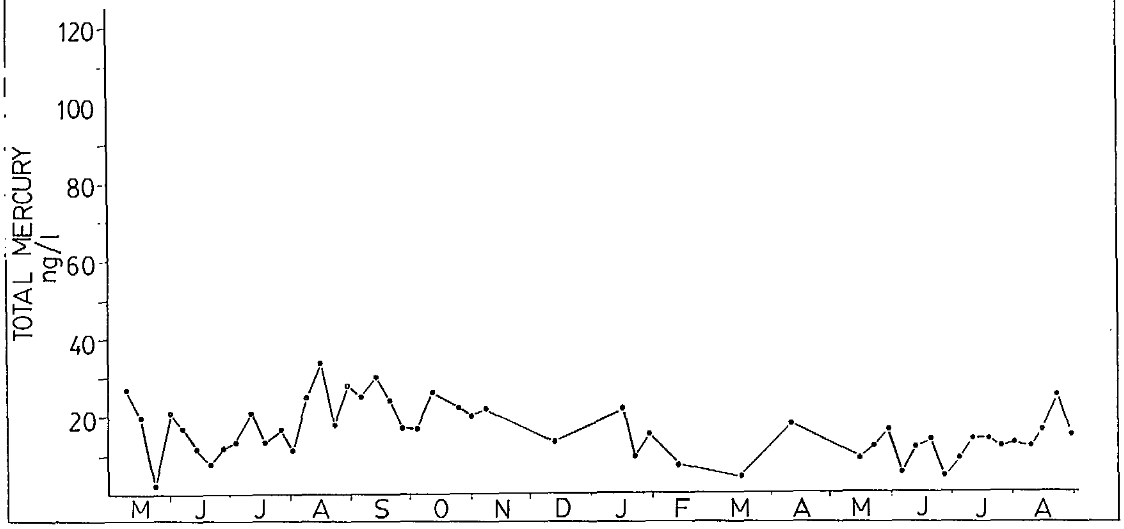


FIGURE 12. Monthly variation in mercury concentration in the epilimnion of the western basin of Clay Lake (Station 7).

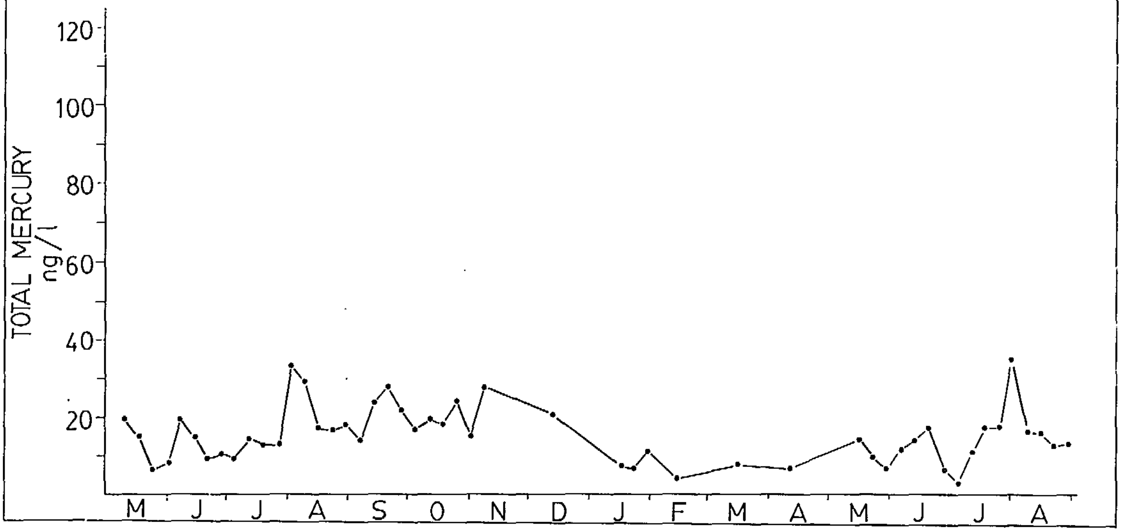


FIGURE 13. Monthly variation in the mercury concentration at the outflow from Clay Lake (Station 8).

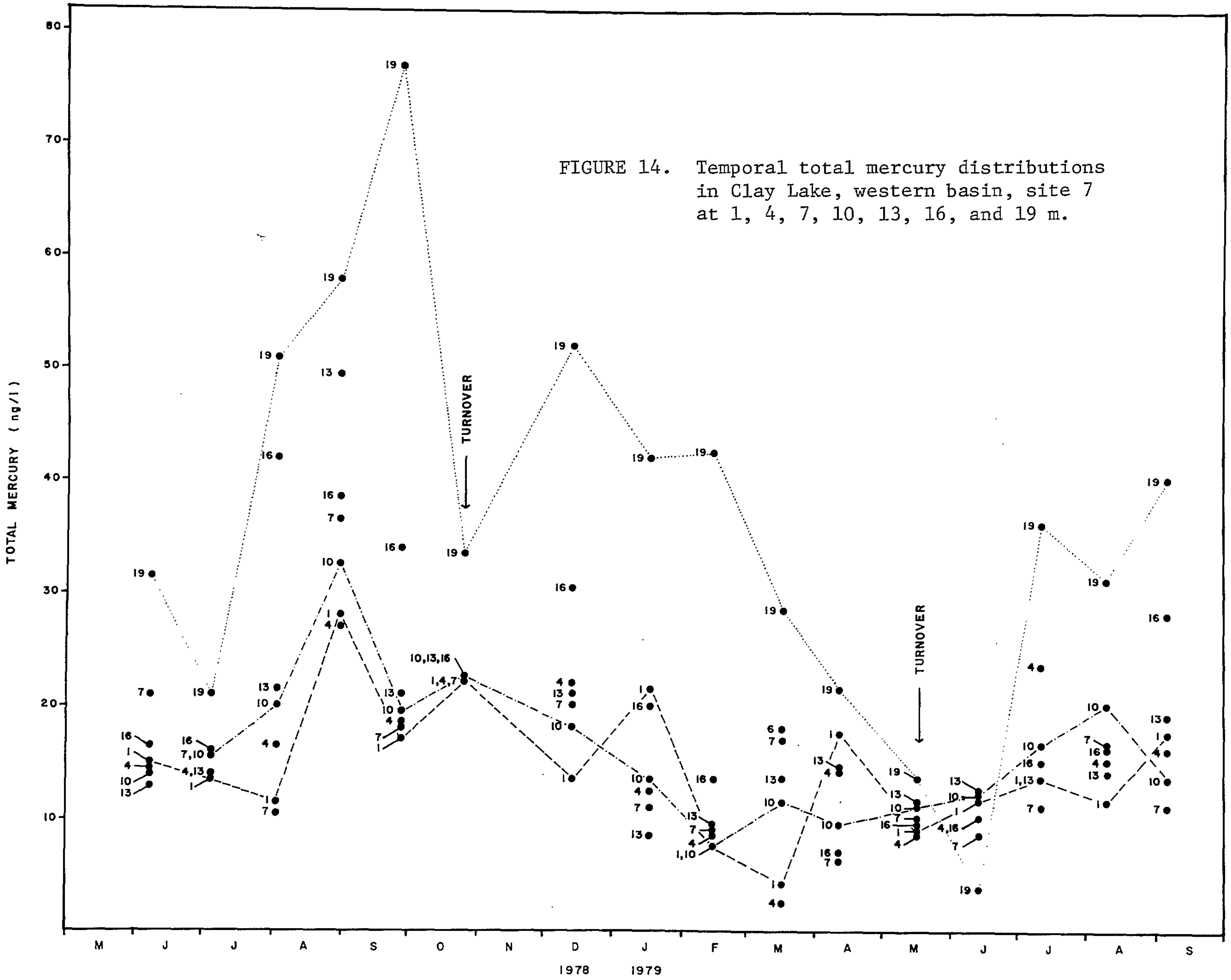


FIGURE 14. Temporal total mercury distributions in Clay Lake, western basin, site 7 at 1, 4, 7, 10, 13, 16, and 19 m.

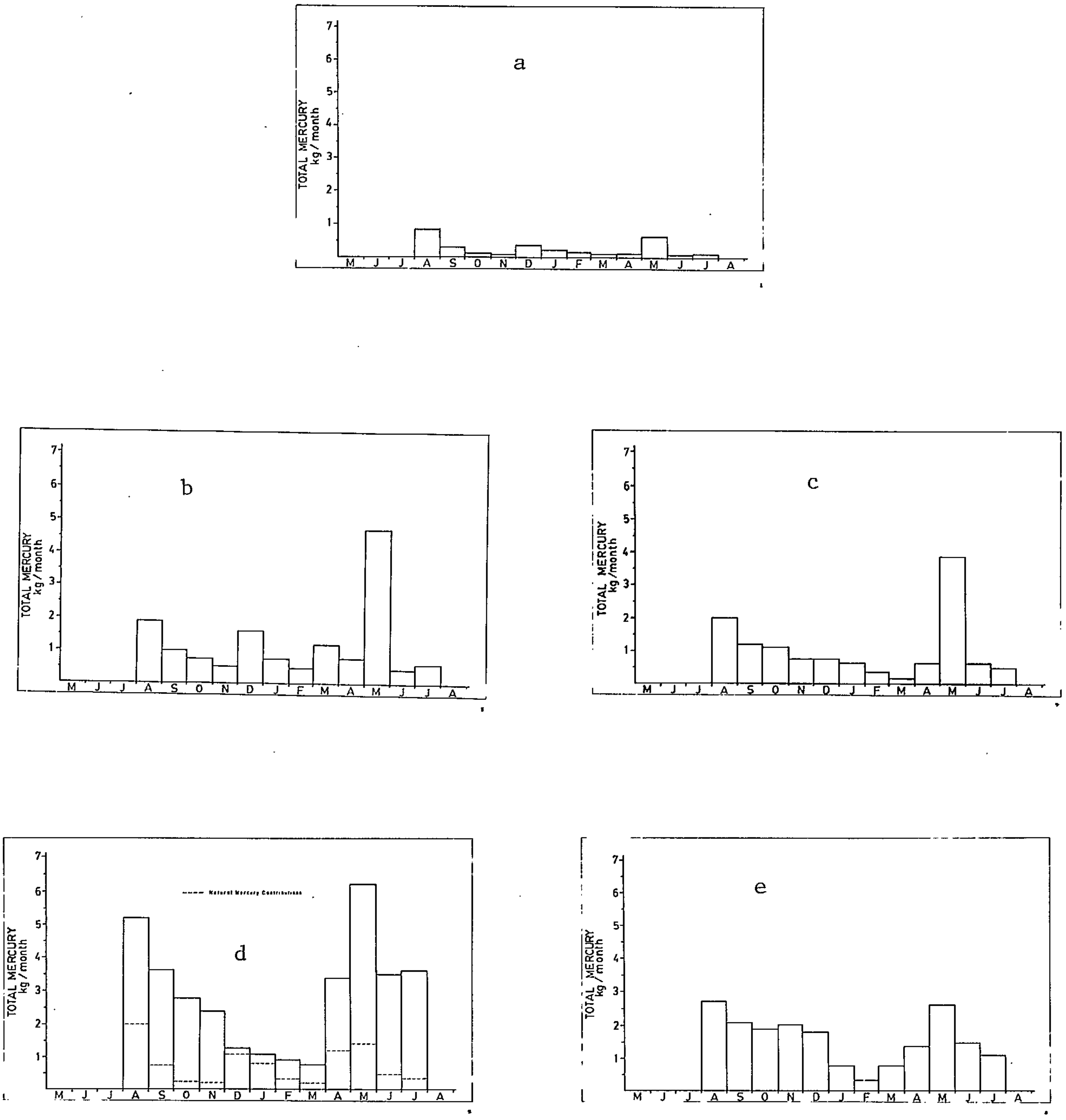


FIGURE 15. Total mercury loadings (kg/month) from August, 1978, to July, 1979, at five sites on the Wabigoon River system.

a - Wabigoon Lake outflow (station 1).
b - Wabigoon River at Highway 17 (station 3).
c - Wabigoon River at Wainwright Dam (station 4).
d - Clay Lake inflow (station 5).
e - Clay Lake outflow (station 8).

TABLE 6. Mean annual total mercury loadings at selected study sites, August 2, 1978 to August 1, 1979.

Study Site	Loading (kg)	Monthly Range (kg)
Site 1	3.0	0.06 - 0.78
Site 2	14.8	N/A
Site 3	14.8	0.46 - 4.7
Site 4	12.4	0.08 - 3.9
Site 5	35.1	0.84 - 6.2
Site 8	19.1	0.29 - 2.6

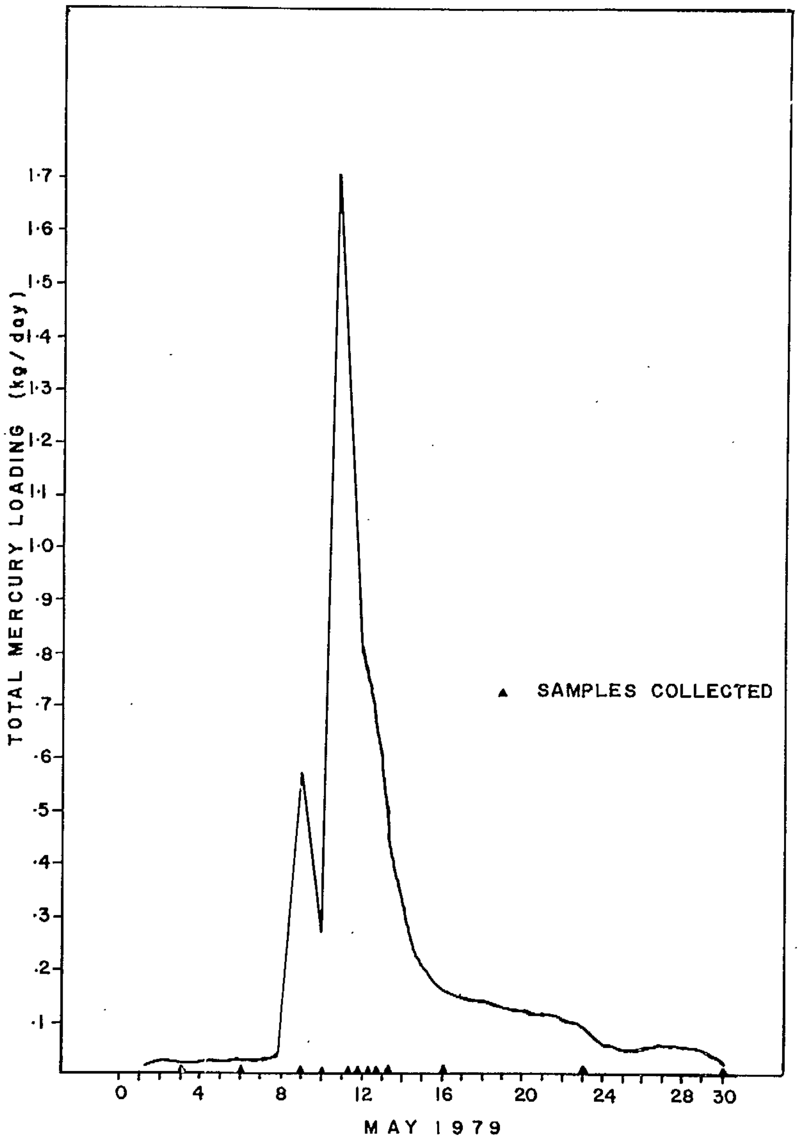


FIGURE 16. Total mercury loading during spring runoff at Station 3.

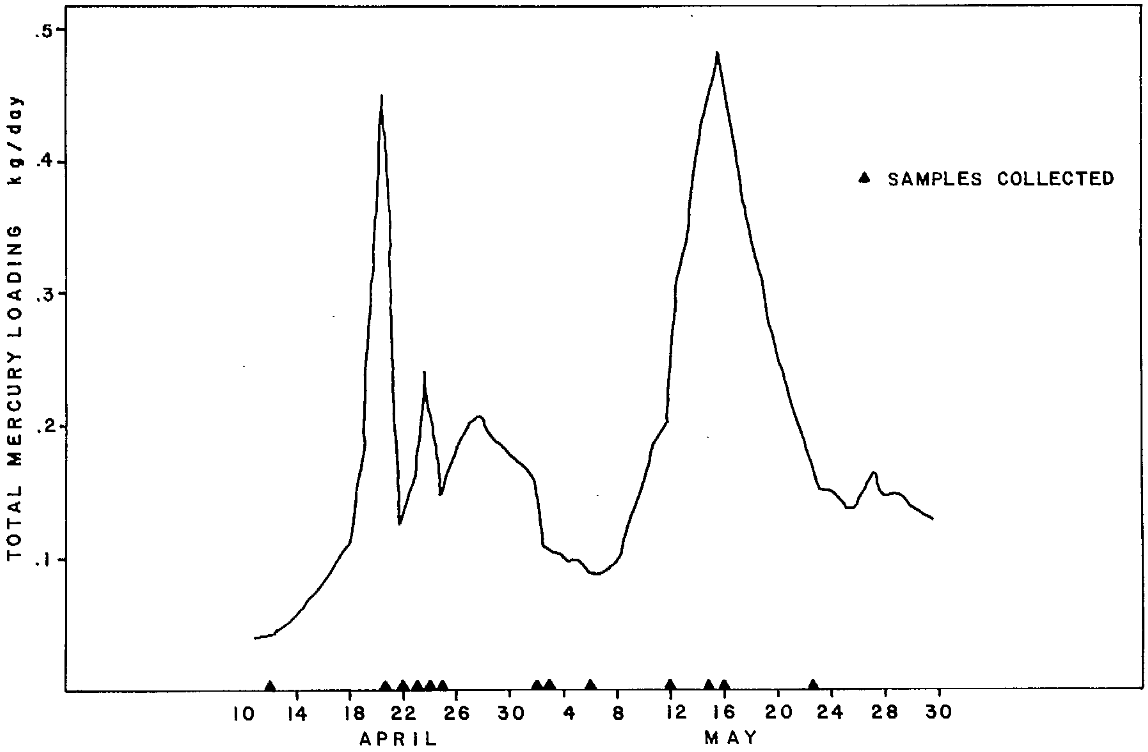


FIGURE 17. Total mercury loading during spring runoff at the inflow to Clay Lake (Station 5).

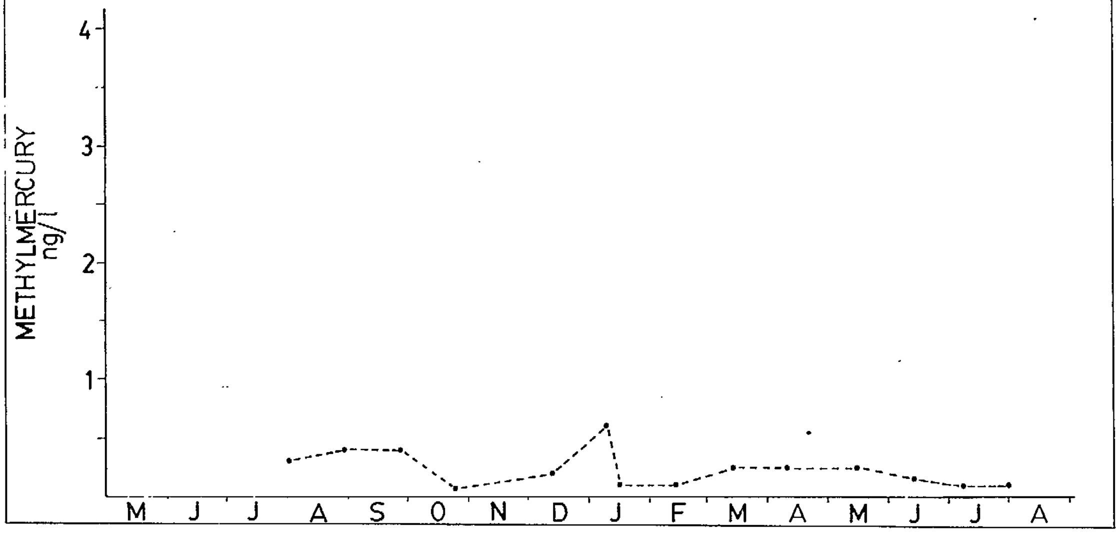


FIGURE 18. Monthly variation in methyl mercury concentration at the outflow from Wabigoon Lake (Station 1).

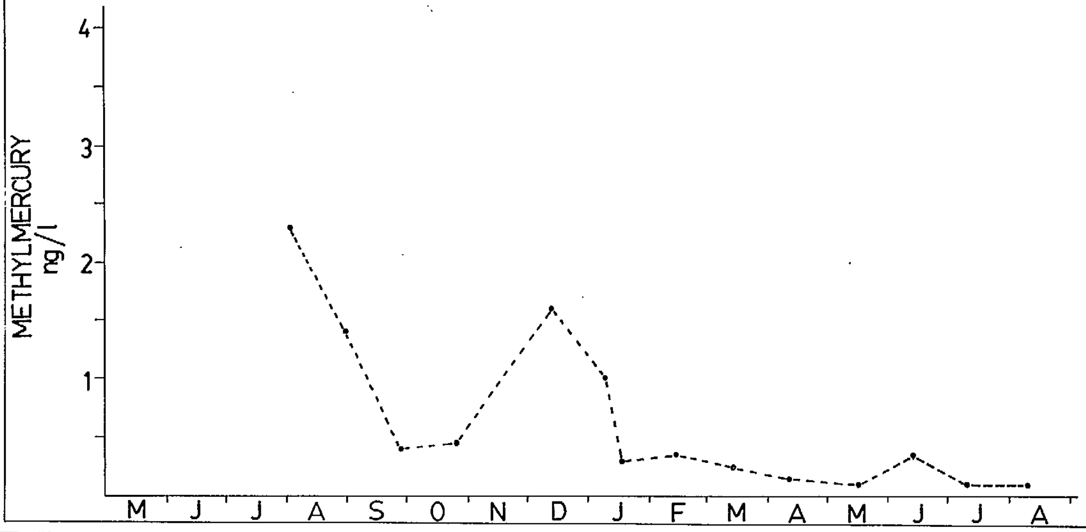


FIGURE 19. Monthly variation in methyl mercury concentration in the Wabigoon River at Highway 17 (Station 3).

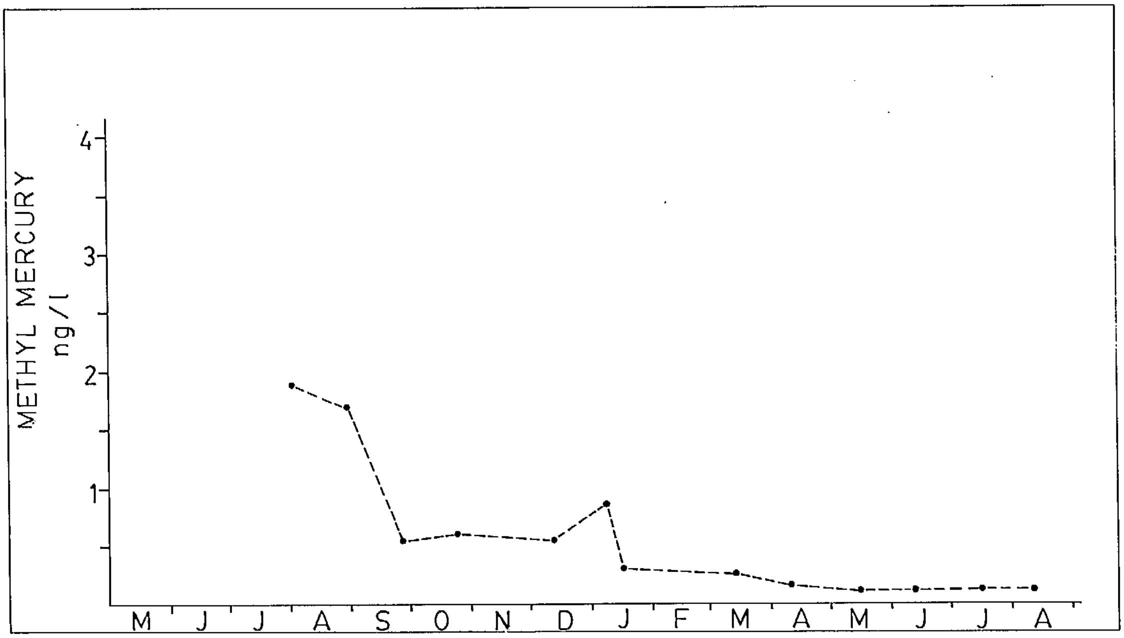


FIGURE 20. Monthly variation in methyl mercury concentration in the Wabigoon River at Wainwright Dam (Station 4).

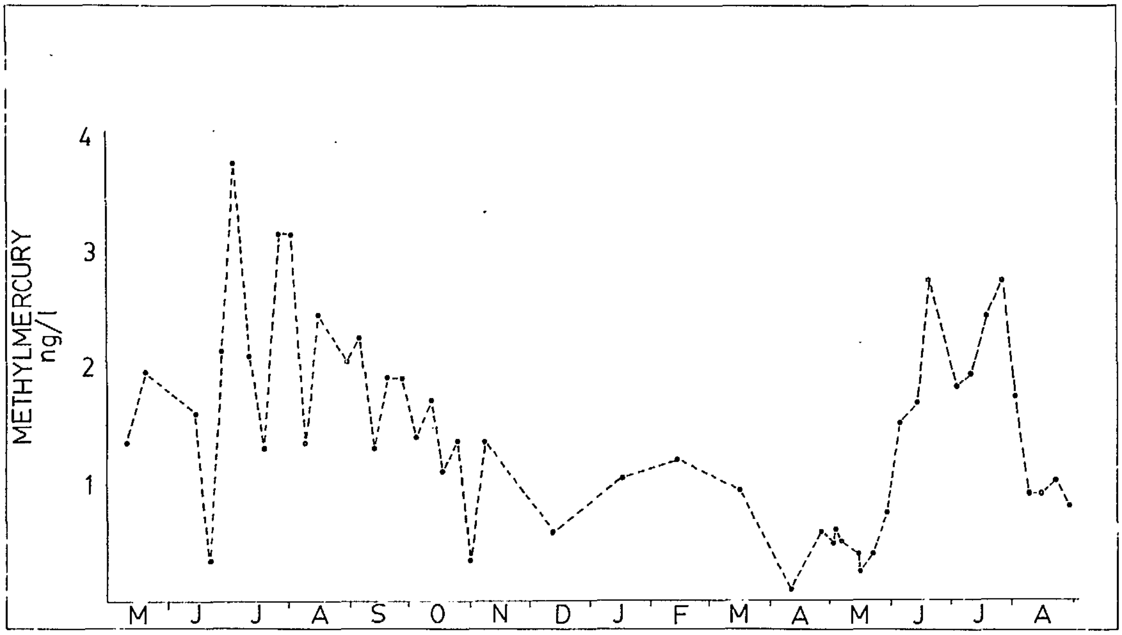


FIGURE 21. Monthly variation in methyl mercury concentration at the inflow to Clay Lake (Station 5).

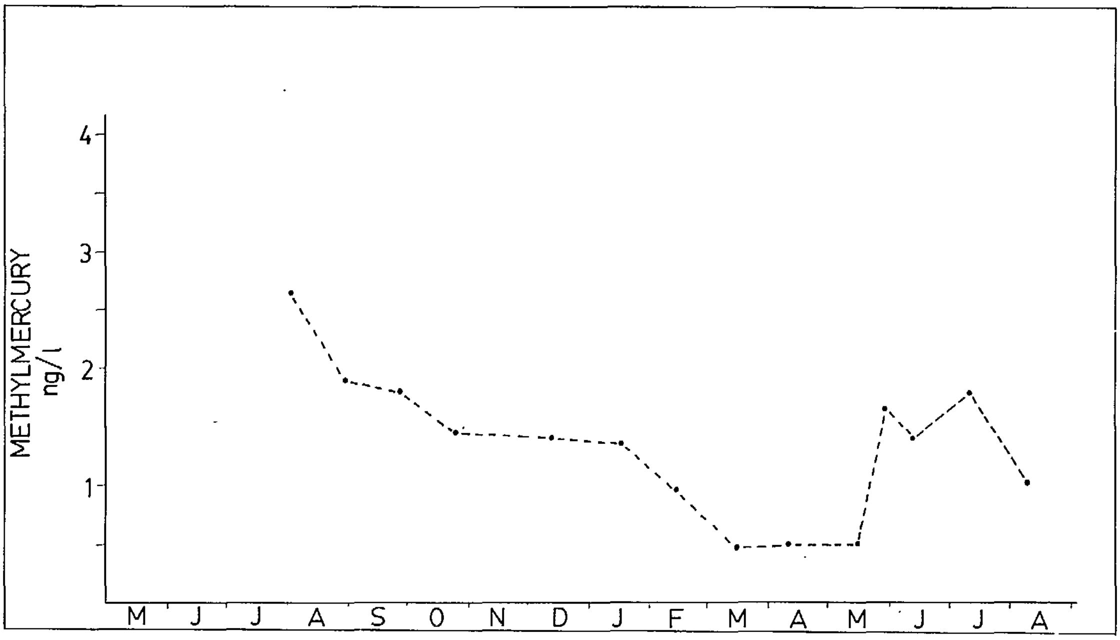


FIGURE 22. Monthly variation in methyl mercury concentration in the eastern basin of Clay Lake (Station 6).

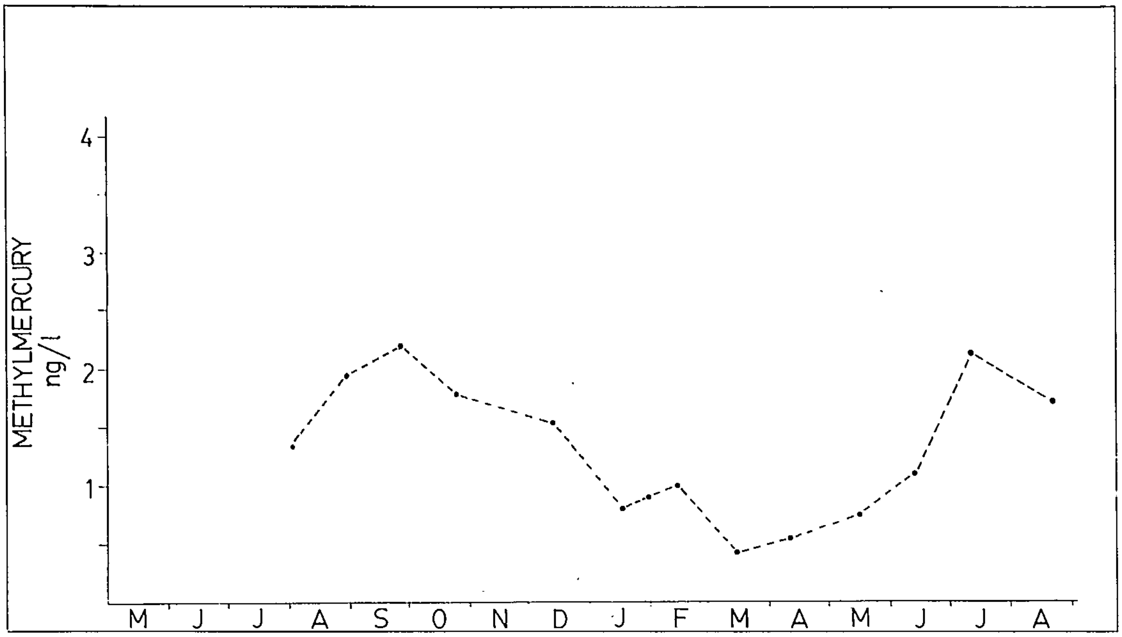


FIGURE 23. Monthly variation in methyl mercury concentration in the epilimnion of the western basin of Clay Lake (Station 7).

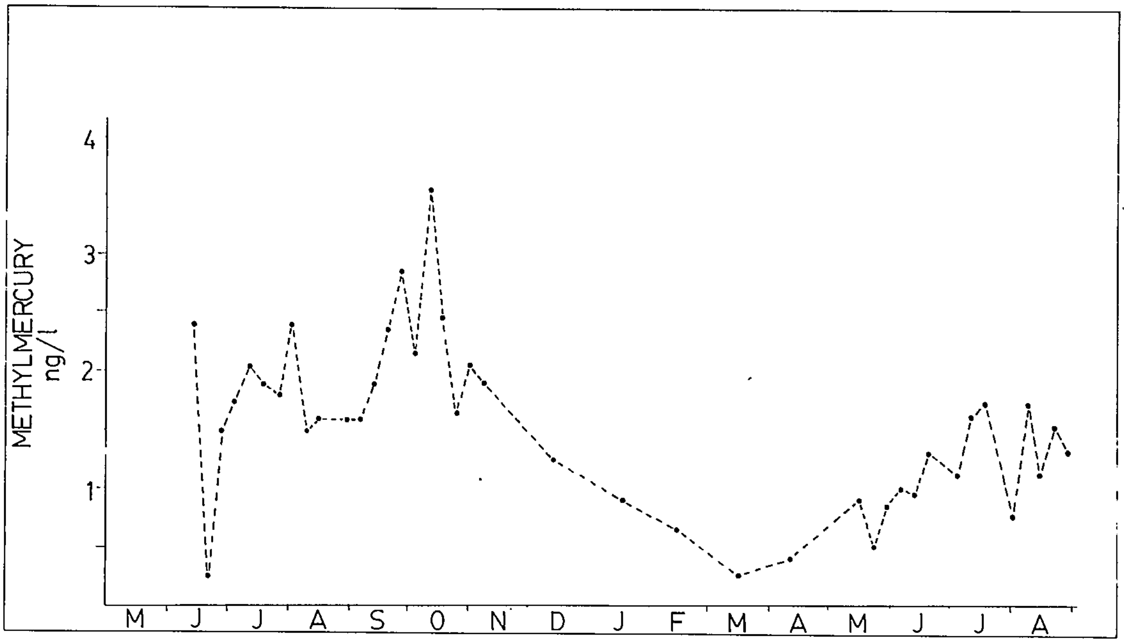


FIGURE 24. Monthly variation in methyl mercury concentration at the outflow of Clay Lake (Station 8).

TABLE 7. Mean concentrations of methyl mercury at study sites, August 2, 1978 to August 1, 1979.

Study Site	Concentration (ng/l)	Monthly Range (ng/l)	Number of Samples
Site 1	.22	.1 - .35	25
Site 3	.61	.1 - 1.8	25
Site 4	.50	.1 - 1.8	25
Site 5	1.3	.6 - 2.2	61
Site 6	1.4	.5 - 2.3	26
Site 7 - Epilimnion	1.3	.4 - 2.2	25
Site 8	1.3	.4 - 2.4	50

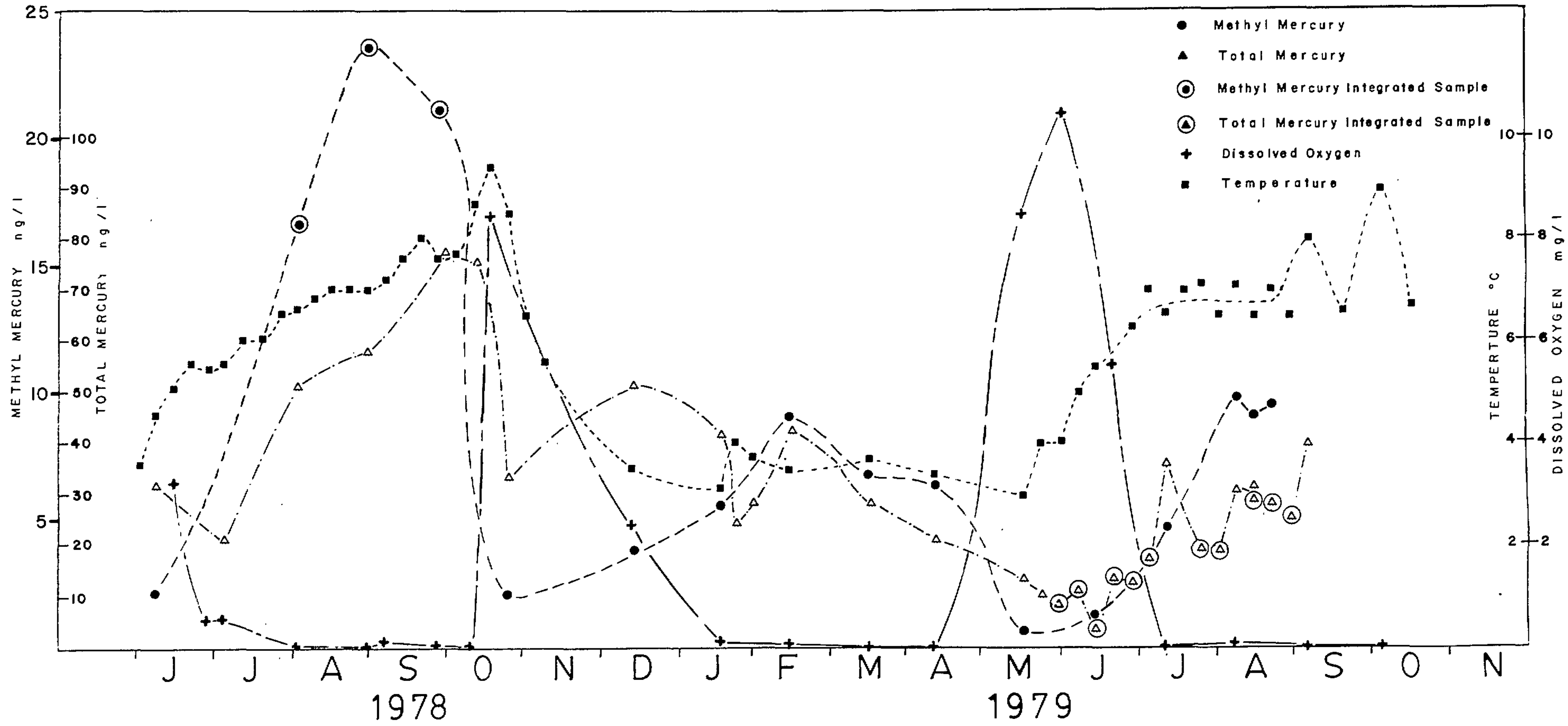


FIGURE 25. Total and methyl mercury values, one meter off bottom, Clay Lake western basin, site 7.

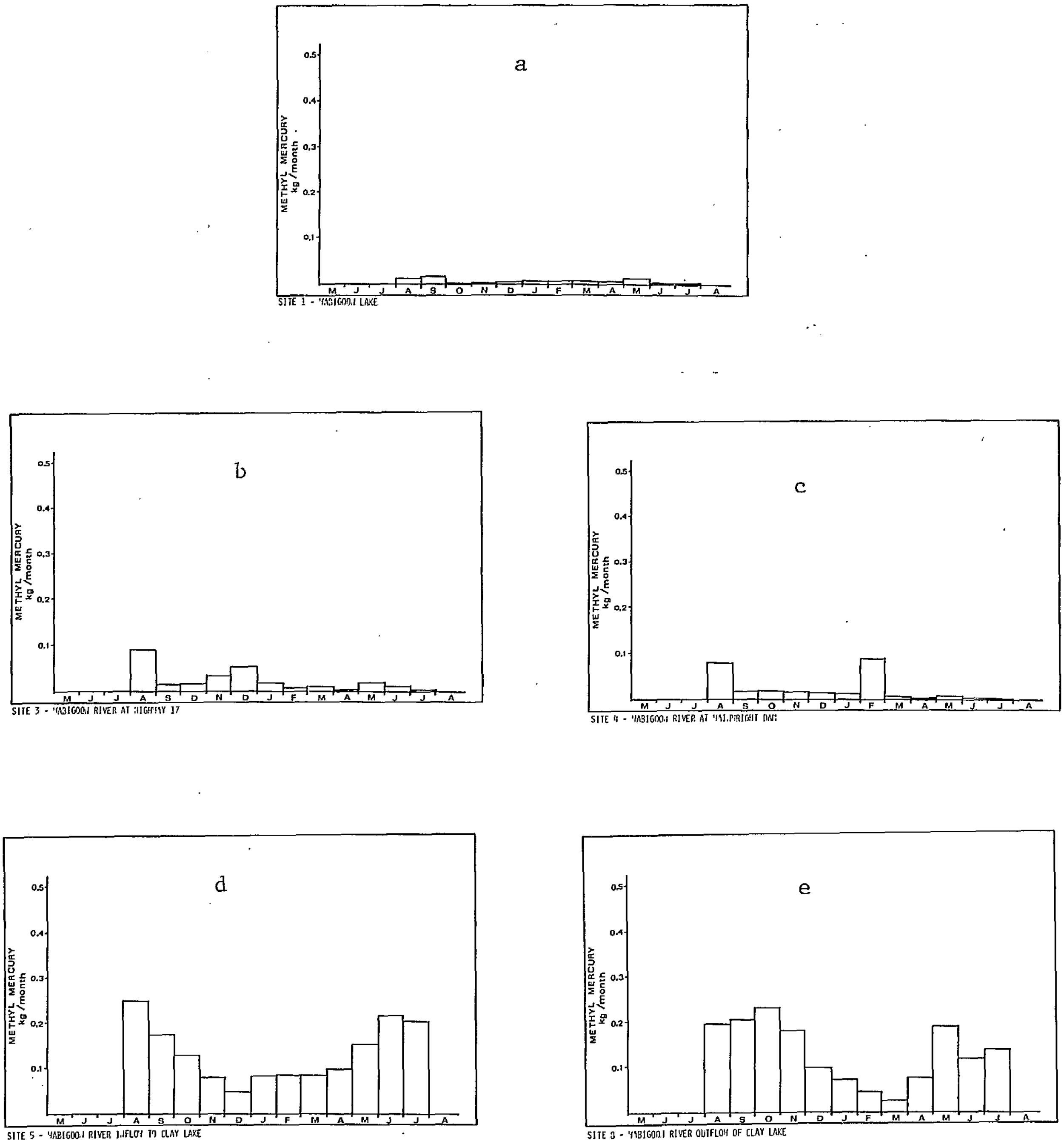


FIGURE 26. Methyl mercury loadings (kg/month) from August, 1978, to July, 1979, at five sites on the Wabigoon River system.

a - Wabigoon Lake outflow (station 1).
b - Wabigoon River at Highway 17 (station 3).
c - Wabigoon River at Wainwright Dam (station 4).
d - Clay Lake inflow (station 5).
e - Clay Lake outflow (station 8).

TABLE 8. Mean annual methyl mercury loadings at selected study sites, August 2, 1978 to August 1, 1979.

Study Site	Loading (kg)	Monthly Range (kg)
Site 1	.09	.002 - .015
Site 3	.29	.002 - .021
Site 4	.22	.003 - .085
Site 5	1.7	.052 - 0.25
Site 8	1.6	.023 - 0.24

general, substantially different from each other. The results from selected sites, therefore, reflect effects from a wide range of lake and river environments. In maximizing the environmental scope of this project, however, only small resources were available for replicate testing; consequently, the following discussion of mercury trends and other dynamic interactions based on one year's results must, in certain respects, be viewed tentatively subject to confirmation by another year's values.

A relatively high variance in some of the duplicate total mercury concentrations collected at the start of the program raised some concern over sampling procedures. Mercury values obtained from the intensive sampling of the Wabigoon River, at Highway 17, in August, however, provided sufficient information to explain data scatter. A significant portion of the mercury in the water column was associated with particulate matter greater than 0.45 u (Table 2). Since a mercuric sulphide particle (2×10^{-2} mm in diameter) in a 250-ml sample of otherwise particulate-free water would produce a mercury concentration in excess of 1,000 ng/l, the presence or absence of mercury containing particulate matter is an obvious potential source of variation in mercury content. Because of the demonstrated water-solid phase characteristics of mercury, replicate results do not appear unreasonable.

All samples downstream of Dryden had significantly higher ($p < .01$) mercury concentrations than those at the control site. Average mercury levels in the Wabigoon River at Highway 17, at Wainwright Dam, at the inflow to Clay Lake, and from the eastern basin of Clay Lake were similar and were approximately three times higher than the concentration (8.6 ng/l) for uncontaminated waters above Dryden. Mean mercury concentrations in the surface waters of the western basin of Clay Lake and outflow of 17 and 14 ng/l, respectively, were significantly less ($p < .01$) than those in other contaminated waters upstream. Concentrations at the outflow of Clay Lake were approximately 45 percent lower than inflow values, though significant seasonal differences were evident.

Mean annual mercury concentrations of 8.6 ng/l (Table 4) at the outlet of Wabigoon Lake appear comparable with values obtained for other shield waters in Canada. Kudo et al (19) reported values of 12 to 13 ng/l for raw water from the Ottawa River unaffected by industrial wastes and A. F. Penn has concluded waters in northwestern Quebec have approximately 10 ng/l (20). In comparison to other published values for total mercury in water, mercury levels reported in this study appear to be low (29).

Of the 80 values obtained from Wabigoon Lake, 50 percent were less than the detection limit of approximately 5 ng/l. After comparing the Eagle and other tributary results (Table 9) with those of Wabigoon Lake and finding no significant difference, we are assuming that control site values are representative of other uncontaminated feeder streams. Temporal trends from the Wabigoon Lake outflow were evident (Figure 6) with summer and winter maxima noted. The winter peak was not observed at all downstream sites due, perhaps, to increased mercury concentrations resulting from present or past industrial discharges. The same general trends at our control site were also found in the Ottawa River (19) in waters not immediately downstream of a source of industrial contamination.

Although the study year began in August, 1978, and complete summer data were not available, the value of 30.5 ng/l observed early in this month was considered to be the maximum for the season. In Clay Lake, where June and July data are available, maximum values were generally found at that same time. The winter peak in December at the control site was unexpected and cannot be explained. It may be an artifact of the sampling site location which is very close to the outlet of the lake. Thus, the site may reflect internal lake dynamics as does site 8 at the outlet of Clay Lake. Here values in December were also elevated.

Mean annual mercury concentrations in the Reed Ltd. total effluent were 294 ng/l. Although these values are typical of other pulp and paper mills with or without chlor-alkali plants (21), many laboratories do not have the capability to accurately determine low concentrations of mercury in many mill discharges.

TABLE 9. Mercury concentrations for five uncontaminated tributaries for the Wabigoon River, August 2, 1978 to August 1, 1979.

Sampling Site	Aug 1978	Sep 1978	Oct 1978	Nov 1978	Dec 1978	Jan 1979	Feb 1979	Mar 1979	Apr 1979	May 1979	Jun 1979	Jul 1979
Site 1	19[a](8)[b]	8 (8)	4 (8)	2 (4)	13 (2)	10 (8)	5 (2)	2 (2)	4 (10)	6 (11)	3 (8)	4 (8)
Eagle River			2 (2)					2 (2)	6 (12)	4 (12)	6 (8)	3 (8)
Aubrey Creek			2 (2)					6 (2)	7 (2)			
Buller Creek			2 (2)						7 (2)			
Hutchinson Creek			2 (2)					2 (2)	10 (3)			
Rugby Creek			2 (2)					2 (2)	4 (2)			

[a] Represents monthly average mercury concentrations.

[b] Indicates the number of samples taken each month.

Average values at site 3 for the Wabigoon River at Highway 17 were 27 ng/l, over three times values observed at the control station. Except during the spring flush, a highly significant total mercury relationship ($p < .01$) was found between results for Reed Ltd. effluent and those at site 3. Total mercury concentrations appear to be time related but, in general, lack the definition observed at most other stations. The lack of temporal clarity, no doubt, reflects the masking effects of Reed Ltd. effluent. Historical loadings of mercury desorbed or resuspended may also play an important role.

Mercury concentrations increased by more than an order of magnitude in the spring during the regulated discharge from the Dryden dam (Figure 27). Highest mercury levels were reported just preceding the maximum stage. This phenomenon is common for sediment bound contaminants eroded during high flow events. It is clear that sediment exhaustion occurs very quickly, thus accounting for a poor relationship between mercury concentrations and flow. The high values found in early August, 1978, may be related more to the increased spill (Figure 2) than to seasonal effects.

No significant difference in total mercury concentration was found between site 4, the outflow of Wainwright Dam and site 3, indicating that the Wainwright Dam has a negligible effect on the total mercury flux in this part of the river. During regulated maximum flow events, similar total mercury levels were also found at sites 3 and 4 (Figure 27). The data suggest that the mercury reservoir reported to exist behind the Wainwright Dam (22) is not acting as a source for mercury contamination farther downstream, rather, the area in question may trap mercury washed from upstream. A significant correlation ($p < .05$) was also found between mercury concentrations at site 4 and results from the mill complex.

Total mercury results at site 5, which exhibit a clear, temporal, sinusoidal pattern, when averaged, are comparable to concentrations observed at station 4. These levels are approximately three times higher than concentrations observed in uncontaminated waters. Since flows are substantially greater than those

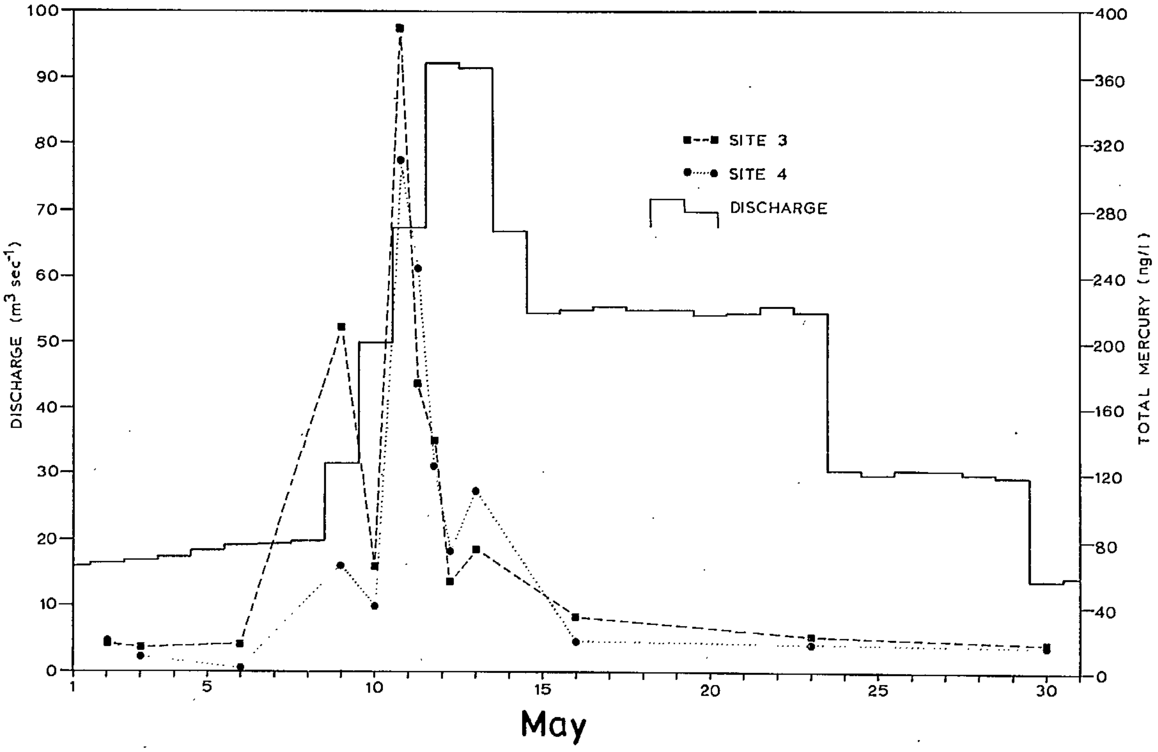


FIGURE 27. Mercury dynamics at sites 3 and 4 during the spring flush, 1978.

at the Wainwright Dam, additional mercury is being introduced into the water column presumably by remobilizion of mercury in contaminated sediments upstream. Excluding spring runoff, mercury concentrations are clearly a function of water temperature which directly affects chemical desorption and microbiological activity. During times of uniform flows it is likely that mercury levels at site 5 are a function of the rate of solubilization of mercury from bed sediments.

In reference to the hydrograph (Figure 2), two maximum stages are obvious during the spring of 1979. The first peak represents the unregulated discharge, comprising watershed contributions resulting from the spring melt, while the second peak exhibits the effect of the regulated discharge of water from the Dryden dam. The regulated discharge would have a greater impact on bed sediments near the head of the study area, where mercury concentrations in the sediments are the highest. Mercury levels increased in both flood episodes but higher mercury concentrations were observed during the regulated discharge, thereby implicating the source of flow, as well as the stage, as a significant factor in mercury mobility in the Wabigoon River. A good portion of the mercury pulses observed during this period are probably related to resuspended sediment.

At site 6, the eastern basin of Clay Lake, the mean mercury concentration of 22 ng/l was similar to the average value at site 5. In addition, temporal effects were clearly evident.

During a six-week period in the summer of 1978, mercury concentrations at site 6 began to increase and on August 16 reached a peak of 65 ng/l (Figure 11). Algae blooms were present on Clay Lake at approximately the same time during both years and it is presumable that the elevated mercury concentrations may be linked to a rise in productivity.

On October 12, 1978 duplicate mercury concentrations of 99 and 107 ng/l were detected at site 6 on Clay Lake. These levels are five times higher than the mean mercury level (21 ng/l) of all samples collected at site 6 for the whole study year. It would appear that the inordinately high mercury concentrations may have their origin in the form of a mercury spike in the Reed Ltd. effluent. In support of this statement are three points of evidence:

(1) Total mercury samples taken at site 6 on October 12, 1978 were in duplicate.

(2) Mercury concentrations in the Reed Ltd. effluent of 900 ng/l and 970 ng/l were reported one week prior to the detection of high mercury levels at site 6. The mercury levels reported in the Reed effluent were the highest values detected during the whole study year and represented concentrations three times higher than the mean of all samples taken at Reed. Because sampling frequency was limited to once per week at this time of the year, the mercury "spike" passing down the Wabigoon River was not detected at the river sampling sites. However, elevated mercury levels were recorded at site 6 on Clay Lake where water residence time is much longer.

(3) Finally, the Federal Research Team was conducting an "in situ" minnow caging experiment at site 5, the inflow to Clay Lake, during the time of the mercury "spike". They reported almost total mortality of their minnows the same week that elevated mercury levels were detected at site 6. The experiment had been carefully monitored for several weeks prior to the incident. The minnow mortalities suggests that other water quality characteristics were influenced at the time of the increase in mercury concentrations.

An alternative explanation may be that Reed Ltd. discharged a slug of chemicals capable of extracting mercury from the bed sediments.

Mean surface values (17 ng/l) for site 7, the western basin of Clay Lake, were significantly lower than those observed in the eastern basin. The sinusoidal curve was pronounced at site 5, moderated at site 6, and further decreased at site 7 (Figure 10, 11 and 12).

Seasonal trends were apparent with maximum mercury concentrations normally found in August. Monthly profiles (Figure 14) generally reflected thermal stratification (see Figures 28, 29 and 30). Generally, there are two distinct trends, separated by spring and fall turnovers when mercury levels in the entire water column are homogeneous. During the summer, mercury levels increased in the hypolimnion with maximum values reached in October, well after the early August peak observed at most surface sites. It is possibly a result of mercury settling out and subsequent trapping in the hypolimnion. Desorption from sediments could also be a contributing factor. As the metalimnion is eroded in September and October, the mercury in the bottom waters is mixed with the epilimnion, thereby raising surface water mercury concentrations. The reasons for not detecting a pronounced increase in surface water mercury concentrations are threefold. First, the hypolimnion by volume constitutes approximately 10 percent of Clay Lake and, secondly, the process whereby the hypolimnion is eliminated is spread over several weeks. Consequently, gradual, not immediate changes would be noted. Finally, if mercury concentrations at site 7 generally followed trends at site 6, mercury levels would drop in September and October. In Clay Lake, however, mercury levels remain elevated through the fall. The trend established during the 1978 summer seems to continue in 1979; however, mercury levels are substantially reduced. After fall turnover, mercury levels rise immediately in bottom waters and decrease through the winter months. This phenomenon cannot be readily explained.

At site 8, the outflow of Clay Lake, a mean mercury level of 14 ng/l was significantly less than the level of 25 ng/l reported at site 5, the inflow to Clay Lake but not significantly different than those obtained at site 6. Temporal trends are obvious and mercury dynamics appear to be related to the effects of internal cycling of the western basin.

At all sites, the changes in mercury concentrations generally followed the same trends (Table 10) with highest values noted in August and lowest values observed in late winter.

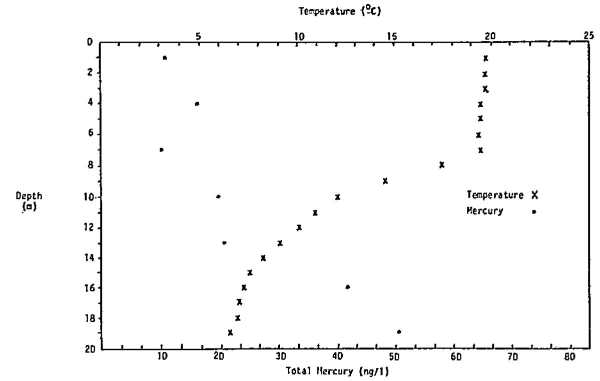


FIGURE 28. Mercury profile of western basin of Clay Lake (Station 7) on August 2, 1978.

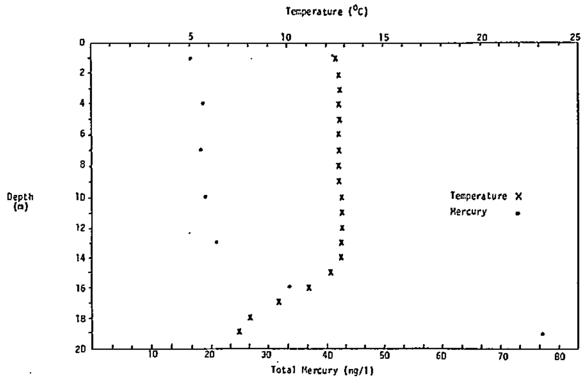


FIGURE 29. Mercury profile of western basin of Clay Lake (Station 7) on September 27, 1978.

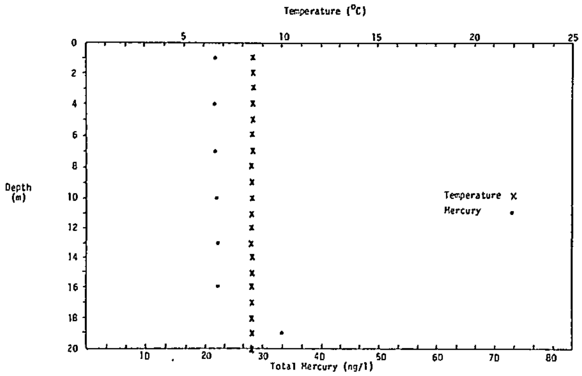


FIGURE 30. Mercury profile of western basin of Clay Lake (Station 7) on October 25, 1978.

TABLE 10. Summary of total mercury dynamics characteristics at study sites.

Study Site	Total Mercury (ng/l)	High		Low		High/Low
		Date	Total Mercury (ng/l)	Date	Total Mercury (ng/l)	
Site 1	9	08/16/78	30	N/A[b]	<5	>12
Site 3	27	08/02/78	78	04/23/78	8	9
Site 4	23	08/02/78	67	02/14/79	<5	>13
Site 5	25	08/09/78[a]	56	03/16/79	9	6
Site 6	22	08/09/78	66	03/16/79	<5	>13
Site 7 - Epilimnion	17	08/16/78	34	03/16/79	4	8
Site 8	14	08/02/78	34	02/14/79	4	8

[a] Omitting October spike.

[b] 50% of all samples were below detection limits. These results were observed in all seasons.

Loadings

Past and present mercury contamination of the Wabigoon River system is much more striking than concentration data indicate due to the increase in flows between Dryden and Clay Lake. The background total mercury loading at the outflow of Wabigoon Lake for the study year was 3.0 kg. At site 3, the first monitoring site on the contaminated watercourse, approximately 5.5 km downstream of Dryden, the mercury loading was 14.8 kg or five times this value. Contributions from Reed Ltd. could account for all of this additional mercury, if all mercury from Reed effluent passed this point. The loading of 12.4 kg at site 4 at the outflow of Wainwright Dam was slightly less than at the inflow, thus indicating that, at present, the Wainwright Dam has a negligible effect on total mercury mobility in this portion of the river. At site 5, the loading increased to 34 kg. After subtracting the natural loading (Figure 15) at this point, 25 kg of anthropogenic mercury was calculated to have entered Clay Lake. Apparently, Clay Lake is a sink for a substantial portion of this load as 42 percent of incoming mercury was retained during the 1978-79 study year.

Of special interest at sites 3 and 4 is the effect of creating near instantaneous flood conditions during the aforementioned May period. During this short interval of seven days, 4.5 kg or 30 percent of the total annual loading occurred at site 3 (Figure 16). In a similar time frame, 35 percent of the annual flux at the outflow of the Wainwright Dam occurred. Resuspension of mercury-laden sediments is, undoubtedly, responsible, as a daily monitoring of Reed Ltd. operations during this period indicated that at best only 8 percent of the site 3 loadings could have been derived from that source. Depending on one's perspectives, this event could be viewed in two ways. If flows at site 3 were maintained at values below those capable of resuspending contaminated sediments, then quite likely loading could be decreased substantially as mercury would be removed by desorption only - a very slow process. Since the total quantity of mercury to be removed from the sediments does not change, application of the above strategy would necessarily involve a longer period for the river to return to normal. If, on the other hand, continual pulses were deliberately contrived, mercury loadings would be elevated sharply but more mercury would be flushed from the river in a shorter time frame.

Loadings at site 5 clearly indicate the effects of past and present mercury discharges on the present mercury loadings to Clay Lake. Most striking are the loadings resulting from the twin flow peaks in April and May (Figure 17) which accounted for 27 percent of the annual flow.

From data for site 5, we can calculate that 25 kg of industrially released mercury has entered Clay Lake during a one-year period of the present study, approximately nine years after mercury releases from Reed Ltd. were sharply reduced to 15 kg per annum. It is not possible to back calculate and determine exactly how much mercury has been flushed from the river during this period because it is probable that annual, industrially related loadings to Clay Lake have not been similar since 1970. Loadings have probably decreased as the sediments containing the highest concentrations of mercury were eroded or desorbed in the early phase. Previous investigations (5, 23) also do not assist in estimating this value. Nonetheless, the Ministry of the Environment estimated a mass balance of the Wabigoon River and Clay Lake system in 1973 suggesting that approximately two tons resided in river sediments at that time. Another intensive sediment sampling of the Wabigoon River in 1980 should also help redefine the mercury reservoir there. If estimates of over a ton are obtained, it is clear that decades are involved before most of the mercury will be removed from the Wabigoon River between Dryden and Clay Lake.

At site 7, loadings reflect lake dynamics more than the dynamics of a true river station. These loadings generally parallel those found at site 1, with the peaks of the spring runoff moderated due presumably to settling out of particulate matter.

METHYL MERCURY

Concentrations

Mean values for surface waters at contaminated stations were two to six times the average control value of approximately 0.22 ng/l. In general, temporal trends appear at most sites with highest values noted during the summer. Considering that most methyl mercury production in natural sediments or waters is believed to be related to the activity of bacterial organisms, this trend is not surprising.

Concentrations of methyl mercury in the Wabigoon Lake outflow were low, with 50 percent of the values below the detection limit (Table 5). Thirteen values from the Eagle River were similar. In the early part of the study, highest levels occurred in late September, possibly due to internal lake dynamics. The winter peak cannot be readily explained.

Average concentrations escalated at site 3, the Wabigoon River at Highway 17, to 0.61 ng/l. Temporal trends similar to the control site are evident; however, highest values were observed in August not January. An increase in Wabigoon River flows in early August (Figure 2) may be partially responsible as bed sediments may have been disturbed. The increased concentrations were presumably caused by mercury methylation and subsequent diffusion from contaminated sediments.

Results from site 4, the outflow from the Wainwright Dam, are not significantly different from those at site 3, though mean concentrations of 0.50 ng/l are slightly less than the inflow concentration. From this limited data, the Wainwright Dam appears to have a slightly demethylating environment. These results indirectly support the hypothesis that most ecologically significant methylation occurs in the surficial sediments. Loosely consolidated sediments behind the Wainwright Dam are composed of mercury-enriched woodwastes and extend to depths of over 10 metres. Gas formation to depths of at least 5 m have been observed and the constant physical disturbance of these sediments would aid methyl mercury produced here to enter the water column. Mercury concentrations in the sediments are also very high (approximately 10 ppm) and organic material is abundant. All the aforementioned conditions appear optimum for methyl mercury formation, yet increased production is not evident.

At site 5, the Wabigoon River inflow to Clay Lake, mean methyl mercury levels were more than double the average concentration at site 4. This increase is presumably derived from the sediments downstream of Wainwright Dam.

Temporal trends are striking, with highest values in July followed by a general decrease to April. During the spring runoff (Figure 31), methyl mercury levels remained unaffected by the total mercury pulse derived from the Dryden dam discharge. These data suggest that disruption of bed sediments by dredging or other mechanical means might not release large pulses of immediately bioavailable mercury, if the dredging were undertaken during the cooler seasons.

Sites 6, 7 and 8 had mean methyl mercury levels comparable to site 5 and likewise temporal trends are similar. Fall values at site 8 (the outflow of Clay Lake) differed, presumably, owing to internal lake dynamics.

At site 7, rates of methyl mercury production in the hypolimnion may be related to anoxic conditions, however, methyl mercury settling out may also be a contributing factor (Figure 25). A parallel between the seasonal variations of total and methyl mercury is evident. The 1979 summer maximum for methyl mercury was markedly less than the 1978 one.

Methyl mercury levels at the outlet of Clay Lake are among the highest found anywhere in the system. The data also suggest that, in general, highest methyl mercury values are observed in August, decreasing to lowest levels in late winter (Table 11).

Loadings

The annual loading from Wabigoon Lake outflow was less than one-third of the value observed at Highway 17. There appears to be a decrease in loading from the Wainwright Dam but it is not significant. A loading of 1.7 kilograms at site 5 probably has a

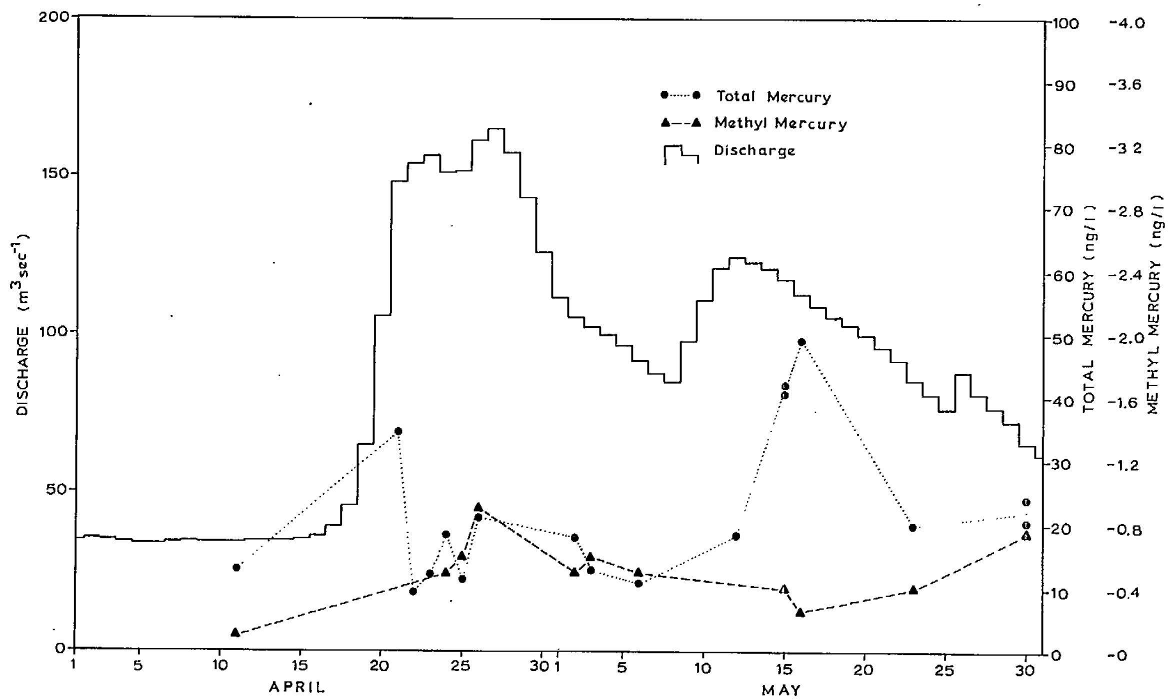


FIGURE 31. Total and methyl mercury dynamics during the spring runoff at the Wabigoon River inflow to Clay Lake, Station 5.

TABLE 11. Summary of methyl mercury dynamics characteristics at study sites.

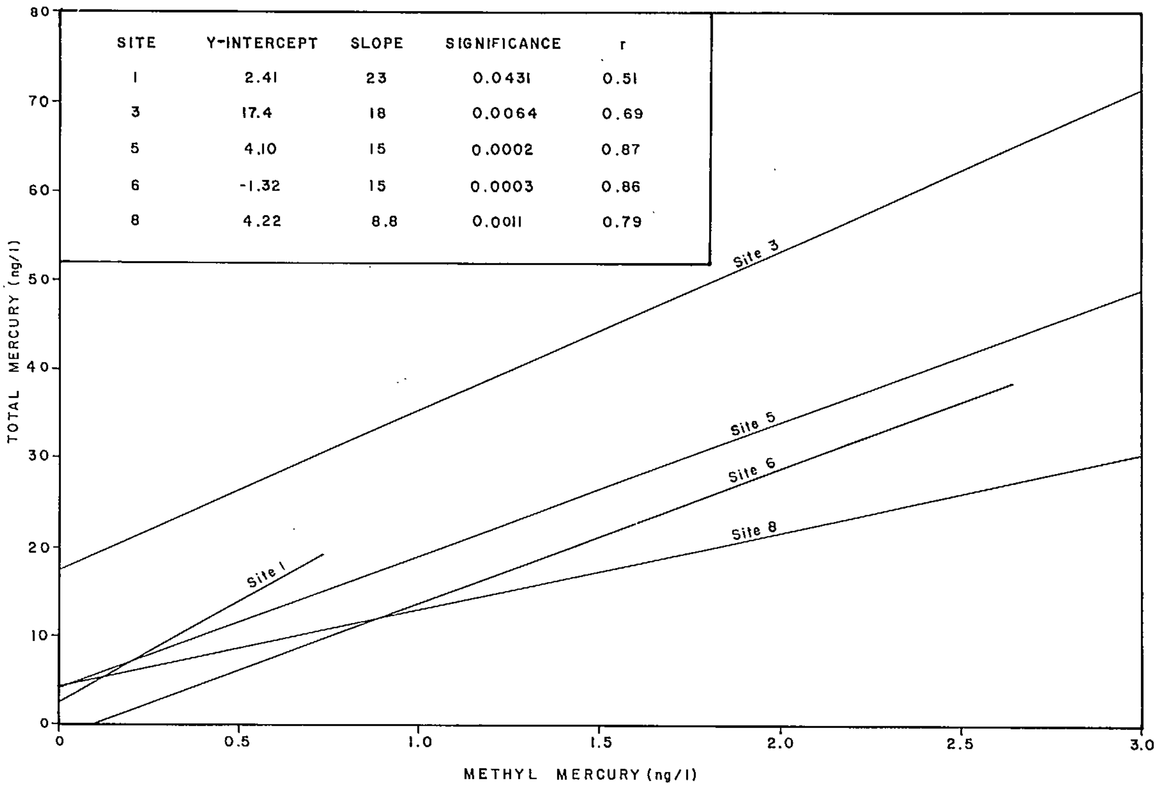
	High		Low		
Study Site	Date	Methyl Mercury (ng/l)	Date	Methyl Mercury (ng/l)	$\frac{\text{High}}{\text{Low}}$
Site 1	01/06/79	0.60	10/25/78	<.2	>3
Site 3	08/02/78	2.30	04/11/79	<.2	>12
Site 4	08/02/78	1.90	04/11/79	<.2	>9
Site 5	08/02/78	3.15	04/11/79	<.2	>16
Site 6	08/02/78	2.65	04/11/79	.50	5.3
Site 7- Epilimnion	09/27/78	2.20	04/11/79	.55	4.0
Site 8	10/12/78	2.55	06/23/78	.25	14.2

major impact on Clay Lake biota. Assuming that other uncontaminated runoff had comparable values to Wabigoon Lake, it would appear that approximately 85 percent of the inflow load came from increased methylation in the contaminated watercourse. The highest methyl mercury loadings at site 5 occurred in August. The similarity in annual loadings at sites 5 and 8 indicated that Clay Lake was not a "net" sink for methyl mercury.

TOTAL MERCURY - METHYL MERCURY INTERRELATIONSHIPS

For ease of presentation and continuity, total mercury and methyl mercury results have been discussed separately. In the following discussion, relationships between the two are examined.

Twelve methyl and total mercury samples collected concomitantly once per month at each site were examined. One set of values from the spring melt at sites 5 and 6 were not included because the presence of eroded sediments gave results atypical of the vast majority of the year. The relationship between mercury and methyl mercury are illustrated in Figure 32. The data indicate that the proportion of methyl mercury to total mercury increases as distance downstream increases. This relationship is also shown in Figure 33. Both of these figures may have several explanations. It would be tempting to hypothesize that these data demonstrate an equilibrium existing in the water column between total and methyl mercury or, at progressive sites downstream, environmental factors favour enhanced methyl mercury production. Arguments could also be forwarded that components such as reduced sulphur-containing constituents in the pulp and paper mill effluent suppress or inhibit methyl mercury production at upstream sites. An examination of Ministry data during a mill shutdown gives a number of parameters which develop inverse trends shown in Figure 33, but these probably just reflect the improvement in the water due to dilution and natural purification processes acting on mill wastes. In the river, increased methyl mercury production is evident with increasing downstream distance. In the lake, a significant portion of the total mercury is removed but not methyl mercury.



SITE	Y-INTERCEPT	SLOPE	SIGNIFICANCE	r
1	2.41	23	0.0431	0.51
3	17.4	18	0.0064	0.69
5	4.10	15	0.0002	0.87
6	-1.32	15	0.0003	0.86
8	4.22	8.8	0.0011	0.79

FIGURE 32. Methyl and total mercury relationships for monthly data from August, 1978 to August, 1979.

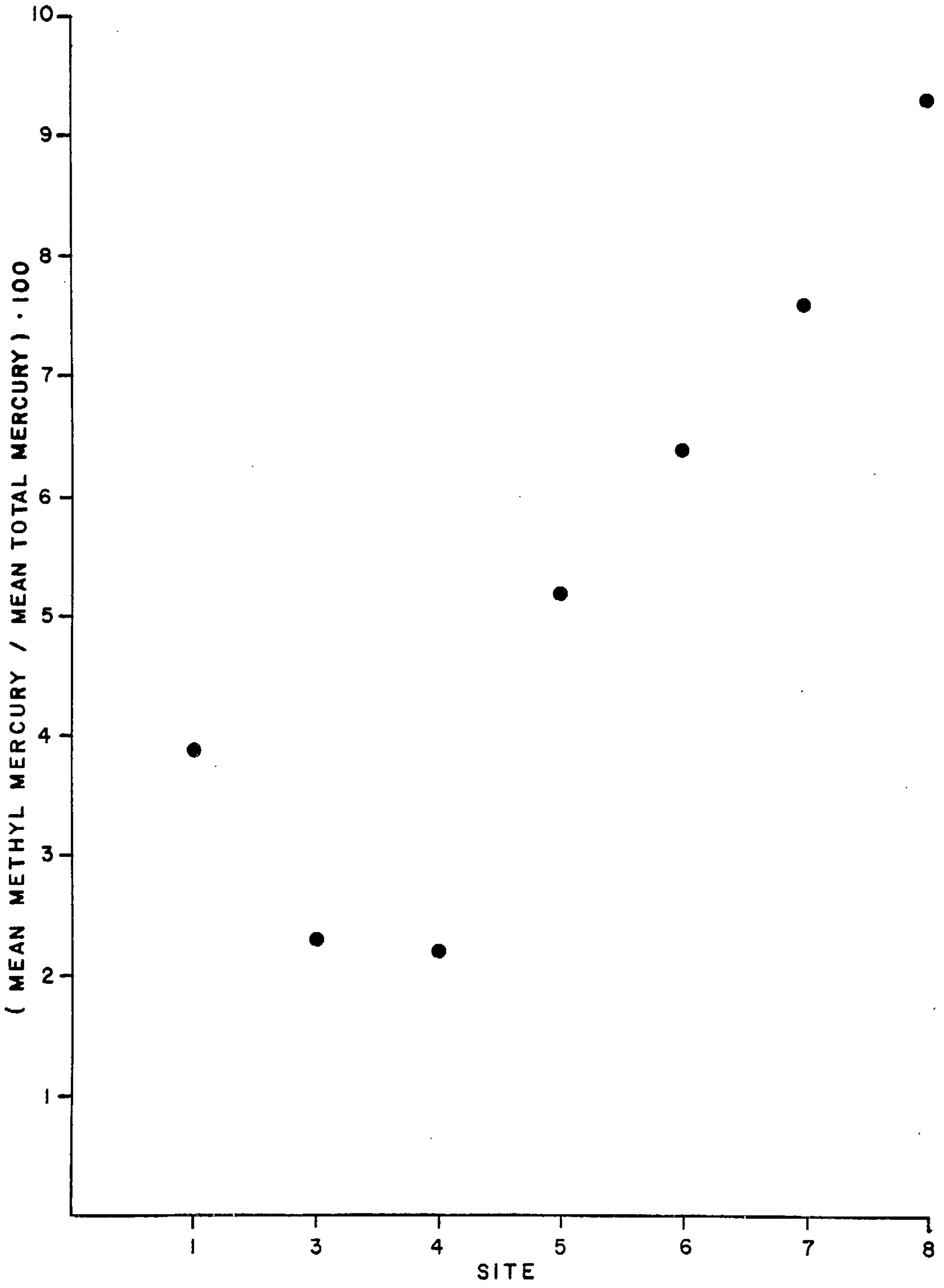


FIGURE 33. Ratio of mean methyl to mean total mercury at study sites.

The most likely explanation is that the river results are a reflection of the time of contact between a water parcel moving downstream and the sediments. There is abundant literature to show that most methylation takes place in the sediments and in such a case the longer the contact or the farther downstream a site is located, the higher the methyl mercury concentrations are expected to be. Also, if the rate of methylation and subsequent release from sediments was temperature dependent, as appears to be for total mercury desorption, then relationships shown in Figure 32 are probably sediment derived, however, methylation in the water column may be significant.

IMPLICATIONS OF PRESENT DAY MERCURY LOADINGS FROM REED LTD.

Reed Ltd. (formerly Dryden Paper Company) discharged approximately 10,000 kg of mercury into the Wabigoon River between 1962 and 1970, primarily from its chlor-alkali operations. Between 1970 and 1971, mercury losses were sharply curtailed and Ministry of the Environment figures (Table 12) show approximately 350 kg lost from the chlor-alkali plant for this period. Current measurements indicate that Reed loadings from the total complex are 15 kg per annum or approximately 1 percent of previously uncontrolled discharges. Results for daily and weekly sampling are presented in Figure 7. Results for complete composite samples only are presented due to the known fluctuations in mercury concentration in industrial effluents. From the sampling methodology employed, it is clear that mercury concentrations integrated daily are relatively uniform on a temporal basis, at least insofar as monitoring industrial effluents is concerned. Since most samples for Reed were collected on a 24-hour composite once a week, some spikes may have occurred in the effluent or at river sites and may have gone unobserved due to sampling frequency. Evidence suggesting occasional spikes was noted in the eastern basin of Clay Lake where, in October, 1978, the high value was attributed to a spike in Reed effluent.

For Clay Lake, there was evidence of only one such spike during the period under study. The wide fluctuations in the

TABLE 12. Annual mercury discharges related to chlor-alkali processes at Reed Ltd.

Year	Quantity per Year (kg)
1962-69	1125
1970	347
1971	9.1
1972	2.3
1973	2.1
1974	1.7
1975	2.0
1976	1.2
1977	1.7

results for intensive hourly sampling reported by Bishop and Neary in earlier studies (24, 25) are signficantly moderated when daily composite values are utilized.

A discussion of the significance of present-day Reed loadings is complicated by the fact that very little is known of the physico-chemical properties of mercury in pulp and paper mill effluents. Prior to 1972, when mercury losses from the plant were very high, the chemistry of mercury in the effluent may have been significantly different due to different industrial processes. Possibly at that time proportionally more mercury was available for subsequent methylation or transport, depending on the nature and concentrations of binding constituents. Limited suspended sediment analyses suggest approximately 50 percent of mercury is associated with particulate matter and possibly the particles settle out quickly in the Wabigoon River. This reasoning does not take into account dynamic physical and biochemical reactions in the receiving stream and as such is of little practical use. For example, mercury adsorbed onto organic particulate matter which does settle out in the river can be re-mobilized by the microbial reduction of organic material or desorption processes. Also, particles bearing mercury which settle under low flow conditions can be eroded during high stage events and, subsequently, transported. Releases of industrial mercury will be partitioned into various parts of the ecosystem, and in this process some will be transported out of the system entirely by direct water transport or through volatization into the atmosphere.

According to estimates of mercury budgets on the Wabigoon River system, approximately 50 percent of previously discharged mercury resides in sediments of Clay Lake and the upper Wabigoon River. At the present time, most methylation in the river may be derived from deposits of mercury from past discharges; however, the significance of ongoing releases may increase as past discharges are removed from the Wabigoon River and covered in Clay Lake by natural means. A lack of quantitative information on mercury/ total mercury, inter-conversions and inter-compartmental transformations and partitioning prevents the precise analysis of the significance of present day discharges; however, there is little doubt that in the absence of former mercury discharges, mercury levels in biota would still be elevated by present discharges of mercury which raise the total loading to the river immediately downstream from Dryden to approximately five times the natural loading.

In the study area, the only significant fishery is a sports fishery on Clay Lake. Mercury contaminated biota here are primarily the result of two processes, the high methyl mercury influx from the Wabigoon River and methyl mercury generated in Clay Lake itself. An accurate definition of the contribution of each is not possible at present since the stability of methyl mercury compounds in different chemical environments is not well understood. Although Reed does not appear to load the system with methyl mercury, the company is responsible for discharging significant quantities of total mercury, a portion of which probably is ultimately transformed into the more toxic form. There appears to have been little change in the past eight to nine years in the rate of mercury uptake in Clay Lake fish. Intrinsically linked with this new equilibrium have been constant loadings from Reed Ltd. which may account for twice the natural mercury loading to Clay Lake. While fundamental reasons can be advanced for claiming that all present mercury loadings from Reed Ltd. do not immediately enter Clay Lake, it is not unreasonable to conclude that on the average over several years this is actually the case; especially, in light of the fact that the Wainwright Dam does not significantly alter the total mercury flux. In the absence of anthropogenic mercury entering Clay Lake, methyl mercury production should decline as a result of clean sediment covering or mixing with previously contaminated substrates. Since 1970, we could expect a minimum of 1 centimetre of new sediment according to sedimentation values published by Armstrong and Hamilton (3). If the sediment were clean, lower methylation rates would be expected, especially in light of studies which demonstrate that the surface millimetres of substrate play the major role in methyl mercury generation in this lake (Rudd et al) (26). In reality, we expected that sediments would remain sharply elevated because particulate matter accumulated in crayfish cages suspended in the Wabigoon River at the inflow to Clay Lake was found to contain mercury at concentrations of a few ppm. The sediment profile by Rudd (26) on the eastern basin, not only confirmed our suspicions, but also demonstrated that maximum mercury levels were encountered at depths of over 3 cm. This finding suggests that probably much of the mercury deposited in Clay Lake prior to 1970 remains effectively removed from further significant interactions. It also demonstrates that Reed Ltd.'s present loadings cannot be considered insignificant in that approximately 65 percent of the industrially related mercury entering Clay Lake this year may have been derived from post-1970 company operations.

Effect of Reed Effluent on Mercury Flux

Two other characteristics of Reed Ltd.'s effluent, namely phosphorus and BOD_5 loadings, may have some significance in the mercury flux. The elevated phosphorus levels in Reed Ltd. effluent which stimulate the eutrophication process in Clay Lake, produce two reactions which are diametrically opposed. Additional phosphorus will stimulate biological growth, which will not only increase growth rates in fish but also will produce organic matter (food) for methyl mercury production. If all other factors were kept constant, increasing the growth rate of fish may decrease the mercury concentration in the flesh but not the total body burden. This fact would suggest that artificially stimulating productivity in Clay Lake would lower mercury levels in fish without an alteration of these contaminated sediments. On the other hand, many studies have shown that one of the prime variables in methyl mercury production is the quantity of organic matter present. The fertilization of Clay Lake would produce more organic matter which could serve as fuel for later methyl mercury generation. Distinguishing the rates of these different processes and their total environmental significance is critical in delineating the effects of phosphorus on the mercury flux in this system.

High BOD_5 levels in the effluent can be regarded as an immediate enrichment process for this river with respect to microbiological activity. Mercury contaminated sediments are washed with this nutrient mixture and elevated methyl mercury production can be expected, as a consequence. Studies using Wabigoon River sediments (27) clearly show the adverse effects of stimulated microbiological activity.

HISTORICAL BIOLOGICAL PERSPECTIVES

Since the discovery of highly contaminated biota in Clay Lake in 1970, continued sampling of selected organisms by Provincial and the Federal governments has produced an extensive data base.

Crayfish (*Orconectes virilis*) are excellent indicators of mercury contamination (3) and have been collected by the Freshwater Institute from 1970 to 1979. To date, these results form the most complete data base and are incorporated by kind permission of Mr. G. McCrae of the Freshwater Institute. The results (Figure 34) are for crayfish over 65 mm only; consequently, the body burdens given are the result of two to three years accumulation. Thus, a lag exists between the time when real aquatic improvements occur and the subsequent reflection in mercury concentrations in crayfish. The exponential decline in mercury levels in this organism does not suggest that further significant improvements will be noted in the near future. Clearly, mercury levels have dropped substantially since 1970; however, 1977, 1978 and 1979 values are reasonably close together and suggest that only slow rates of change are likely in future years in Clay Lake. Values for this period are approximately one order in magnitude higher than results for similar-sized crayfish in Wabigoon Lake.

Extensive sampling for walleye (*Stizostedion vitreum*), an important game fish, has been conducted by the Ministry of the Environment and the Freshwater Institute during 1970, 1972, 1975, 1976, 1977 and 1979. Mercury levels for walleye, in Figure 34, also show an exponential decline. The standard walleye mercury concentration in 1979 was 6.5 ppm, more than an order of magnitude higher than 0.5 ppm, the maximum level for unrestricted human

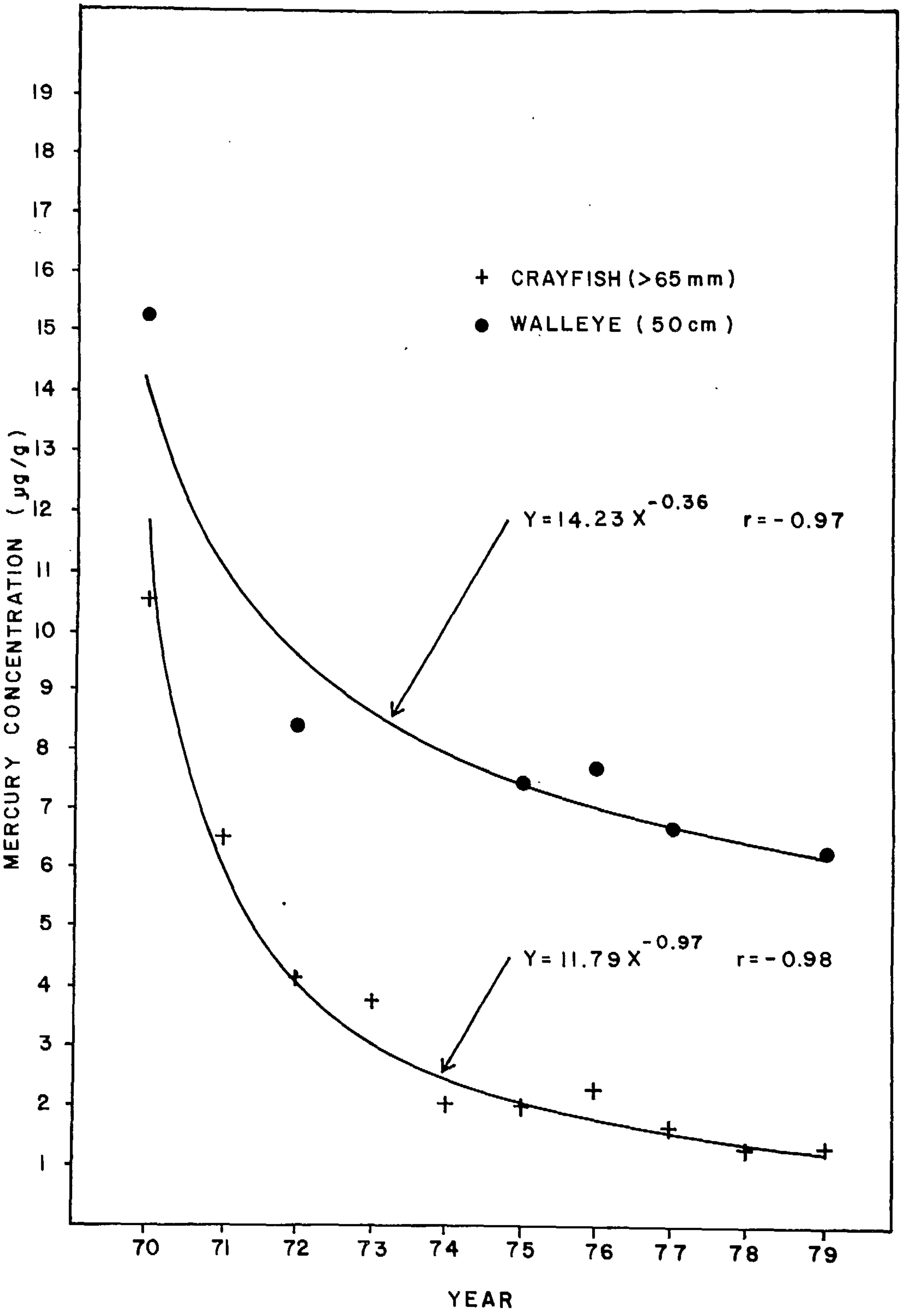


FIGURE 34. Summary of annual crayfish and walleye mercury concentrations in Clay Lake, 1970-1979.

consumption (the Canadian Food and Drug Act). Results are based on a "standard" 50 cm walleye value obtained by linearly regressing log mercury concentration versus log length on a minimum sample of at least twenty specimens. Results of mercury testing on more than 1,500 fish of four species in 1972 and 1976 by the Freshwater Institute are not reported; however, a preliminary assessment indicates that the rate of mercury uptake between 1972 and 1976 has not changed (Dr. D. P. Scott, Personal Communication). Dr. Scott also indicated that growth rates have increased and the decrease in mercury concentration is related.

The standard walleye in Clay Lake have an estimated age of 5 to 7 years for the early 1970's; consequently, a time lag similar to that for crayfish is expected.

Crayfish and walleye data strongly indicate that 80 to 90 percent of the improvement in the aquatic environment took place almost immediately after cessation of high mercury loadings in 1971. Under these circumstances, a major portion of the mercury body burden in biota captured in 1970 would have been derived from the water column rather than by release from sediments, a situation previously suggested by A. L. Hamilton (28).

REFERENCES

1. JENSEN, S., AND A. JERNELOV. 1969. Biological methylation of mercury in aquatic organisms. Nature: 223:753-754.

2. DITRI, F. 1978. Mercury pollution perspective, Water Spectrum. 7 p.

3. ARMSTRONG, F. A. J., AND A. L. HAMILTON. 1973. Trace metals and metal organic interactions in natural waters. P. C. Singer, ed. Ann Arbour Science Publishers. 131-156.

4. BISHOP, J. N., AND B. P. NEARY. 1976. Mercury levels in fish from Northwestern Ontario, 1970-1975. Inorganic Trace Contaminants Section, Laboratory Services Branch, Ontario Ministry of the Environment. 85 p.

5. PARKS, J. W. 1976. Mercury in sediment and water in the Wabigoon/English River system, 1970-75. Ontario Ministry of the Environment, Northwestern Region. 29 p.

6. NATIONAL RESEARCH COUNCIL. 1978. An assessment of mercury in the environment. National Academy of Sciences, Washington, D.C. 185 p.

7. NATIONAL RESEARCH COUNCIL OF CANADA. 1977. Ottawa River Project, Final Report. Vol. 1 and 2.

8. KRENKEL, P. A. 1973. Mercury environmental considerations, C.R.C. Vol. 3:303-373.

9. KOTHNY, E. 1973. The three-phase equilibrium of mercury in nature, in trace elements in the environment. American Chemical Society, Washington, D.C. 32 p.

10. GAVIS, J., AND J. FERGUSON. 1972. The cycling of mercury through the environment, water research. Vol. 6:989-1008.

11. JONASSON, I. R. 1979. Mercury in the natural environment: A review of recent work. Geological Survey of Canada, Department of Energy, Mines and Resources. Paper 70-57:39 p.

12. ZOLTAI, S. C. 1974. Forest sites of site regions 55 and 45, Northwestern Ontario. Ontario Ministry of Natural Resources, Forest Research Branch, Maple, Ontario. Vol. II.

13. ARMSTRONG, F. A. J., AND D. W. SCHINDLER. 1971. Preliminary chemical characterization of waters in the Experimental Lakes Area, Northwestern Ontario. J. Fish. Res. Board Can. 28:171-187.

14. GERMAN, M. J. 1969. Water pollution survey of the Wabigoon River. Ontario Ministry of the Environment. 24 p.

15. ONTARIO WATER RESOURCES COMMISSION. 1970. Water use study of the Wabigoon River below Dryden. 22 p.

16. RUST, B. R. 1977. The distribution of sediment-associated mercury, in Ch. 6. Ottawa River Project, Final Report. National Research Council of Canada. Vol. 1:49 p.

17. ONGLY, E. D. 1977. Sediment and nutrient loadings to Lake Ontario: Methodological arguments. Can. J. Earth Sci. Vol. 14:1555-1565.

18. LUTZ, A. W. 1979. Unpublished manuscript. Environment Canada, Winnipeg, Manitoba.

19. KUDO, A., ET AL. 1977. Mercury contents in Ottawa River water, in Ch. 14. Ottawa River Project, Final Project Report. National Research Council of Canada. Vol. 1:14 p.

20. PENN, A. F. 1978. The distribution of mercury, selenium and certain heavy metals in major fish species. Grand Council of the Crees of Quebec. 395 p.

21. BETTS, J., Chief, Pulp and Paper Division, Per. Comm. Water Pollution Control, Environmental Protection Service, Ottawa.

22. JACKSON, T. The geochemistry, dynamics and distribution of mercury in the Wabigoon/English River system. Interim report to the Steering Committee for the Canada-Ontario Study of Mercury Pollution in the Wabigoon River.

23. BISHOP, J. N., AND B. P. NEARY. Summary of mercury concentrations in sediments and fish from the Wabigoon/English River system, 1970-74. Laboratory Services Branch, Ministry of the Environment. Draft Report.

24. MINISTRY OF THE ENVIRONMENT, INORGANIC TRACE CONTAMINANTS SECTION, LABORATORY SERVICES BRANCH. 1975. Mercury in the effluents from chlor-alkali plants: First survey at Dryden, July, 1975. 34 p.

25. MINISTRY OF THE ENVIRONMENT, INORGANIC TRACE CONTAMINANTS SECTION, LABORATORY SERVICES BRANCH. 1976. Mercury in the effluents from chlor-alkali plants: Second survey at Dryden, October, 1975. 57 p.

26. RUDD, J., ET AL. Mercury dynamics and amelioration studies of Clay Lake, Ontario. Interim report to the Steering Committee for the Canada-Ontario study of mercury pollution in the Wabigoon River.

27. WRIGHT, D., AND R. HAMILTON. Methyl mercury release from sediments at low temperatures and with nutrient enrichment, submitted for publication in Applied Microbiology. 16 p.

28. HAMILTON, A. L. 1972. Pond experiments on the uptake and elimination of mercury by selected freshwater organisms, in mercury in the aquatic environment: A summary of research carried out by The Freshwater Institute. 1970-1971. Fisheries Research Board of Canada. Manuscript report series 1167:163 p.

29. DITRI, F. M. 1973. Mercury in the aquatic ecosystem, in Bioassay Techniques and Environmental Chemistry. Ann Arbor Science Publishers. 69 p.

THE GEOCHEMISTRY AND DISTRIBUTION OF MERCURY IN THE WABIGOON RIVER SYSTEM

by

Togwell A. Jackson

and

Robert N. Woychuk

Department of the Environment
Freshwater Institute
501 University Crescent
Winnipeg, Manitoba R3T 2N6

TABLE OF CONTENTS

RESULTS AND INTERPRETATIONS

(1) Distribution and chemical speciation of mercury in bottom sediments.

TENTATIVE CONCLUSIONS AND RECOMMENDATIONS

(1) Methyl mercury is currently being generated in the polluted surficial sediments of the Wabigoon River and its associated lakes.

(2) Release of methyl mercury and other forms of mercury from the sediments by diffusion and bottom scour is causing contamination of the lake and river waters. Surface waters of the lakes are being contaminated by methyl mercury introduced by the river from sources in the riverbed upstream from Clay Lake; deeper lake waters are apparently being contaminated by methyl mercury generated locally in the bottom sediments of the lakes.

(3) Accumulation of mercury by pelagic fish (e.g. walleye) is ascribed primarily to the riverborne methyl mercury transported into lake surface water by the river from sources between Dryden and Clay Lake. Only bottom-feeding animals (e.g. suckers and crayfish) show a strong effect of methyl mercury generated in local bottom sediments.

(4) Unless remedial measures are taken, contamination of water and fish is likely to continue for an indefinitely long time. From the standpoint of reducing the mercury levels in pelagic fish, the most effective method for restoring the lake-river system would probably be to dredge the mercury-contaminated sediments out of the riverbed between Dryden and the inflow to Clay Lake. A possible alternative procedure would be to accumulate this mercury in a series of settling ponds, immobilize it by chemical treatments, and eventually dredge it out. Unless the mercury in this portion of the river system is removed or immobilized, no other scheme for lake restoration is likely to succeed.

(5) The total quantity of anthropogenic mercury in the bottom sediments of the riverbed between the plant at Dryden and the inflow of Clay Lake is estimated to be approximately 2.6 (1.2-3.9) metric tons, ~80-94% of which is upstream from Wainwright dam. Correction of an estimate by Armstrong and Hamilton (1973) gives a comparable value for Clay Lake sediments, signifying that about 5 metric tons of mercury (half of the total quantity discharged) has been transported beyond Clay Lake. At least part of this mercury has accumulated in Ball Lake sediments. Both Clay Lake and Ball Lake function as natural settling ponds for partial entrapment of riverborne mercury. The mercury is bound to iron oxides, organic matter, and (in Clay Lake) sulfide in the sediments.

(6) Methyl mercury levels in surficial bottom sediments of the Wabigoon River system depend primarily on environmental variables rather than total mercury supply. Total mercury concentrations in sediments decline sharply and progressively downstream from the source of pollution at Dryden, but methyl mercury levels remain relatively high throughout and even increase from Clay Lake to Ball Lake. Methylation in the riverbed is most intense at the sediment-water interface (where release to the water column is most probable) regardless of the vertical distribution of total mercury, which is generally most abundant several centimeters below the surface owing to deposition of less contaminated detritus after 1970, when uncontrolled mercury discharges officially ceased.

Mercury speciation in surficial bottom sediments from Dryden to Ball Lake varies with the composition of the sediments and interstitial water, reflecting a gradational change from deposits of decomposing wood fragments and slime, and high chloride levels, near Dryden to clay-silt muds associated with iron-manganese oxides, and lower chloride levels, further downstream. In the organic deposits between Dryden and

Clay Lake, methyl mercury production is enhanced by low pH levels (in the range 4-7), high concentrations of organic nutrients, and microbial activities involving the methionine biosynthetic pathway; but in Ball Lake mud, methyl mercury levels are limited by sorption-desorption processes involving iron-manganese oxides and cation exchange sites. Situated between these two environmental extremes, Clay Lake is a transition zone where methyl mercury levels are related to methionine biosynthesis and chloride concentration (demonstrating the influence of riverborne pollutants) as well as reactions on iron-manganese oxides. Methylation in Clay Lake may be slightly depressed owing to anomalously high sulfide concentrations.

Weakly sorbed, "exchangeable" mercury increases in proportion to total mercury from Dryden to Ball Lake, roughly paralleling the tendency shown by methyl mercury. Weak sorption of mercury by cation exchange sites probably promotes methyl mercury formation, whereas strong chemisorption by amorphous oxides inhibits it. An increase in the concentration of exchangeable mercury relative to "amorphous-oxide bound" mercury may account for the increase in sedimentary methyl mercury levels from Clay Lake to Ball Lake.

(7) In the determination of total mercury concentrations in sediments, digestion of the samples with HNO_3/H_2SO_4 by the method of Hendzel and Jamieson (1976) is preferable to the HNO_3/HCl method of the Dow Chemical Company. With the Dow procedure, the mercury values are systematically underestimated by factors ranging from less than 2 (as with Clay Lake and Lake Ontario muds) to greater than 5 (as with Ball Lake mud).

INTRODUCTION

The biological effects of mercury (Hg) in an aquatic environment depend not merely on the total Hg content of the water and sediments but also on the forms, or "chemical species," of the metal. The production and subsequent fate of these Hg species are governed in turn by environmental variables. Hg introduced into an aquatic environment is rapidly sorbed by particulate matter and accumulates in bottom sediments, where further transformations, including methylation, may occur. Some of this sediment-bound Hg may be released back into the water column by outward diffusion of water-soluble species or by the scouring action of currents, as in a river during the spring flood. Soluble Hg species may then be taken up by organisms in the water.

Monomethyl mercury (CH_3Hg^+), which is formed from Hg^{2+} ions by free-living micro-organisms, is probably the most dangerous form of Hg in aquatic ecosystems. Being a low molecular-weight, water-soluble as well as fat-soluble species, it is readily accumulated by fish and is very toxic when ingested. Dimethyl mercury ($(CH_3)_2Hg$) is considered less harmful, because it is volatile and tends to evaporate from the water. Hg strongly fixed to bottom sediments in the form of stable, highly insoluble precipitates (e.g. HgS) or complexes is probably to a large extent biologically inert and not readily available for methylation unless the Hg^{2+} ions are remobilized (e.g. by oxidation of HgS) owing to a change in environment. For more detailed general information on Hg speciation, consult Fagerström and Jernelöv (1972) and Jernelöv (1972).

The research results presented in this chapter principally concern the chemical speciation and distribution of Hg in the bottom sediments of the Wabigoon River system, including Wainwright Reservoir, Clay Lake, and Ball Lake (Fig. 1). Particular attention is devoted to environmental factors affecting the abundance of CH_3Hg^+ and other Hg species which are likely to be available for accumulation by organisms. The mobilization

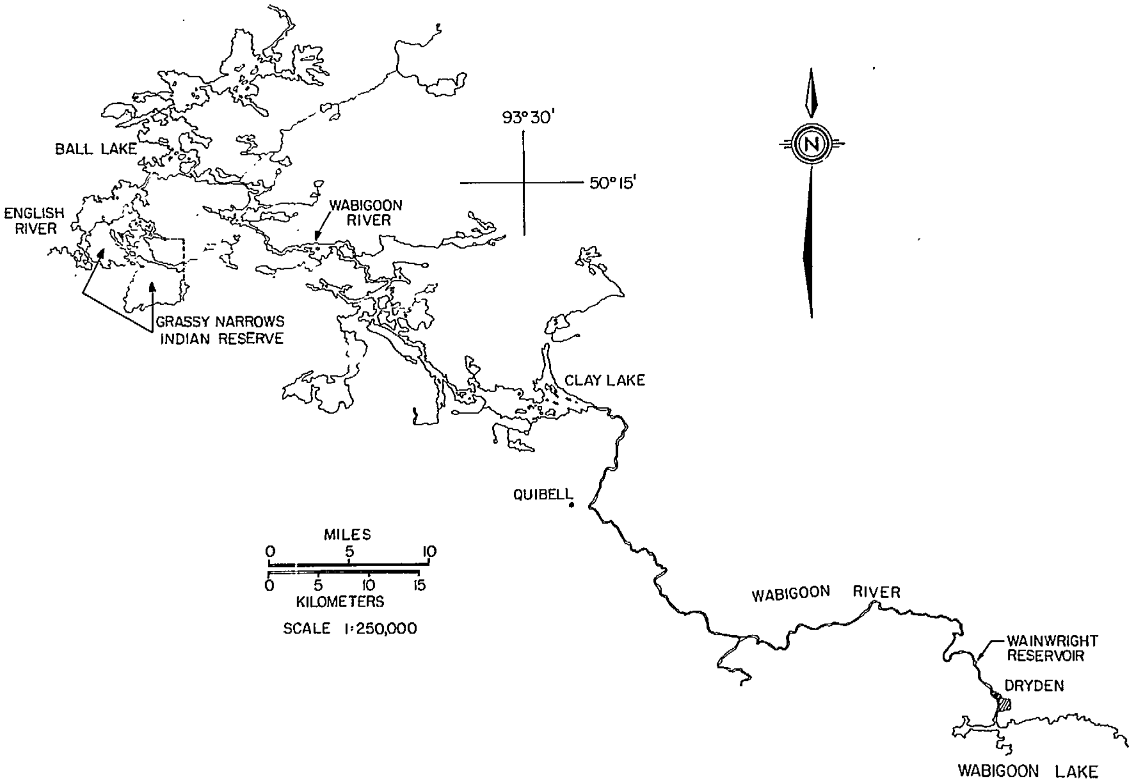


Figure 1. Map of the Wabigoon-English River system from Wabigoon Lake to Ball Lake.

of CH_3Hg^+ from fluvial and lacustrine sediments to the overlying water, and the transport and distribution of CH_3Hg^+ and other forms of Hg in the water, are also discussed, with particular reference to the spring flood. In addition, a preliminary attempt was made to estimate the total quantity of sediment-bound Hg trapped behind Wainwright dam and elsewhere in the river system. Finally, a comparative study of different methods for determining the total Hg content of sediments was undertaken.

This research is still in progress; a more complete account of it will be published in the future.

MATERIALS, METHODS, AND FIELD OBSERVATIONS

All field work was conducted during the spring and summer of 1978.

For the study of Hg transport during the spring flood, water samples were collected by Van Dorn bottle at seven sampling stations between Dryden and Quibell during two time-intervals: (1) April 21-24, when the current velocity was increasing toward its maximum, and (2) May 9-11, when the velocity was declining. In the April-May flooding episode, most of the water came from the watershed north of the Wabigoon River. A second flooding episode not dealt with in this report occurred in June. Analytical data for the river water, together with daily discharge rates at Quibell (Water Survey of Canada, personal communication), were used to estimate the total Hg and CH_3Hg^+ loading to Clay Lake per day during the spring flood.

During July 17-20, water samples were collected at the surface and near the bottom in the east and west basins of Clay Lake and in the south basin of Ball Lake, and temperature profiles were recorded.

During April, grab samples of bottom sediment were collected at different sampling sites between Dryden and Quibell, including two sites in Wainwright Reservoir. In July grab samples of mud were taken from the east and west basins of Clay Lake, from a region of the Wabigoon River just downstream from Clay Lake, and from the north and south basins of Ball Lake. Most of the river sediments collected upstream from Clay Lake consisted of grey mud overlain by grey slime and/or wood chips, and the Wainwright reservoir sediment was composed entirely of decayed wood fragments. In contrast, nearly all of the sediment samples from Clay Lake, Ball Lake, and the intervening stretch of river consisted of grey or brownish-grey clay-rich mud. Iron-manganese nodules were found at scattered localities in Ball Lake, but not in Clay Lake. None of the sediments had sufficient H_2S to be detected by odor.

Finally, on August 24, cores were taken by hand and by Benthos corer from the Wainwright Reservoir and from a stretch of river upstream from the reservoir. In order to obtain a complete stratigraphic sequence extending into the original, pre-impoundment river bed, the coring operation in the reservoir had to be confined to sites near the shore, where the sediment trapped behind the dam thins to a feather edge. Each core from the river or reservoir comprised an upper stratum of decayed wood particles underlain by the fine-grained mineral sediment of the pristine river bed.

From the mean Hg content of the wood-chip sediment (on a wet-weight basis) and estimates of the volume and density of the contaminated sediment trapped behind the dam, the total quantity of anthropogenic Hg retained in the sediments of the reservoir and the stretch of river extending upstream from it to Dryden was estimated. Similarly, the total anthropogenic Hg burden of the river sediments downstream as far as Clay Lake was estimated from the mean Hg content of the grab samples. The volume of the wedge of wood-chip sediment in the reservoir was estimated on the basis of (1) a bottom profile measured with an echo-sounder and line, (2) the length and breadth of the reservoir according to a 1:50,000 scale map, (3) the maximum thickness of the wood-chip layer as given by Parks (1976) or computed as the distance from the base of the dam to the water level on the date of sampling (Ontario Ministry of the Environment, personal communication) minus the depth of water, and (4) the assumption that the shape of the wedge of sediment approximates a prism with triangular ends (modified to correct for a deep hole at the narrow upstream end of the reservoir). Downstream from Wainwright dam, the thickness of the contaminated surface zone of the sediment was assumed to be 5 cm. (Parks, 1976); upstream from the reservoir, the core data were used to gauge the thickness of this zone.

The procedures used for analysis of the samples may be summarized briefly as follows.

Unfiltered water samples stabilized in the field by acid treatments, together with grab samples and 5-12 cm. thick core sections, were analyzed for total Hg using flameless atomic absorption (Hendzel and Jamieson, 1976) and for CH_3Hg^+ using gas chromatography (Uthe et al., 1972). Prior to total Hg analysis, the water was digested with $KMnO_4/H_2SO_4$ and $K_2S_2O_8$ under ultraviolet light, but the sediments were digested with H_2SO_4/HNO_3 (4:1, v/v) at 160°C. CH_3Hg^+ was extracted from water and sediments with benzene and toluene, respectively, and with $NaBr/H_2SO_4$ and $CuSO_4$. The water samples were also analyzed for pH and conductivity, for organic carbon before and after filtration with 0.4 μm Nuclepore membranes, and for dissolved and particulate nitrogen. Filtered water samples were analyzed for Hg, but the data were useless owing to Hg contamination from the filter pads. The sediment samples were analyzed for pH, E_h (using platinum and calomel electrodes), organic carbon (org. C), nitrogen (N), phosphorus (P), free (volatile) and bound (HCl-soluble, nonvolatile) sulfide (S^{2-}), total iron (Fe), manganese (Mn), cobalt (Co), cadmium (Cd), copper (Cu), and zinc (Zn), and for Mn and Fe oxides (as represented by the Mn and Fe fractions extracted with $NH_2OH \cdot HCl/HNO_3$ followed by citrate/bicarbonate/dithionite). S^{2-}, having been expelled from the sediments in the form of H_2S, was collected in an alkali trap and estimated by ultraviolet spectrophotometry (Armstrong, 1975); the bound sulfide was converted to H_2S by treatment with boiling 6N HCl prior to analysis. Analytical data for sediments were calculated on the basis of oven-dry weight (at 105°C). The amino acid content of the sediments was determined with a Beckman ion-exchange analyzer following acid hydrolysis under vacuum.

Interstitial water was sampled by centrifugation of sediments at 10,000 rpm. Conductivity, pH, and org. C content were determined, and the water was analyzed for total Hg, Fe, Mn, Cu, Zn, Cd, sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), chloride (Cl^-), sulfate (SO_4^{2-}), and N following digestion with H_2SO_4/H_2O_2 under ultraviolet radiation. The centrifuged sediments were then rinsed twice with de-aerated (nitrogen-purged) water, and different solvent-extractable Hg fractions were isolated with nitrogen-purged solvents using the extraction schemes outlined as follows:

2.5% acetic acid (pH 2.5) → 0.1N NaOH (pH 13)
1N Ca acetate → 1N $CaCl_2$
1N NH_4 acetate → 0.1M $NH_2OH \cdot HCl$/0.01M HNO_3 (pH 2) →
citrate/bicarbonate/dithionite (CBD).
Electrodialysis (yielding separate anionic and cationic fractions)
0.005 M Diethylenetriaminepentaacetic acid (DTPA) /0.01M $CaCl_2$/0.1M triethanolamine (TEA) [the entire solvent system is designated "DTPA" for brevity].
Benzene/methanol (1:1, v/v).

The extracts were wet-ashed with H_2SO_4/H_2O_2 under ultraviolet radiation and then analyzed for Hg, which was normalized to the dry weight of the sediment. The Hg fractions extracted by acetic acid, acetate salts, $CaCl_2$, and electrodialysis were presumably the more weakly bound forms of the metal -- species which, in nature, might be readily taken up by organisms and readily solubilized when brought into contact with waters of higher salinity or lower pH. DTPA, a chelating agent similar to EDTA, was expected to solubilize somewhat more strongly bound but nonetheless potentially bio-available forms of Hg. This reagent is commonly used to analyze soils for heavy metal fractions that are available to plants. NaOH, benzene/methanol, $NH_2OH \cdot HCl/HNO_3$, and CBD were expected to yield estimates of the quantities of Hg strongly chemi-sorbed or complexed by humic and proteinaceous substances, lipids or bitumens (e.g. alkyl species and degraded chlorophyll), Mn oxide + "amorphous" Fe oxide, and relatively crystalline Fe oxide, respectively. Metallic Hg would be included in the benzene/methanol fraction.

In previous investigations of the Wabigoon-English River system (e.g. Armstrong and Hamilton, 1973; Jackson, 1979) hot (100°C) aqua regia (HNO_3/HCl) was used to digest sediments for total Hg dtermination, but the use of this reagent could lead to systematic underestimation of Hg concentrations owing to (1) loss of Hg by volatilization as chloride complexes and (2) incomplete decomposition of organic matter. Therefore, HNO_3/HCl was replaced with HNO_3/H_2SO_4 in the present study. The two methods of wet-ashing were compared by means of quality control experiments involving replicate analyses of homogenized sediment samples. The experimentation is still in progress, and a detailed account of the results will be presented elsewhere.

Additional research on frozen sediment samples is currently underway. This work will include, if possible, the study of grain size, clay mineralogy, permeability, humic complexes, cobalamine (a factor in the methylation of Hg), electrodialyzable anionic complexes, and the ability of the sediments to adsorb Hg^{2+} and CH_3Hg^+, as well as examination of Hg distribution among microscopic sediment components (e.g. benthic organisms) by electron microprobe. A pilot study of stable Hg isotopes as possible indicators of Hg source is also anticipated.

RESULTS AND INTERPRETATIONS

(1) Distribution and chemical speciation of mercury in bottom sediments.

A. Monomethyl Hg and total Hg.

The distribution of CH_3Hg^+ and total Hg in the bottom sediments of major depositional basins situated between Dryden and the outlet of Ball Lake is summarized in Table 1. Other chemical data for the sediments are given in Tables 2 and 3.

The total Hg levels are highest in the surficial wood-chip sediments behind Wainwright dam near Dryden and tend to decrease downstream (cf. Parks, 1976; Jackson, 1979), presumably owing to dilution with uncontaminated sediments. A plot of total Hg against org. C (Fig. 2) revealed that the surficial sediments collected between Dryden and the outlet of

Table 1. Methyl and total mercury concentrations of bottom sediments, and total mercury concentrations of interstitial water, in the Wabigoon-English River system. Notation: Number of samples: N; mean: $\bar{X}$; standard deviation: stand. dev.

	BULK SEDIMENT									INTERSTITIAL WATER			
	ppb CH_3Hg^+				ppm Total Hg				$\frac{CH_3Hg^+}{\text{Total Hg}} \times 10^3$	µg Hg/L			
Sample material	N	$\bar{X}$	range	Stand. dev.	N	$\bar{X}$	range	Stand. dev.		N	$\bar{X}$	range	Stand. dev.
Wainwright Reservoir, grab samples (rotten wood)	2	18	14-22	5.7	2	0.878	0.589-1.17	0.409	24.7	-	-	-	-
Wabigoon River between Dryden & Quibell, grab samples (chiefly mud; some scum + wood) [not incl. Wainwright Reservoir]	8	9.05	5.5-11	2.0	8	2.03	1.21-2.99	0.605	4.78	-	-	-	-
Wabigoon River cores taken between Dryden & Wainwright Reservoir													
wood-chip layer	5	15.0	3.29-43.0	16.5	5	22.1	6.83-43.2	13.7	0.843	-	-	-	-
clay layer	3	1.1	0.58-1.3	0.43	3	0.729	0.571-0.896	0.163	1.5	-	-	-	-
Wainwright Reservoir cores													
wood-chip layer	16	19.4	4.63-44.1	12.7	16	30.2	5.20-66.0	18.5	1.18	-	-	-	-
wood/clay transition	5	1.0	0.66-1.5	0.37	5	3.13	1.30-7.90	2.73	0.46	-	-	-	-
clay layer	4	1.8	0.30-4.58	2.0	4	0.38-0.41	<0.061-1.21	0.55-0.57	>2.36	-	-	-	-
Clay Lake grab samples (mud)													
East basin	13	12.0	7.08-21.6	4.10	13	7.86	2.66-13.7	3.86	1.87	13	0.570	0.287-0.840	0.201
West basin	6	12.3	8.79-15.6	2.32	6	8.68	4.97-12.9	3.06	1.55	6	0.602	0.445-0.760	0.126
Wabigoon River grab samples (mud) taken downstream from Clay Lake	5	16.5	12.9-21.7	3.56	5	3.12	1.60-6.19	1.89	6.52	5	0.234	0.200-0.287	0.0321
Ball Lake grab samples (mud)													
South basin	12	20.3	8.42-43.1	10.6	14	1.18	0.517-1.86	0.418	18.4	14	0.130	0.102-0.187	0.0221
North basin	6	15.4	12.0-22.7	4.37	6	0.637	0.348-0.967	0.215	28.6	6	0.115	0.090-0.133	0.0151

Table 2A. Depth of water at sampling sites, and pH and E_h values of sediment samples. Notation: Number of samples: N; mean: $\bar{X}$; standard deviation: stand. dev.

	Depth (m.)				pH				E_h (mV)			
Sample	N	$\bar{X}$	range	Stand. dev.	N	$\bar{X}$	range	Stand. dev.	N	$\bar{X}$	range	Stand. dev.
Wainwright Reservoir, grab samples (rotten wood)	-	-	-	-	6	4.80	4.40-5.20	0.298	6	-108	-140 to -70	27.3
Wabigoon River between Dryden & Quibell, grab samples												
Mud (+ some scum & wood)	-	-	-	-	21	6.57	6.05-6.95	0.280	21	-273	-420 to -170	67.9
Organic scum	-	-	-	-	7	5.71	5.40-6.30	0.475	7	-180	-210 to -160	16.6
Wabigoon River cores, between Dryden & Wainwright Reservoir												
Wood-chip layer	-	-	-	-	5	6.23	5.40-6.90	0.552	5	-284	-350 to -200	66.6
Clay layer	-	-	-	-	3	6.75	6.50-6.95	0.229	3	-300	-350 to -250	50.0
Wainwright Reservoir cores												
Wood-chip layer	-	-	-	-	16	6.05	5.18-7.00	0.515	16	-245	-420 to -90	82.9
Wood/clay transition	-	-	-	-	5	6.76	5.95-7.40	0.519	5	-214	-350 to -50	117
Clay layer	-	-	-	-	4	6.69	6.60-6.75	0.0629	4	-173	-300 to -120	86.2
Clay Lake, grab samples (mud)												
East basin	13	3.4	1.8-5.2	1.1	13	6.53	6.10-6.85	0.206	13	-244	-325 to -160	62.0
West basin	6	19.0	18.5-19.5	0.46	6	6.62	6.50-6.73	0.0914	6	-288	-300 to -280	9.83
Wabigoon River downstream from Clay Lake, grab samples (mud)	5	11.9	8.5-14.5	2.70	5	6.76	6.40-7.10	0.265	5	-280	-315 to -255	23.1
Ball Lake, grab samples (mud)												
South basin	14	22.7	15.5-32.5	5.6	13	6.92	6.55-7.30	0.183	13	-298	-340 to -260	30.0
North basin	6	21	19-24	1.8	6	6.82	6.75-6.95	0.0753	6	-298	-360 to -260	36.6

Table 2B. Analytical data for sediment samples. Same notation as in 2A.

	μg org. C/mg				μg N/mg				N/org.C	ppm bound S^{2-}			
Sample	N	$\bar{X}$	range	Stand. dev.	N	$\bar{X}$	range	Stand. dev.	$\bar{X}$	N	$\bar{X}$	range	Stand. dev.
Wainwright Reservoir, grab samples (rotten wood)	-	-	-	-	-	-	-	-		2	1.69	0.125-3.26	2.22
Wabigoon River between Dryden & Quibell, grab samples													
Mud (+ some scum & wood)	-	-	-	-	-	-	-	-	-	10	5.02	0-14.2	5.49
Organic scum	-	-	-	-	-	-	-	-	-	2	4.75	0-9.49	6.71
Wabigoon River cores, between Dryden & Wainwright Reservoir													
Wood-chip layer	5	179	122-236	41.1	5	6.69	4.50-8.30	1.40	0.0401	5	1.09	0.784-1.45	0.243
Clay layer	3	99.3	20-180	81.1	3	6.42	2.75-8.50	3.19	0.0892	2	0.549	0.373-0.725	0.249
Wainwright Reservoir cores													
Wood-chip layer	16	267	208-389	47.2	16	8.25	4.80-15.7	2.34	0.0314	16	1.73	0.925-2.95	0.588
Wood/clay transition	5	143	36.0-245	76.3	5	3.83	1.10-5.30	1.84	0.0294	5	1.03	0.457-1.61	0.418
Clay layer	4	58.3	17.5-109	45.6	4	2.03	0.85-4.00	1.43	0.0402	4	0.453	0.359-0.535	0.0923
Clay Lake, grab samples (mud)													
East basin	13	37	33-41	2.8	13	2.9	2.1-4.3	0.70	0.078	6	23.7	10.8-40.2	10.0
West basin	5	46	42-49	3.0	5	4.4	3.8-5.4	0.63	0.097	5	32.4	22.2-44.4	7.93
Wabigoon River downstream from Clay Lake, grab samples (mud)	5	48	36.5-54	7.2	5	4.8	2.9-6.0	1.2	0.099	4	15.6	10.2-19.8	4.67
Ball Lake, grab samples (mud)													
South basin	13	29	13-38	7.2	13	3.3	0.65-4.9	1.5	0.11	5	19.1	9.60-34.6	10.3
North basin	6	25	7.5-29	8.7	6	3.4	0.5-4.6	1.5	0.14	4	14.2	9.60-20.5	4.80

Table 2C. Analytical data for sediment samples.
Same notation as in 2A.

	µg. Fe/mg				µg. Mn/mg				Fe/Mn
Sample	N	$\bar{X}$	range	Stand. dev.	N	$\bar{X}$	range	Stand. dev.	$\bar{X}$
Wainwright Reservoir, grab samples (rotten wood)	-	-	-	-	-	-	-	-	-
Wabigoon River between Dryden & Quibell, grab samples									
Mud (+ some scum & wood)	-	-	-	-	-	-	-	-	-
Organic scum	-	-	-	-	-	-	-	-	-
Wabigoon River cores, between Dryden & Wainwright Reservoir									
Wood-chip layer	-	-	-	-	-	-	-	-	-
Clay layer	-	-	-	-	-	-	-	-	-
Wainwright Reservoir cores									
Wood-chip layer	-	-	-	-	-	-	-	-	-
Wood/clay transition	-	-	-	-	-	-	-	-	-
Clay layer	-	-	-	-	-	-	-	-	-
Clay Lake, grab samples (mud)									
East basin	13	33.4	21.0-42.2	8.00	13	0.565	0.330-1.00	0.192	60.9
West basin	5	48.0	47.0-49.5	0.953	5	1.05	0.994-1.13	0.0561	45.9
Wabigoon River downstream from Clay Lake, grab samples (mud)	5	45.4	43.7-49.0	2.17	5	1.16	0.915-1.45	0.236	40.6
Ball Lake, grab samples (mud)									
South basin	13	33.5	13.3-41.0	7.59	13	1.27	0.458-1.61	0.494	32.3
North basin	6	33.6	10.6-39.8	11.3	6	0.830	0.512-0.992	0.172	39.3

Table 3A. Analytical data for interstitial water of sediment samples.
Notation: Number of samples: N; mean: $\bar{X}$.

	N	pH			Conductivity (μmhos/cm)			mg Cl^-/L			mg SO_4^{2-}/L		
Sample		$\bar{X}$	range	Stand. dev.	$\bar{X}$	range	Stand. dev.	$\bar{X}$	range	Stand. dev.	$\bar{X}$	range	Stand. dev.
Clay Lake grab samples (mud)													
East basin	13	6.93	6.78-7.21	0.149	181	155-220	21.7	8.37	6.00-12.0	1.86	5.56	2.60-11.4	2.75
West basin	6	7.08	6.90-7.30	0.130	153	120-195	25.7	3.10	1.80-4.50	1.08	0.89	0.54-1.80	0.510
Wabigoon River grab samples (mud) taken downstream from Clay Lake	5	7.19	7.07-7.34	0.115	163	112-227	52.2	4.76	4.00-6.00	0.780	1.80	1.20-3.00	0.735
Ball Lake grab samples (mud)													
South basin	14	7.25	7.00-7.32	0.108	227	190-250	17.7	2.11	1.80-2.40	0.262	3.08	1.80-5.40	1.07
North basin	6	6.85	6.79-6.90	0.0528	226	180-258	26.1	2.10	1.80-2.40	0.276	3.70	2.40-4.80	1.02

Table 3B. Analytical data for interstitial water of sediment samples.
Same notation as in 3A.

	mg Na/L				mg K/L				mg Ca/L				mg Mg/L			
Sample	N	$\bar{X}$	range	Stand. dev.	N	$\bar{X}$	range	Stand. dev.	N	$\bar{X}$	range	Stand. dev.	N	$\bar{X}$	range	Stand. dev.
Clay Lake grab samples (mud)																
East basin	13	10.2	8.07-12.9	1.66	13	5.62	4.01-8.64	1.61	6	1.39	0.69-1.77	0.402	13	8.55	6.60-11.9	1.79
West basin	6	3.43	2.13-4.56	0.800	6	1.55	1.00-2.46	0.581	4	0.923	0.85-1.00	0.0613	6	2.81	2.00-3.78	0.570
Wabigoon River grab samples (mud) taken downstream from Clay Lake	5	5.02	3.20-6.51	1.20	5	2.33	1.56-2.91	0.542	4	1.67	1.31-2.54	0.582	5	4.34	3.30-5.61	0.946
Ball Lake grab samples (mud)																
South basin	14	3.40	3.06-3.75	0.210	14	2.20	1.50-3.15	0.498	6	1.62	1.31-2.08	0.310	14	5.24	3.54-6.66	0.829
North basin	6	2.62	2.25-3.06	0.372	6	1.81	1.35-2.22	0.393	4	1.91	1.69-2.08	0.172	6	5.99	5.13-6.33	0.447

Table 3C. Analytical data for interstitial water of sediment samples. Same notation as in 3A.

Sample	mg Fe/L				mg Mn/L				Fe/Mn	mg org. C/L				mg N/L				N/org. C
	N	$\bar{X}$	range	Stand. dev.	N	$\bar{X}$	range	Stand. dev.	$\bar{X}$	N	$\bar{X}$	range	Stand. dev.	N	$\bar{X}$	range	Stand. dev.	$\bar{X}$
Clay Lake grab samples (mud)																		
East basin	6	1.69	1.12-2.47	0.502	6	0.814	0.125-2.13	0.726	4.53	13	340	226-453	74.7	13	5.43	3.27-7.92	1.70	0.0160
West basin	4	1.52	1.24-1.91	0.295	4	0.719	0.500-0.875	0.157	2.27	6	475	452-499	18.5	6	2.18	1.42-3.45	0.813	0.00462
Wabigoon River grab samples (mud) taken downstream from Clay Lake	4	1.29	1.12-1.46	0.146	4	1.31	0.875-2.00	0.505	1.06	5	205	157-272	48.2	5	2.26	1.77-2.64	0.314	0.0113
Ball Lake grab samples (mud)																		
South basin	6	1.07	1.01-1.24	0.121	6	2.15	1.75-3.00	0.442	0.470	14	141	121-162	12.6	14	2.33	1.40-3.54	0.588	0.0166
North basin	4	1.41	1.24-1.69	0.195	4	1.66	1.50-1.75	0.119	0.858	6	138	127-146	7.50	6	2.68	1.89-3.60	0.758	0.0195

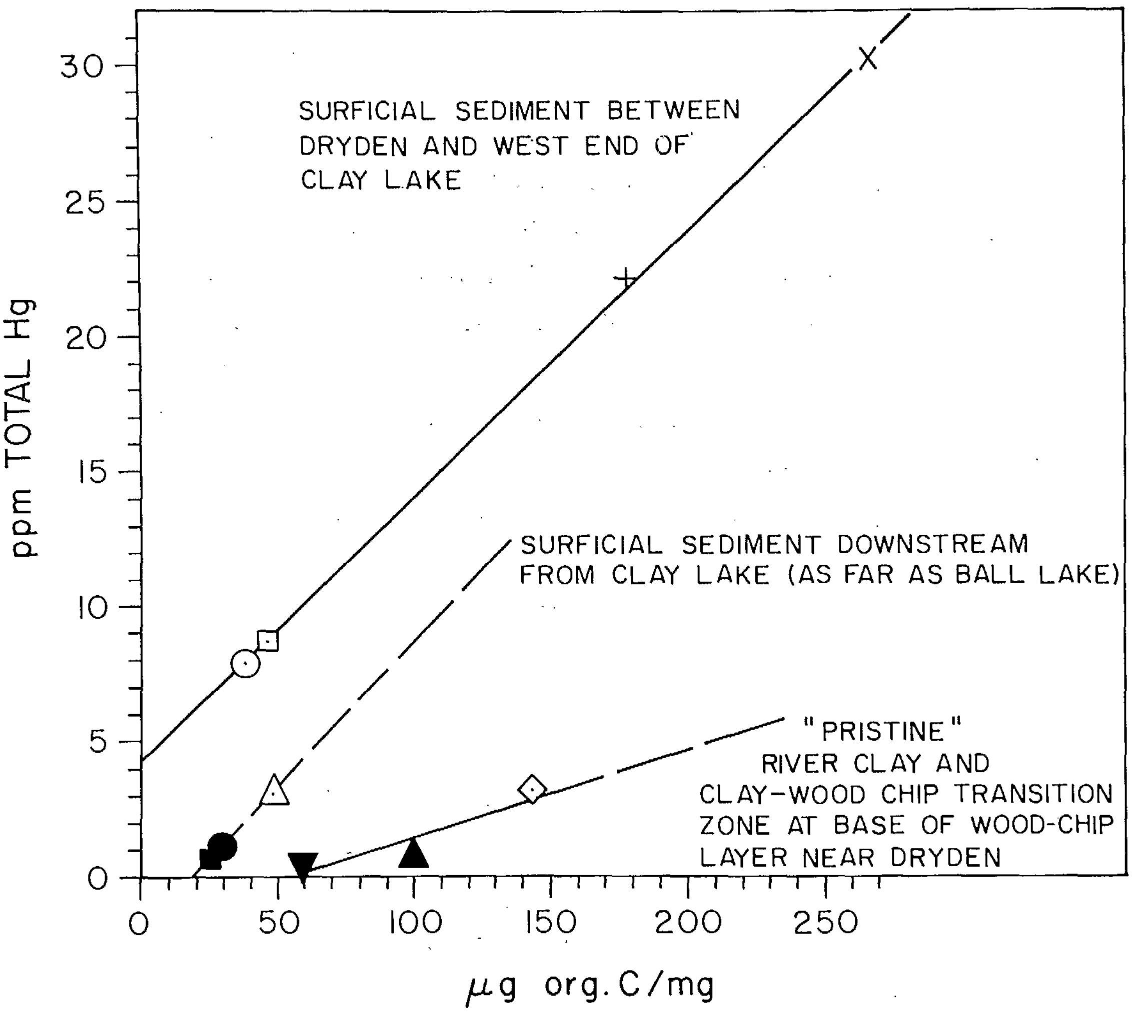


Figure 2. Relationship between mean total Hg and mean organic carbon concentrations of bottom sediments in the Wabigoon-English River system. Explanation of symbols: Wabigoon R. upstream from Wainwright Reservoir: wood-chip layer, + ; clay layer, ▲ ; wood-clay transition, ◇ .
Wainwright Reservoir: wood-chip layer, X ; clay layer, ▼ .
Clay Lake: east basin, ○ ; west basin, □ . Wabigoon River downstream from Clay Lake: △ . Ball Lake: south basin, ● ; north basin, ■ .

Ball Lake have higher Hg concentrations per unit concentration of org. C than do the essentially uncontaminated sediments underlying the contaminated wood-chip layer, suggesting that particulate Hg from Dryden has been transported at least as far downstream as Ball Lake (cf. Parks, 1976). The discontinuity between the trends for sediments above and below the outlet of Clay Lake (Fig. 2) may be an indication of Clay Lake's role as a settling pond for partial entrapment of Hg during its journey downstream (cf. Jackson, 1979; Armstrong and Hamilton, 1973).

In contrast to the total Hg, CH_3Hg^+ does not vary greatly with distance from Dryden. The mean CH_3Hg^+ levels are somewhat lower in the two basins of Clay Lake than in the wood-chip layer near Dryden but then increase from Clay Lake to Ball Lake, being about the same in the south basin of Ball Lake as in Wainwright Reservoir (in fact, slightly higher). Consequently, the CH_3Hg^+/Total Hg ratio increases progressively from Dryden to Ball Lake, and is an order of magnitude higher in Ball Lake than elsewhere in the system (Table 1). Nowhere in the river-lake system do the surficial sediments show a significant relationship between CH_3Hg^+ and total Hg (Fig. 3), although a strong positive correlation was observed in the case of the "pristine" clay underlying the coatings of slime and rotten wood chips on the riverbed between Dryden and Quibell (Fig. 4). Except in this subsurface mineral sediment, CH_3Hg^+ concentration is evidently limited primarily by environmental conditions rather than Hg supply. Let us, therefore, examine the relationships between CH_3Hg^+ concentration and sedimentary environment in different parts of the river-lake system. Interpretation of the analytical data in terms of biogeochemical processes is difficult without additional information, because CH_3Hg^+ concentration is not necessarily proportional to CH_3Hg^+ production rate (Wood, 1974). CH_3Hg^+ concentration may be the net result of the interaction of many quite different variables, such as the rates of methylation and demethylation, the ability of the sediment to adsorb CH_3Hg^+, and the rates of desorption and outward diffusion. Presumably these factors depend on the composition, grain size frequency, permeability, and other properties of the sediment, as well as the nature of the biota and the composition and dynamics of the overlying water. Nevertheless, the results

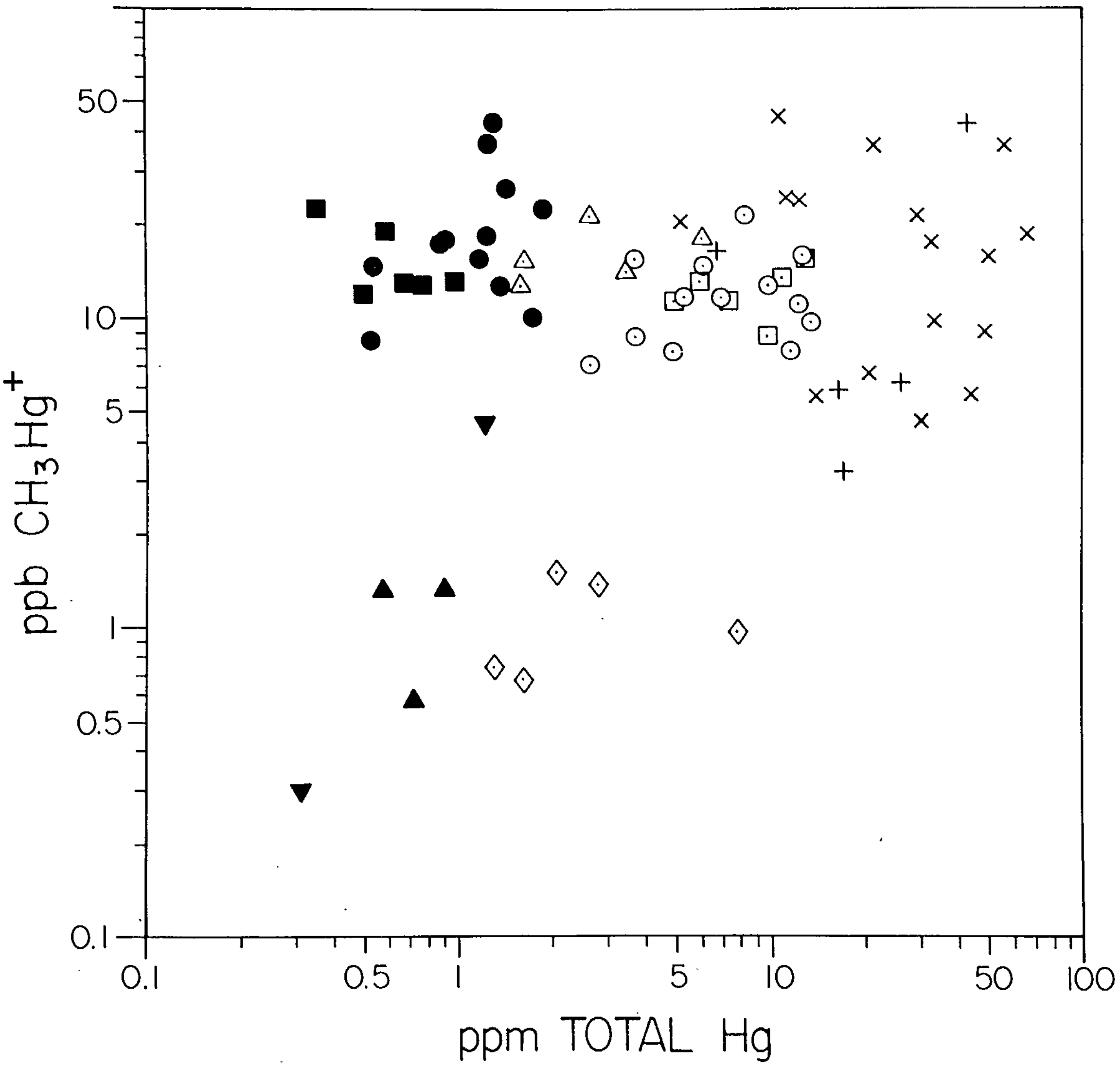


Figure 3. Relationship between CH_3Hg^+ and total Hg in bottom sediments of the Wabigoon-English River system. Explanation of symbols: Wabigoon R. upstream from Wainwright Reservoir: Wood-chip layer, + ; clay layer, ▲ ; wood-clay transition, ◇. Wainwright Reservoir: Wood-chip layer, X ; clay layer, ▼. Clay Lake: East basin, ○ , west basin, □ . Wabigoon River downstream from Clay Lake: △ . Ball Lake: South basin, ● ; north basin, ■ .

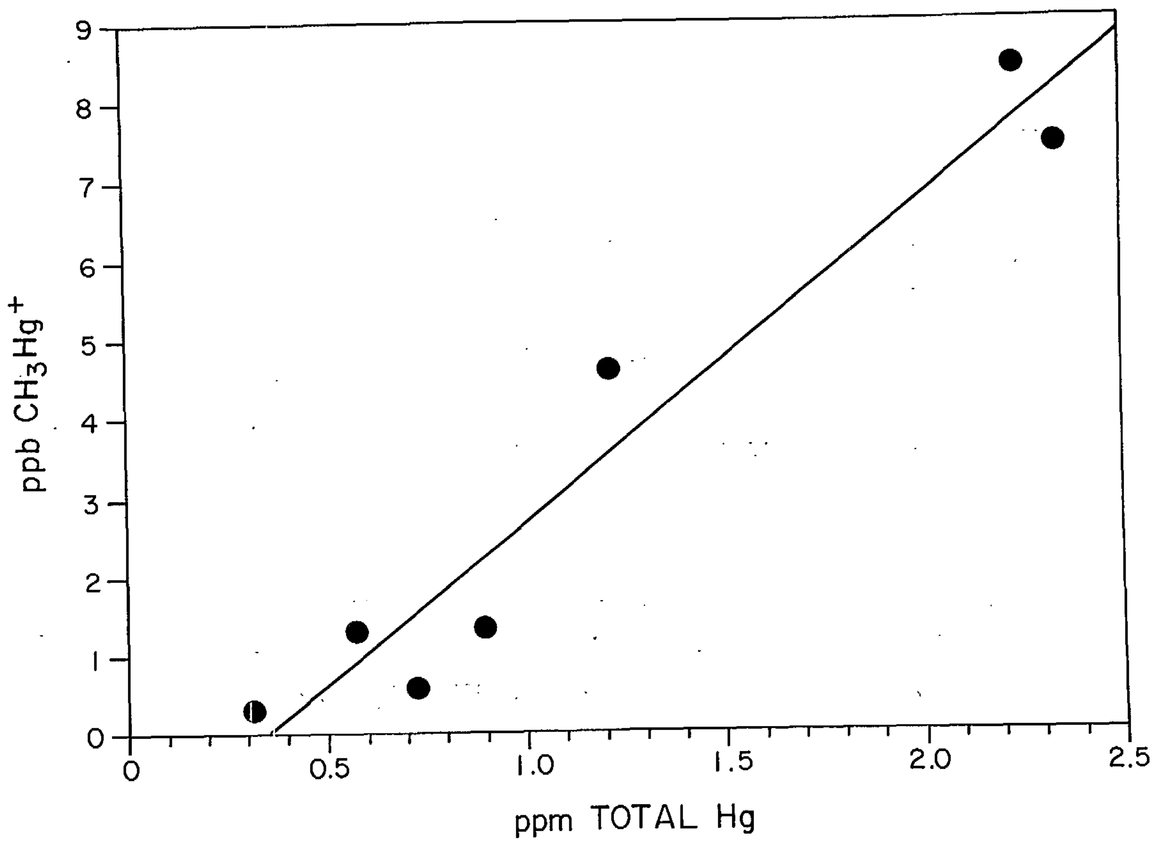


Figure 4. Relationship between CH_3Hg^+ and total Hg concentrations in "pristine" Wabigoon River mud underlying surficial slime and wood-chip layers in Wabigoon River between Dryden and Quibell ($r = 0.969$; $p < 0.001$).

obtained thus far permit the formulation of reasonable working hypotheses, which may serve as starting points for future research.

The cores taken behind Wainwright dam generally showed that the CH_3Hg^+ content of the wood-chip layer was greatest at or near the sediment-water interface, whereas total Hg tended to be most abundant several centimeters below the interface (Fig. 5). The observed distribution of CH_3Hg^+ can be explained by the existence of particularly favorable conditions for microbial CH_3Hg^+ synthesis at the sediment-water interface, whereas the distribution of total Hg probably reflects the deposition of less contaminated sediment on top of the more severely contaminated material after 1970, when uncontrolled Hg discharges officially ceased. In one of the three cores taken from the riverbed (no. 13) the maximum total Hg concentration occurred in the top 6 cm., suggesting erosion and resuspension of the less Hg-rich surface material by current action, with concomitant release of sedimentary CH_3Hg^+ into the water.

The CH_3Hg^+ content of the wood-chip sediment varies with the amino acid composition of the sediment. Thus, CH_3Hg^+ concentration gave strong positive correlations with the methionine/threonine and methionine/serine ratios (Fig. 6A) as well as weaker correlations with the methionine/cystine and methionine/glycine ratios and with the absolute concentration of methionine. These relationships suggest that micro-organisms in the sediments methylate Hg by a process involving methionine or in some way linked to the methionine biosynthetic pathway (cf. Landner, 1971; Wood, 1971; Vonk and Sijpesteijn, 1973). In addition, CH_3Hg^+ content tends to increase with total N concentration (Fig. 6B) or with the N x org. C product, probably reflecting the dependence of methylation rate on nutrient availability and the general level of microbial activity (Fagerström and Jernelöv, 1972; Langley, 1973; Shin and Krenkel, 1976). Experimental studies have demonstrated that methylation rate depends in part on the product of organic carbon and organic nitrogen, defined as the "organic sediment index" (Langley, 1973); org. C x total N -- the parameter used in this report -- probably estimates this index reasonably well.

The CH_3Hg^+ levels in the wood chips and surficial organic slime of the riverbed between Dryden and Quibell also tended to increase as the

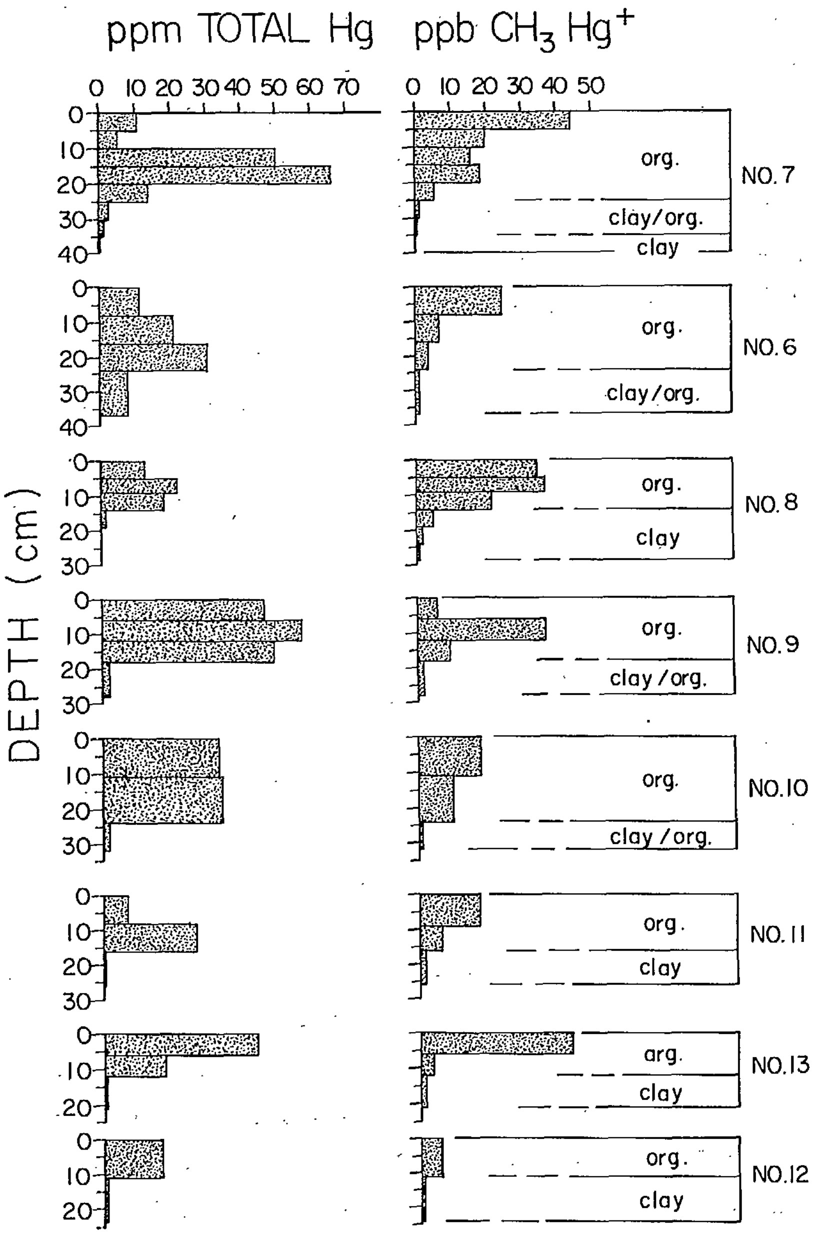


Figure 5. Profiles of CH_3Hg^+ and total Hg in cores from Wainwright Reservoir (no. 6-10) and the Wabigoon River upstream from it (no. 11-13). "Organic" refers to wood-chip sediment.

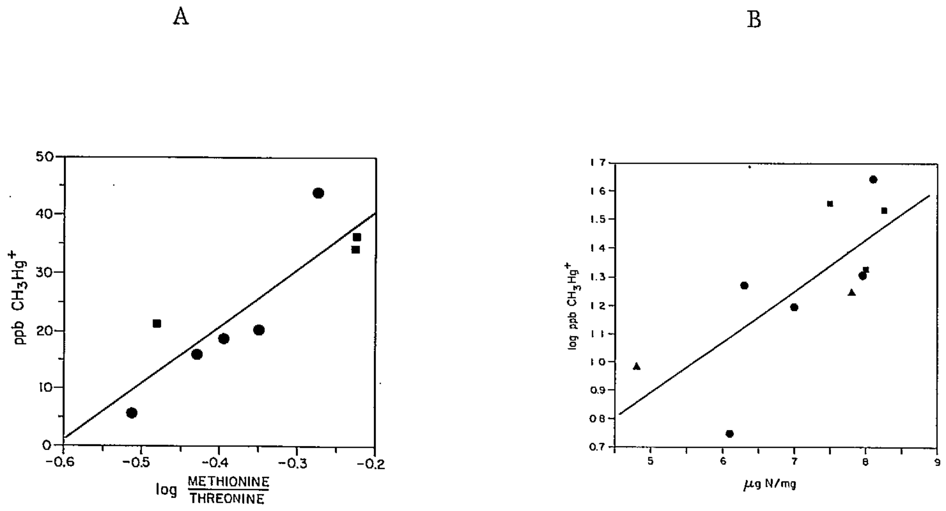


Figure 6. Variation of CH_3Hg^+ concentration with respect to (A) methionine/threonine ratio ($r = 0.873$; $p = 0.001$-0.01) and (B) total nitrogen concentration ($r = 0.745$; $p = 0.01$-0.02) in wood-chip sediments of Wainwright Reservoir. The graphs represent cores 7 (●), 8 (■), and 10 (▲), which were taken from approximately the same place, on the west side of the reservoir.

pH of the sediment decreased, at least within the observed pH range of 4-7 (Fig. 7, A & B). A likely reason for this relationship is the experimentally established fact that CH_3Hg^+ increases in abundance at the expense of $(CH_3)_2Hg$ with decreasing pH (Fagerström and Jernelöv, 1972; Jernelöv, 1972). In the wood-chip zone the pH is lowest at the sediment-water interface, probably owing to particularly favorable conditions for microbial decomposition of the wood. On the other hand, in the essentially inorganic clay or silt muds of the riverbed between Dryden and Quibell CH_3Hg^+ concentration increased with decreasing E_h (Fig. 7C), not pH. This trend may reflect the fact that anaerobic (oxygen-poor) conditions foster net CH_3Hg^+ production, provided that little or no sulfide is present (Fagerström and Jernelöv, 1972; Jernelöv, 1972; Olson and Cooper, 1976), as is the case here (Table 2B). Another possible explanation is that CH_3Hg^+ is sorbed more efficiently, or diffuses outward more slowly, in the more anaerobic sediments.

In summary, the analytical data for surficial organic sediments deposited between Dryden and Clay Lake are consistent with the tentative conclusion that the observed variations in CH_3Hg^+ concentration were due primarily to variations in CH_3Hg^+ production rate, which in turn was a function of pH, nutrient availability, and the metabolic activity of micro-organisms employing the methionine biosynthetic pathway for methylation.

With increasing distance downstream from the source of pollution, the surface deposits of putrefying wood and scum grade into sand, silt, and clay associated with humic matter and hydrated Fe/Mn oxides. This transition is accompanied by progressive changes in the physico-chemical properties of the bottom sediments -- for instance, a decrease in the interstitial Cl^- concentration and an increase in the sedimentary pH, N/org. C ratio, and Mn concentration (both in absolute terms and in proportion to Fe) (Tables 2 and 3). A downstream decrease in the concentration of suspended particles has also been noted (Rudd, J.W.M., personal communication). Not surprisingly, the chemistry of CH_3Hg^+ and other forms of Hg reflects this downstream gradient in sedimentary environment as well as the idiosyncrasies of individual basins of deposition. Variations in the nature of the sediments within the depositional basins had to be taken

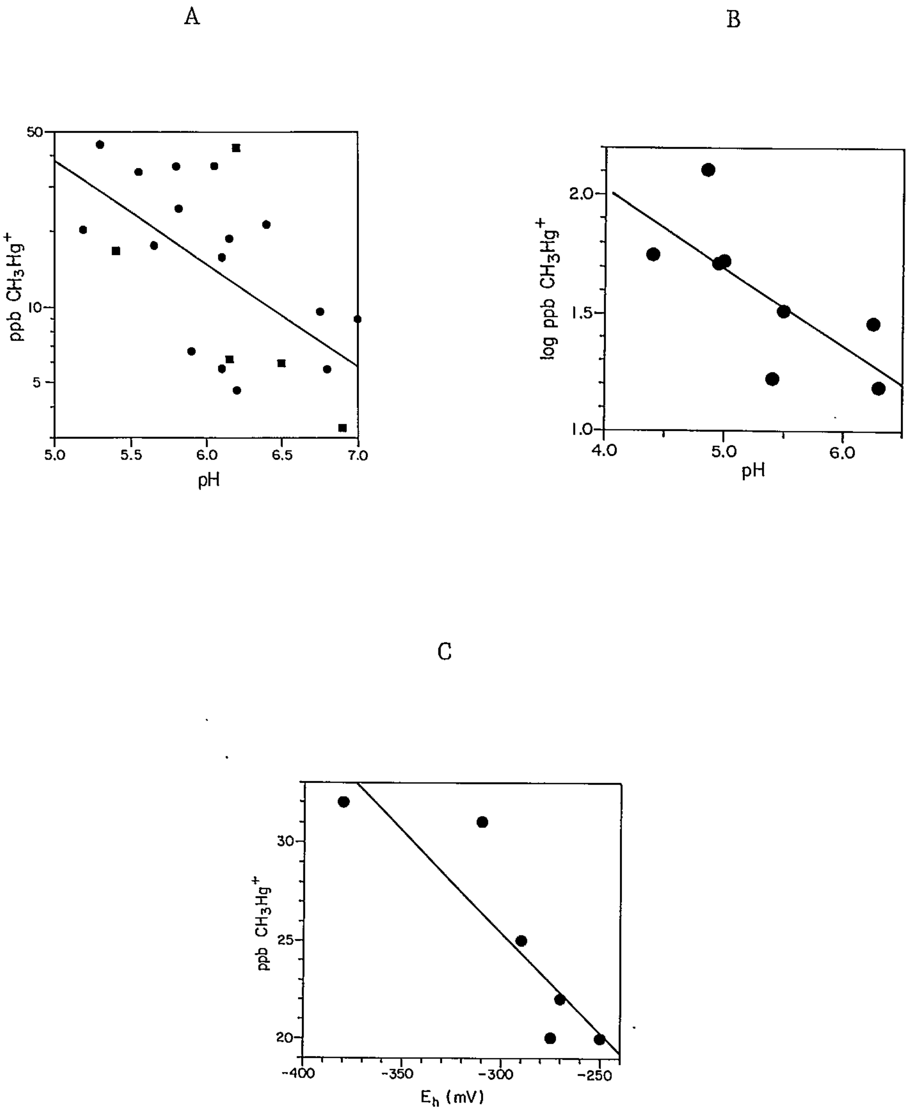


Figure 7. Variation of CH_3Hg^+ concentration with (A) pH in wood-chip sediments in Wainwright Reservoir (●) and Wabigoon River (■) cores ($r = -0.596$; $p = 0.001-0.01$), (B) pH in surficial wood and slime deposits dredged from the riverbed between Dryden and Quibell ($r = -0.723$; $p = 0.02-0.05$), and (C) E_h in surficial and subsurface river mud collected between Dryden and Quibell ($r = -0.882$; $p = 0.02$). Note: The CH_3Hg^+ data in (B) and (C) were obtained from samples that were frozen soon after collection and analyzed 20 months later.

into account as well. Inspection of the analytical data revealed that the sediment samples from the east basin of Clay Lake could be subdivided into two sets (groups 1 and 2), which, though outwardly similar, differed from each other in physico-chemical characteristics and areal distribution. Group 1, which came from the east end of the basin, was distinguished by relatively high levels of interstitial dissolved Cl^- (7.80-12.0 mg/L) and dissolved N (5.94-7.92 mg/L) and high E_h values (-220 to -160 mV), whereas group 2, which came from the western part of the basin, had lower concentrations of interstitial Cl^- (6.00-7.60 mg/L) and N (3.27-4.50 mg/L) and lower E_h values (-325 to -260 mV). The samples from the south basin of Ball Lake were also divided into two sub-groups on the basis of a systematic difference in properties. In this case, group 1 had aberrantly high CH_3Hg^+ levels with respect to group 2, as will be discussed below.

The CH_3Hg^+ concentrations in the group-1 east basin sediments of Clay Lake gave significant positive correlations with the ratios of methionine to certain other amino acids, including alanine (Fig. 8A), serine, and glutamic acid (but not threonine), suggesting that the biochemical mechanisms of CH_3Hg^+ production were similar to those prevailing in the wood-chip deposits near Dryden (cf. Fig. 6A). On the other hand, there was no pH effect, probably because the pH range was too narrow (Table 2A). CH_3Hg^+ was also positively correlated with the ratio of CBD-extractable Fe to $NH_2OH{\cdot}HCl$-extractable Mn (Fig. 8B), possibly indicating that CH_3Hg^+ production is inhibited by the adsorption of certain reactants by colloidal Mn oxide. In addition, the CH_3Hg^+ level reaches a maximum at an interstitial Cl^- concentration of about 10 mg/L and falls off above or below this value (Fig. 8C); this may be the optimal Cl^- level for CH_3Hg^+ synthesis in this particular environment (cf. Shin and Krenkel, 1976).

The group-2 east basin samples showed none of these effects but did give a positive correlation between CH_3Hg^+ content and the ratio of CBD-extractable Fe to $NH_2OH{\cdot}HCl$-extractable Fe (Fig. 9). The group-2 CH_3Hg^+ data also gave a negative correlation with N, org. C, and N X org. C (Fig. 10A) -- the reverse of what would be expected if the N and org. C levels were indicators of the availability of organic nutrients to methylating micro-organisms (Langley, 1973). An hypothesis consistent with the data would be that the sorption

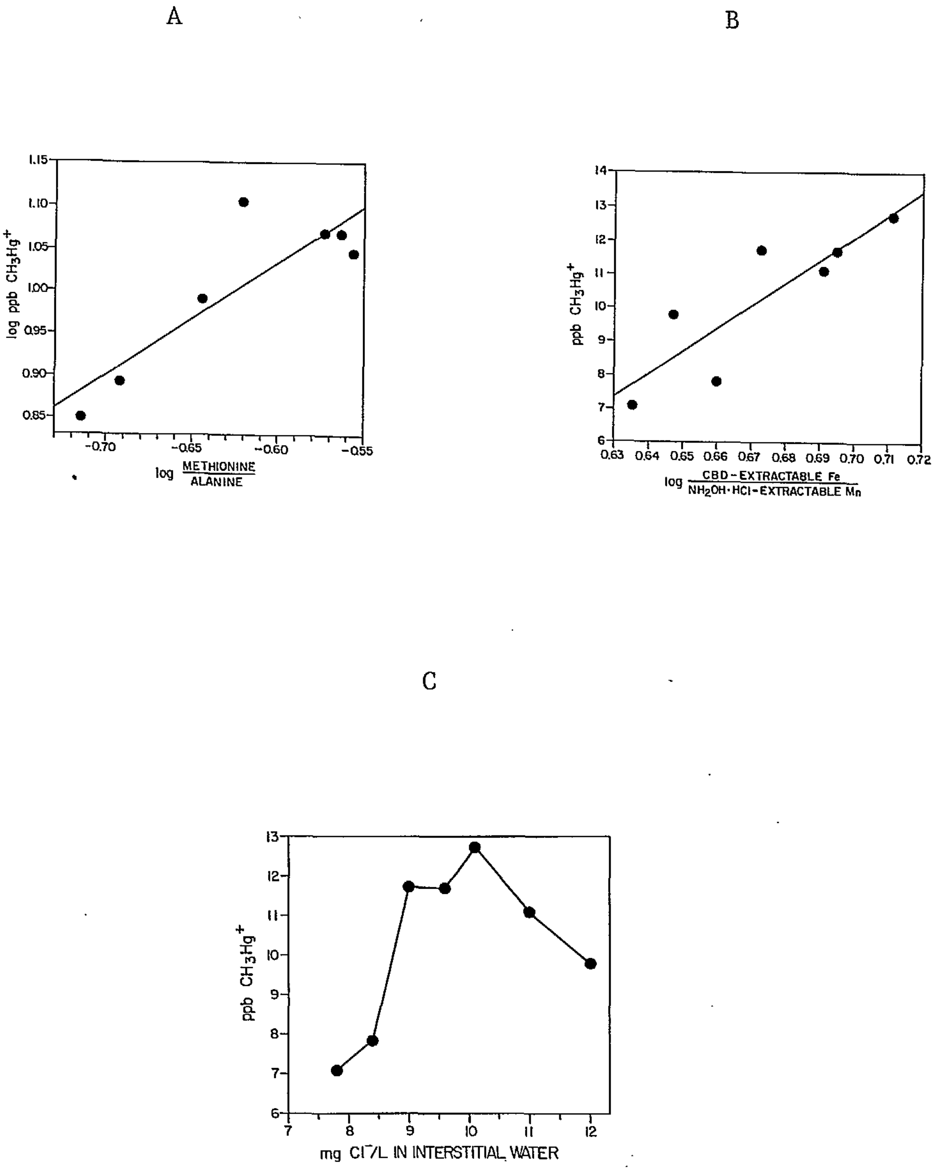


Figure 8. Variation of CH_3Hg^+ content with (A) methionine/alanine ratio ($r = 0.868$; $p = 0.01$-0.02, (B) ratio of CBD-extractable iron to $NH_2OH \cdot HCl/HNO_3$-extractable manganese ($r = 0.867$; $p = 0.01$-0.02), and (C) dissolved interstitial chloride in group-1 sediments from east basin of Clay Lake.

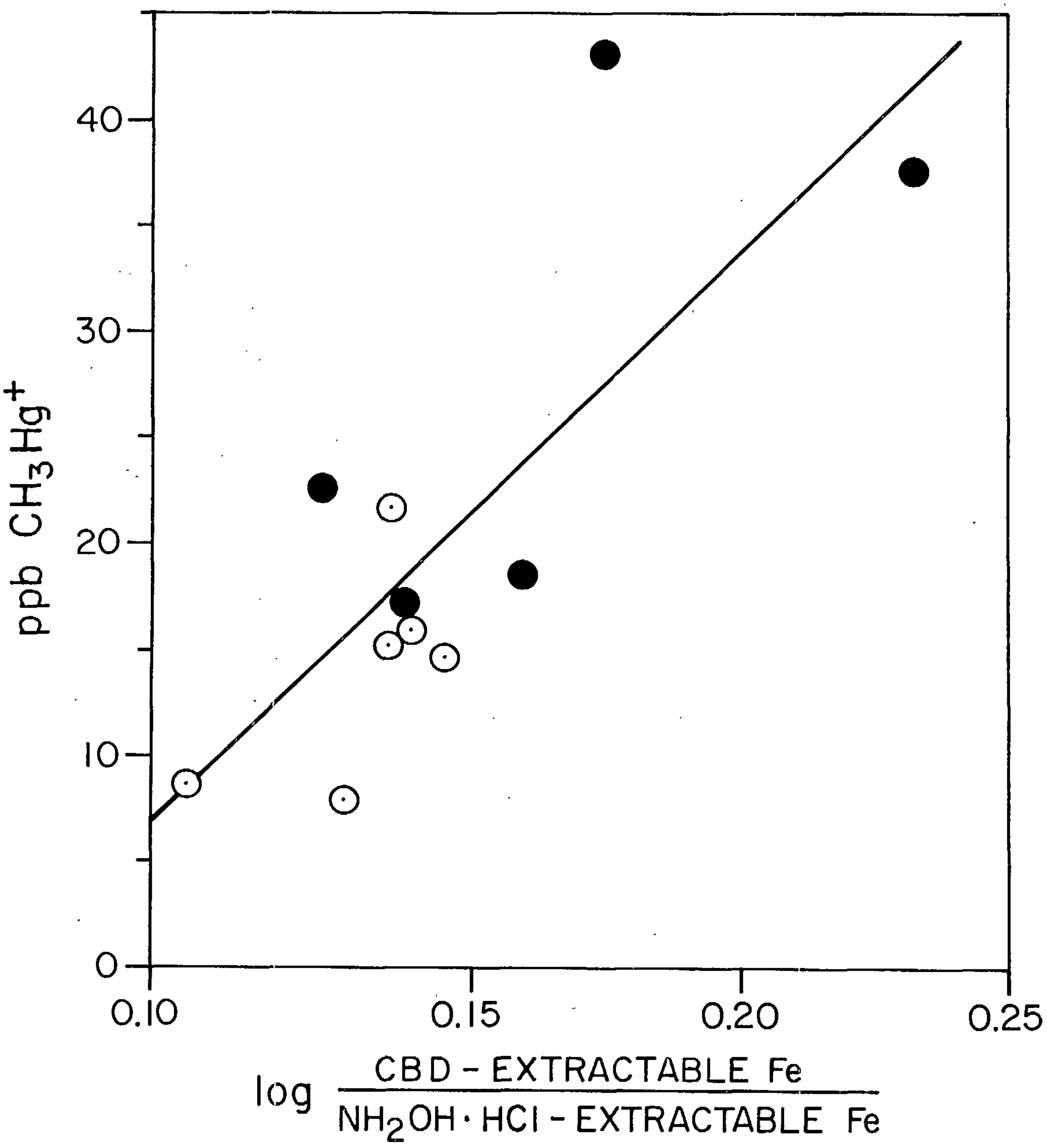


Figure 9. Variation of CH_3Hg^+ content with the ratio of CBD-extractable iron to $NH_2OH \cdot HCl/HNO_3$-extractable iron in group-2 sediments from the east basin of Clay Lake (○) and group-1 sediments from the south basin of Ball Lake (●) ($r = 0.780$; $p = 0.001$-0.01).

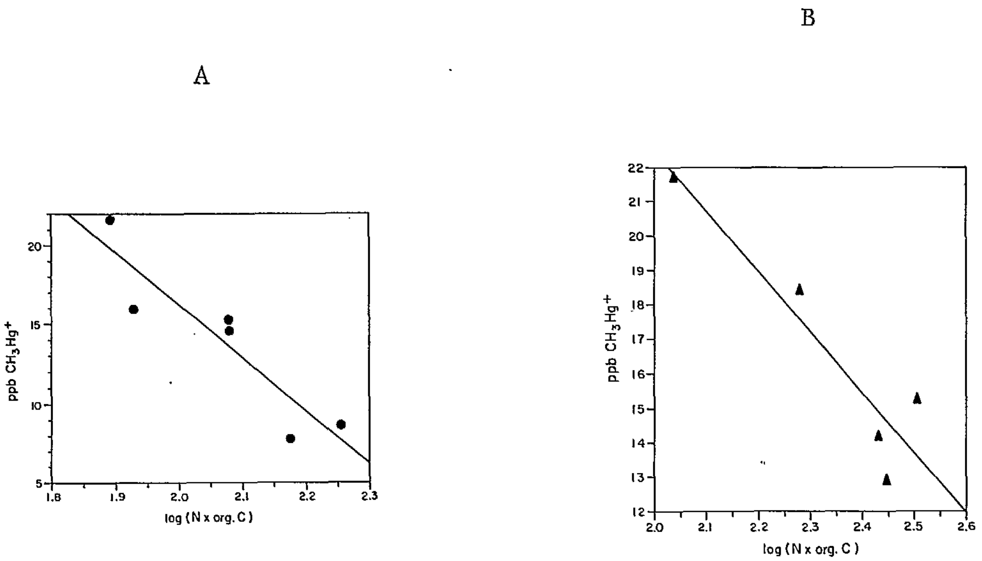


Figure 10. Variation of CH_3Hg^+ content with product of total nitrogen and organic carbon in (A) group-2 sediments from east basin of Clay Lake (r = -0.914; p = 0.001-0.01) and (B) Wabigoon River sediments just downstream from Clay Lake (r = -0.928; p = 0.02-0.05).

of certain Hg species (perhaps Hg^{2+} ions) by amorphous colloidal Fe oxides ($NH_2OH \cdot HCl$-extractable Fe) and associated humic matter (represented by N and org. C) tends to inhibit CH_3Hg^+ formation in these sediments.

Samples from the west basin of Clay Lake and the riverbed just beyond it showed positive correlations between CH_3Hg^+ and the ratios of methionine to serine, aspartic acid, glutamic acid, and alanine, but the relationships were insignificant at the 5% level. The river samples, moreover, showed an inverse relationship between CH_3Hg^+ and N or N x org. C (Fig. 10B) as in the case of the group-2 east basin samples (Fig. 10A).

In brief, the data on CH_3Hg^+ chemistry in the bottom muds of Clay Lake and the river beyond seem to imply that the influence of organic nutrients and dissolved salts introduced by the Wabigoon River from sources in and near Dryden is strongest in east basin sediments of the group-1 type, which lie nearest the inflow. Toward the west (in the downstream direction) this influence understandably becomes increasingly feeble, whereas the role of Fe/Mn oxides, humic substances, and clay minerals becomes increasingly important. In Ball Lake, which is still more remote from the sources of pollution, any influence of river-borne organic matter and salts was undetectable by the criteria employed.

In the south basin of Ball Lake, the deepest depositional basin investigated (Table 2A), sedimentary CH_3Hg^+ concentration decreases with increasing depth (Fig. 11A). The CH_3Hg^+ data form two parallel trends, apparently indicating the existence of two different classes of sediment. The samples forming the upper curve (i.e. those which were anomalously rich in CH_3Hg^+) were called "group 1," and those forming the lower curve were designated "group 2." The observed pattern of variation is related to depth-dependent variation in the proportion of Fe to Mn oxide: The lower the Fe/Mn ratio of the combined $NH_2OH \cdot HCl$- and CBD-extractable fractions, the greater the CH_3Hg^+ concentration in group 1 or group 2 (Fig. 11B). Despite the parallels between groups 1 and 2, the biogeochemistry of CH_3Hg^+ differs markedly in the two groups of samples. The group-1 CH_3Hg^+ data (together with the group-2 CH_3Hg^+ data from the east basin of Clay Lake) were positively correlated with the ratio of CBD- to $NH_2OH.HCl$-extractable Fe (Fig. 9), besides giving a strong

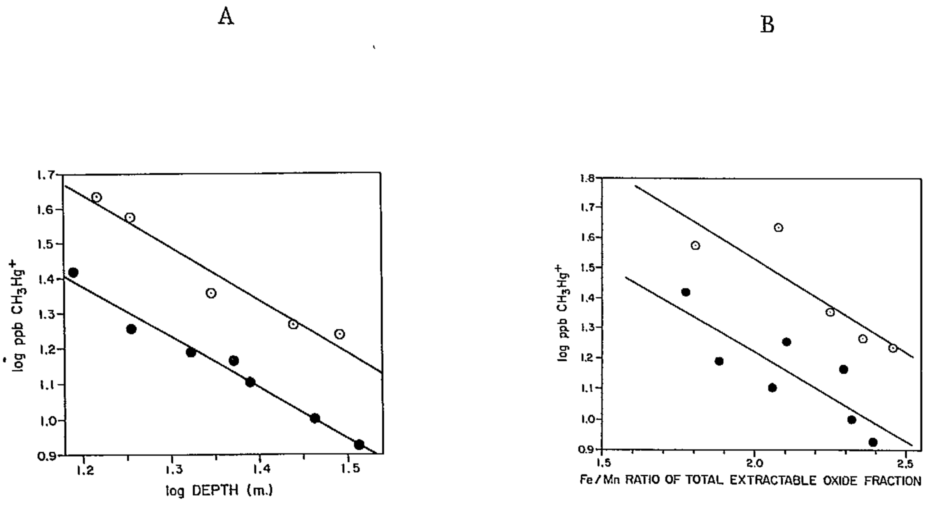


Figure 11. Relationships between CH_3Hg^+ concentrations and environmental parameters in group-1 (○) and group-2 (●) sediments in south basin of Ball Lake.

(A) Variation of CH_3Hg^+ content with depth of water at sampling site (group 1: r = -0.976; r = 0.001-0.01; group 2: r = -0.988; $p < 0.001$).

(B) Variation of CH_3Hg^+ content with the iron/manganese ratio of the combined $NH_2OH \cdot HCl/HNO_3$- and CBD-extractable oxide fractions (group 1: r = -0.872; p = 0.05-0.1; group 2: r = -0.833; $p \simeq 0.02$).

negative correlation with the N x org. C value for the interstitial water (Fig. 12). On the other hand, the CH_3Hg^+ data for group 2 as well as for the north basin gave a rather weak but significant positive correlation with the ratio of cystine (and/or cysteine) to methionine (Fig. 13) (in contrast to the wood-chip sediments in the Wainwright Reservoir, which gave a negative correlation with the cystine/methionine ratio). The north basin samples yielded a negative correlation with the ratio of CBD-extractable Fe to $NH_2OH{\cdot}HCl$-extractable Fe (Fig. 14A) as well as with the interstitial sulfate content (Fig. 14B) and N x org. C value.

The Ball Lake data are difficult to interpret without additional information, but they suggest that adsorption of Hg species -- possibly including CH_3Hg^+ itself -- by Fe and Mn oxides plays an important role in the chemistry of CH_3Hg^+. They also appear to indicate that the role of amino acid composition is very different than in Clay Lake and the riverbed near Dryden. Further work is needed to establish the cause-and-effect relations. The primary role of the Fe/Mn oxides and associated organic matter could be either to adsorb and accumulate the CH_3Hg^+ or to control the rate of CH_3Hg^+ biosynthesis by adsorption, coprecipitation, and catalytic transformation of other species, or both. The data suggest, however, that oxides and associated humic substances may perform more than one function. For instance, the data for the north basin could be interpreted as reflecting preferential adsorption of CH_3Hg^+ by "amorphous," freshly precipitated Fe oxides (Fig. 14A), whereas it makes more sense to infer that the major role of these oxides in the group-1 south-basin sediments is to interfere with CH_3Hg^+ synthesis (Fig. 9). On the other hand, the possible importance of variations in CH_3Hg^+ diffusion rates owing to differences in grain size and permeability cannot be ignored. An additional complication is the possibility that SO_4^{2-} plays an antagonistic role in CH_3Hg^+ production in the north basin (Fig. 14B). Additional research, which is currently underway, may help to clear up some of these ambiguities.

Data on the chemical affinities of the total Hg provided additional information on the variations in Hg speciation as functions of sedimentary

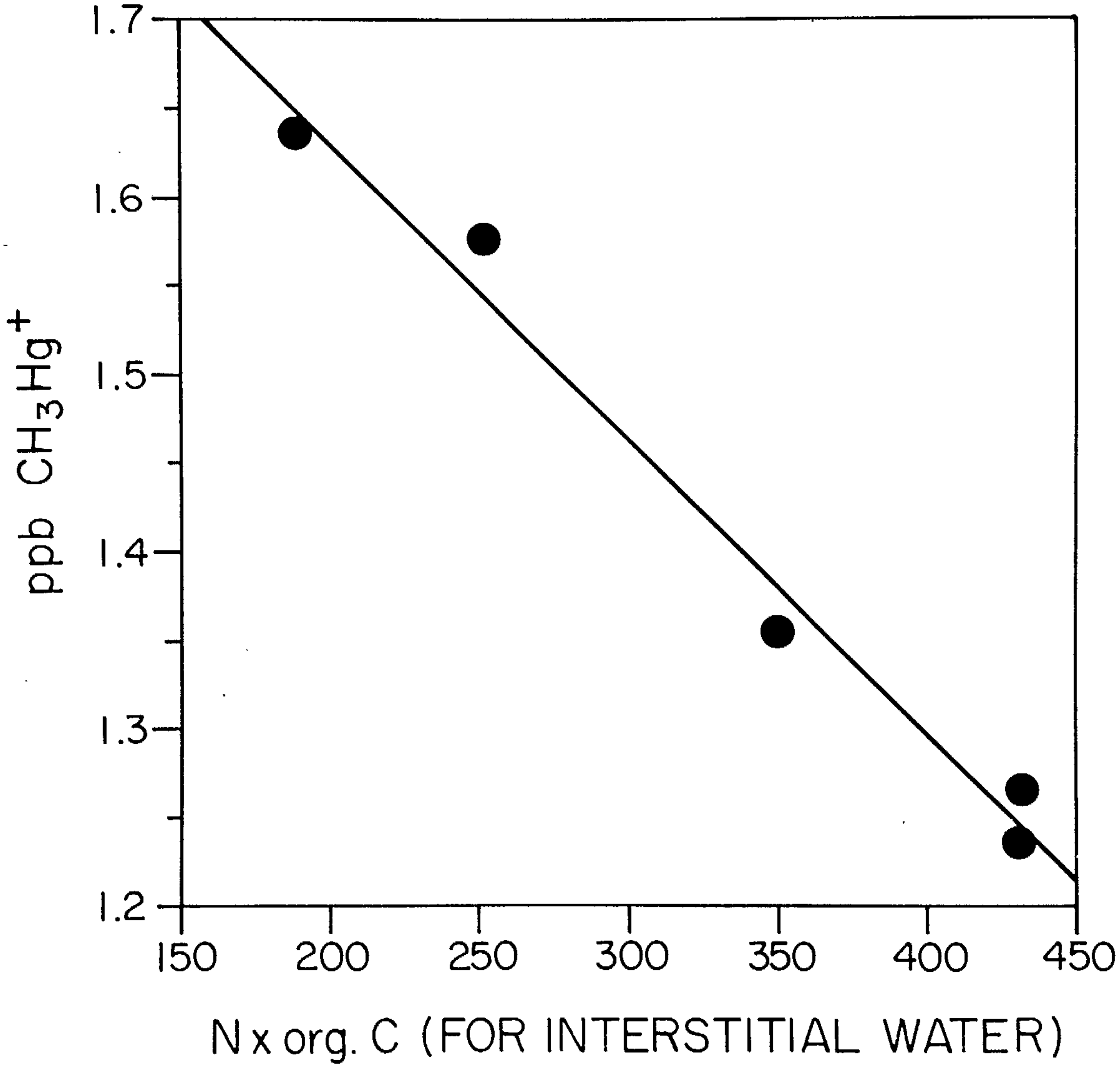


Figure 12. Relationship between CH_3Hg^+ and the product of total nitrogen and organic carbon in the interstitial water in group-1 south basin sediments from Ball Lake ($r = -0.991$; $p = 0.001$).

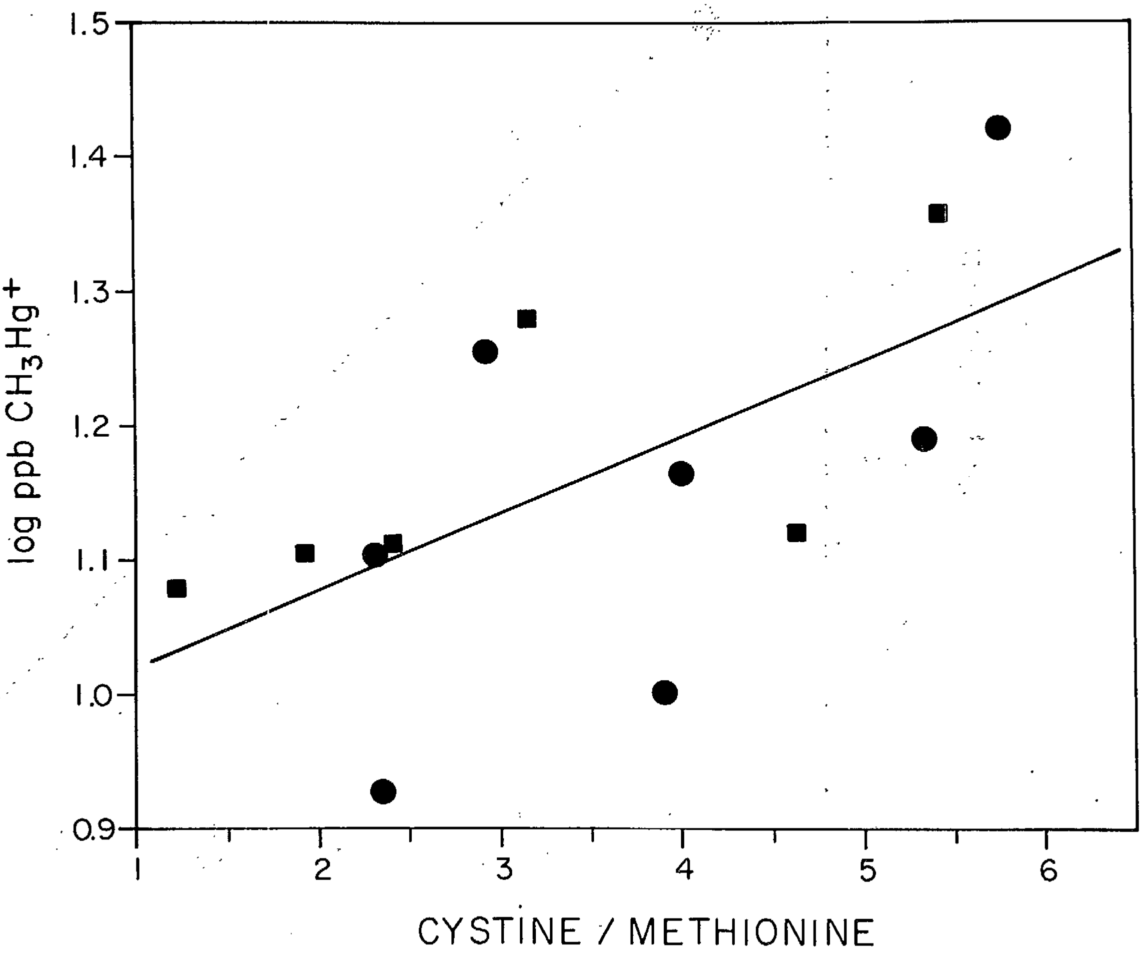


Figure 13. Relationship between CH_3Hg^+ content and the cystine/methionine ratio in north basin (■) and group-2 south basin (●) sediments from Ball Lake (r = 0.608; p = 0.02-0.05).

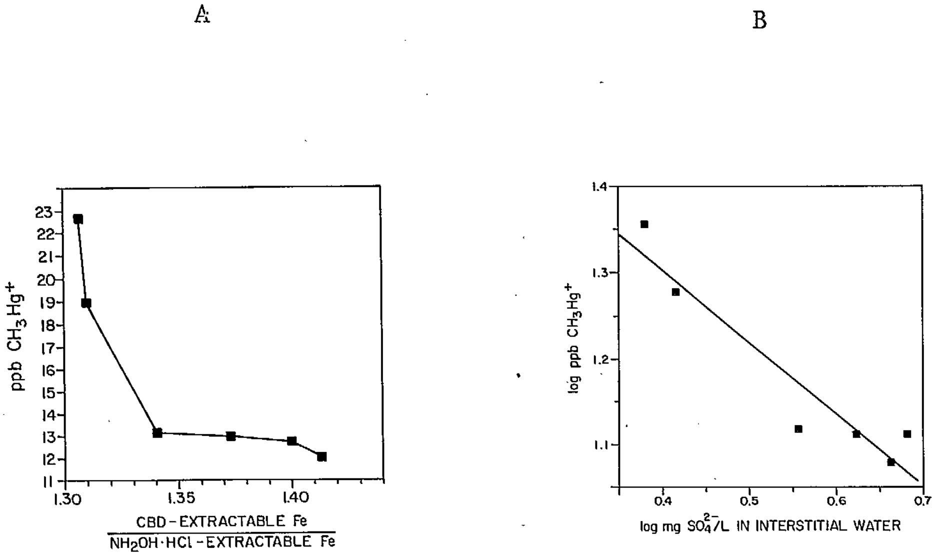


Figure 14. Variation of CH_3Hg^+ content with (A) the ratio of CBD-extractable iron to $NH_2OH.HCl/HNO_3$-extractable iron (for a log-log plot, r = -0.873; p = 0.02-0.05) and (B) interstitial dissolved sulfate (r = -0.948; p = 0.001-0.01) in sediments from the north basin of Ball Lake.

environment. In the wood-chip environment behind Wainwright dam, the distribution of Hg seems to be unrelated to the measured variations in sediment properties, and was probably determined by rates of input from the Reed plant. In Clay Lake and beyond, however, the Hg distribution in the bottom mud is largely determined by association with various metal-binding agents.

In the group-1 east-basin samples of Clay Lake, total Hg is strongly associated with total Fe (Fig. 15A) and Mn and with the total extractable Fe "oxide" fraction, suggesting that most of the Hg is bound to Fe/Mn oxides. These samples -- and these alone -- also show an almost perfect correlation between total Hg and interstitial Cl^- (Fig. 15B). The Hg and Cl^- were probably discharged simultaneously from the chlor-alkali plant and were transported to Clay Lake together -- perhaps as Hg-Cl complexes adsorbed to suspended particles. Besides tending to confirm the provenance of the Hg, the relationship is a further indication of the especially strong influence of inflowing river water on the group-1 sediments.

In contrast, the group-2 east-basin samples and the samples from the west basin gave a highly significant correlation between Hg and "bound" S^{2-}, indicating that Hg deposition in these sediments is largely controlled by precipitation of HgS or the formation of organic sulfide complexes, or both. Possibly this accounts (at least in part) for the slightly depressed mean CH_3Hg^+ levels in Clay Lake (Table 1). Note that Clay Lake mud is richer in S^{2-} than any of the other sampling areas (Table 2), presumably reflecting stimulation of biological production by nutrients (e.g. phosphate) derived from sewage effluents discharged into the river at Dryden.

Hg in the group-2 south-basin sediments of Ball Lake was very strongly associated with total Fe (Fig. 16A) and less strongly with org. C (Fig. 16B), suggesting sorption by Fe oxides complexed by organic matter. However, for reasons not yet understood, the Hg in the group-1 sediments gave a negative correlation with both org. C (Fig. 16C) and Fe; a possible explanation is that the Hg is largely adsorbed to inorganic detrital particles whose abundance varies inversely with organic content.

B. Selective extraction of Hg species from sediments.

The quantity of Hg extracted from each sediment sample by a particular method of extraction was plotted against total Hg. The concentrations of

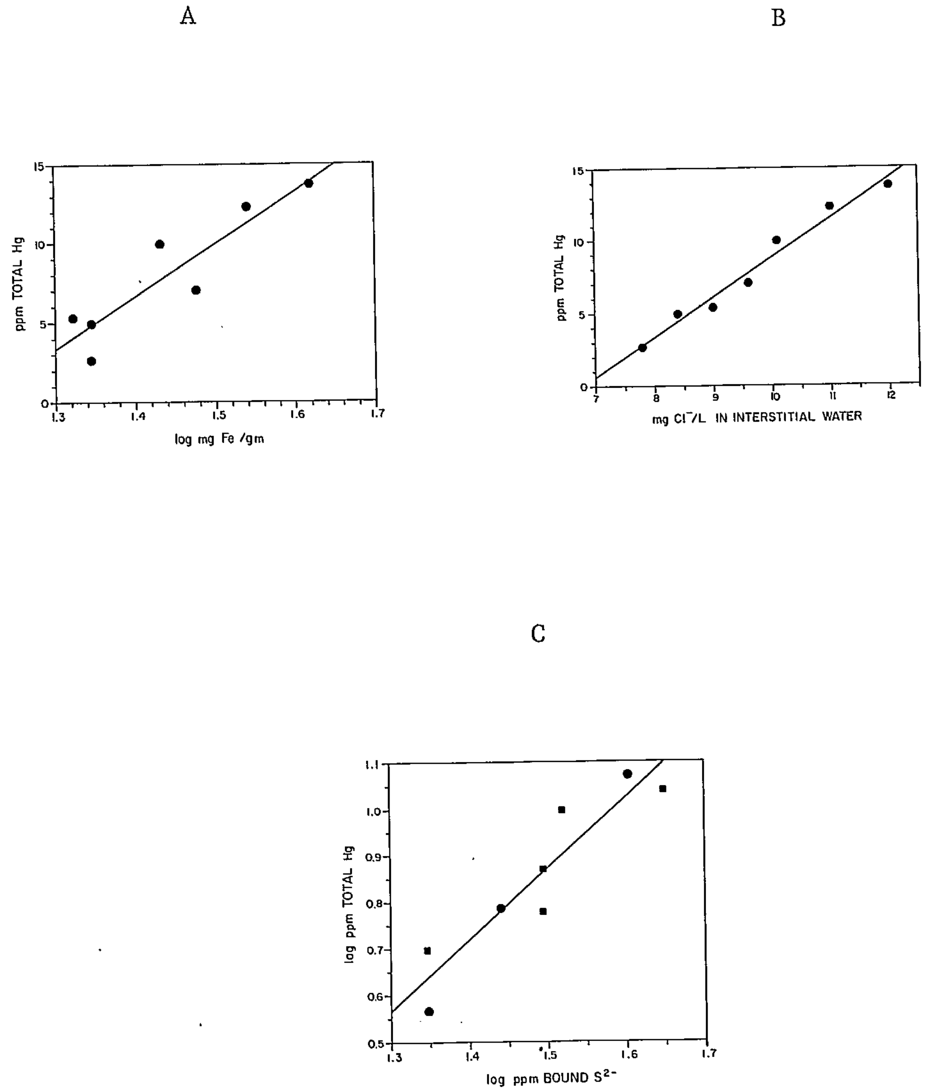


Figure 15. Chemical affinities of mercury in Clay Lake sediments. Variation of total Hg with (A) iron in group-1 east basin mud ($r = 0.912$; $p = 0.001-0.01$), (B) interstitial dissolved chloride in group-1 east basin mud ($r = 0.985$; $p < 0.001$), and (C) "bound" sulfide in west basin (■) and group-2 east basin (●) mud ($r = 0.930$; $p < 0.001$).

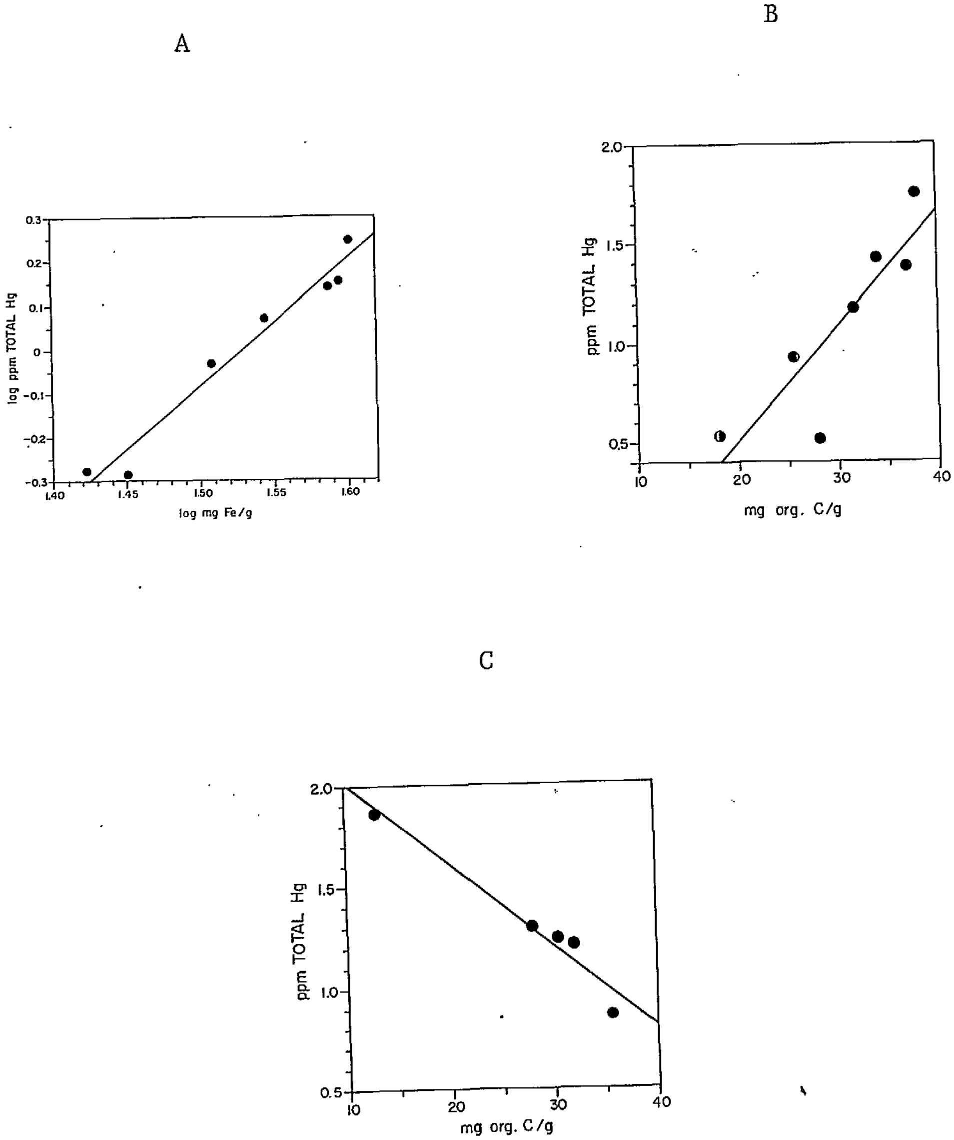


Figure 16. Chemical affinities of mercury in sediments from the south basin of Ball Lake: variation of total Hg with (A) total iron in group-2 mud ($r = 0.982$; $p < 0.001$), (B) organic carbon in group-2 mud ($r = 0.878$; $p = 0.001-0.01$), and (C) organic carbon in group-1 mud ($r = 0.974$; $p = 0.001-0.01$).

the various Hg fractions were commonly, though not invariably, proportional to the concentration of total Hg; but the trends for different regions or sedimentary environments within the Wabigoon system (e.g. Clay Lake and Ball Lake) frequently failed to coincide, indicating environmentally determined variations in the relative abundances of the Hg species (Figs. 17 and 18).

Extraction of sediments with mild reagents such as calcium acetate, calcium chloride, and dilute acetic acid yielded results demonstrating a progressive increase in the relative abundance of the more weakly bound forms of Hg with increasing distance from the source of pollution (Fig. 17). Thus, the quantity of Hg extracted per unit of total sediment-bound Hg increased in the following order: Wainwright Reservoir/Wabigoon River wood-chip layer < Clay Lake/Wabigoon River mud < Ball Lake mud. As with the observed variations in the chemistry of CH_3Hg^+, this gradational change in Hg species composition apparently reflects the downstream transition from organic paper-mill detritus to natural silt and clay associated with Fe/Mn oxides and humic matter. Evidently Hg tends to be more strongly fixed to the wood-chip detritus than to the mineral particles. This could be due to stronger binding of Hg by ligands in the rotten wood and its microflora, or to greater availability of weakly-bonding cation-exchange sites in the more finely divided mineral sediment, or both. The observed pattern of variation could reflect a progressive downstream decrease in grain size as well as a change in sediment composition. Future research on grain-size frequencies should help to resolve this question.

An interesting feature of each of the plots shown in Figure 17 is that the trend given by the clay underlying the contaminated wood-chip sediment behind Wainwright dam coincides perfectly with the trend formed by the Ball Lake mud, whereas the wood-chip sediments themselves have more in common with Clay Lake mud. This may indicate that Ball Lake mud and pristine Wabigoon River clay, being similar in composition, bind Hg in much the same way. A possible alternative interpretation is that the sedimentary Hg in Ball Lake is natural and predates the input of Hg by Reed, Ltd., implying that relatively little of the Hg discharged by

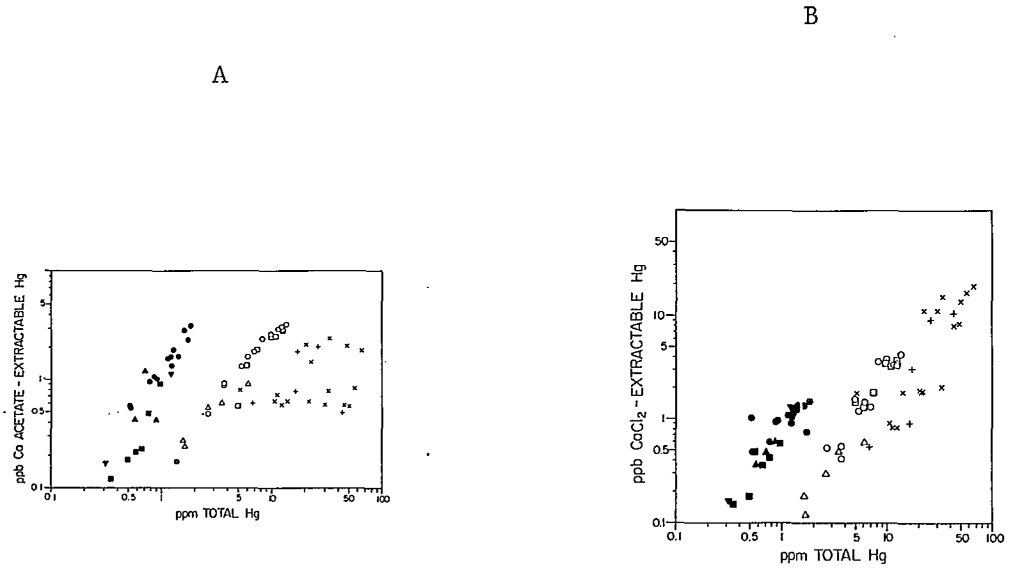


Figure 17. Variation of (A) calcium acetate-extractable Hg and (B) calcium chloride-extractable Hg with total Hg in sediment samples from Wainwright Reservoir (wood chips, X ; clay, ▼), the Wabigoon River upstream from the reservoir (wood chips, + ; clay, ▲), Clay Lake (east basin, ○ ; west basin, □), the Wabigoon River downstream from Clay Lake (△), and Ball Lake (south basin, ●; north basin, ■).

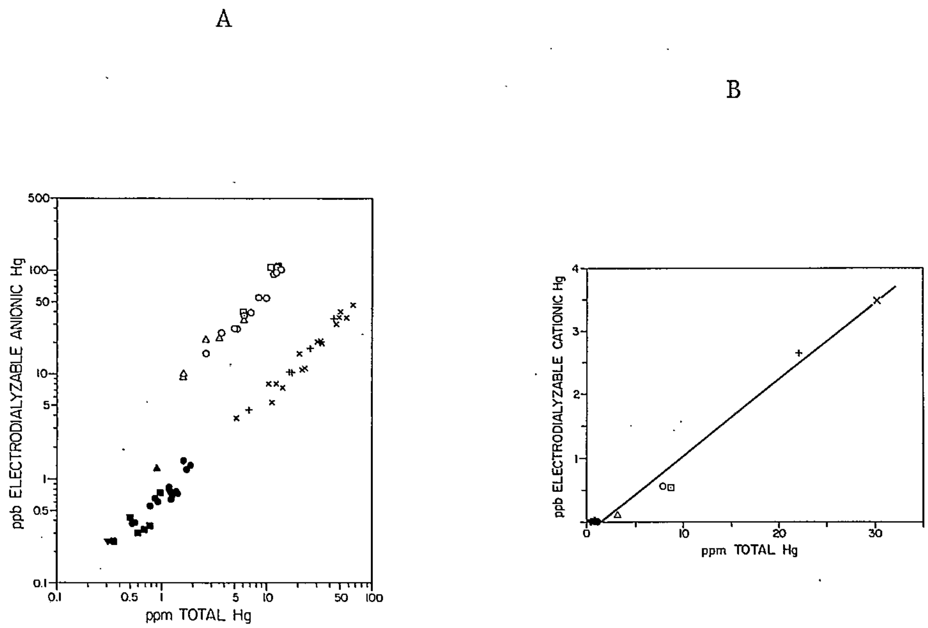


Figure 18. Variation of (A) anionic and (B) cationic electrodialyzable Hg species with total Hg in sediment samples from Wainwright Reservoir (wood chips, X ; clay, ▼), the Wabigoon River upstream from the reservoir (wood chips, + ; clay ▲), Clay Lake (east basin, ○ ; west basin, □), the Wabigoon River downstream from Clay Lake (△), and Ball Lake (south basin, ● ; north basin, ■). Note: The points in Figure 18B represent mean values only.

the Reed plant has been transported beyond Clay Lake. This second possibility, however, is unlikely: It conflicts with the evidence illustrated in Figure 2, as well as with data from cores demonstrating recent Hg contamination of sediments far downstream from Clay Lake (Parks, 1976).

The data for electrodialyzable anionic Hg complexes gave an altogether different pattern of variation (Fig. 18A). The Ball Lake mud samples and sediments from behind Wainwright dam form a single well-defined trend; but Clay Lake mud and river mud collected downstream from the lake form a parallel trend displaced upward, indicating that an anomalously high proportion of the Hg is in the form of low molecular-weight (dialyzable) negatively charged complexes. On the other hand, the Hg in Clay Lake mud and nearby river mud is, if anything, slightly deficient in electrodialyzable cationic forms (Fig. 18B). These plots may be relevant to the problem of understanding the factors that limit the production of CH_3Hg^+, inasmuch as Clay Lake mud was found to have a lower average CH_3Hg^+ content than either Ball Lake mud or the Wainwright/Wabigoon wood-chip sediments deposited near Dryden. The data suggest the as yet unproven possibility that anomalously high concentrations of negatively charged dialyzable complexing agents tend to interfere with methylation in Clay Lake sediments by forming stable complexes with Hg. The nature of the complexing agents is still under investigation, but the anomalously high S^{2-} content of Clay Lake mud supports the suspicion that they might include soluble sulfides.

Solubilization of the more strongly chemisorbed or complexed Hg fractions associated with sedimentary organic matter and oxides by extraction with NaOH, $NH_2OH \cdot HCl/HNO_3$, and benzene/methanol showed a less pronounced, less clear-cut disparity between Clay Lake and Ball Lake than did the milder methods of extraction. In each case, some, if not all, of the samples from one lake conformed to the trend produced by the other lake (e.g. Fig. 19). Therefore, the major differences between Clay Lake and Ball Lake mainly involve the more loosely sorbed, exchangeable forms of Hg -- i.e. the Hg species that are most likely to be available for

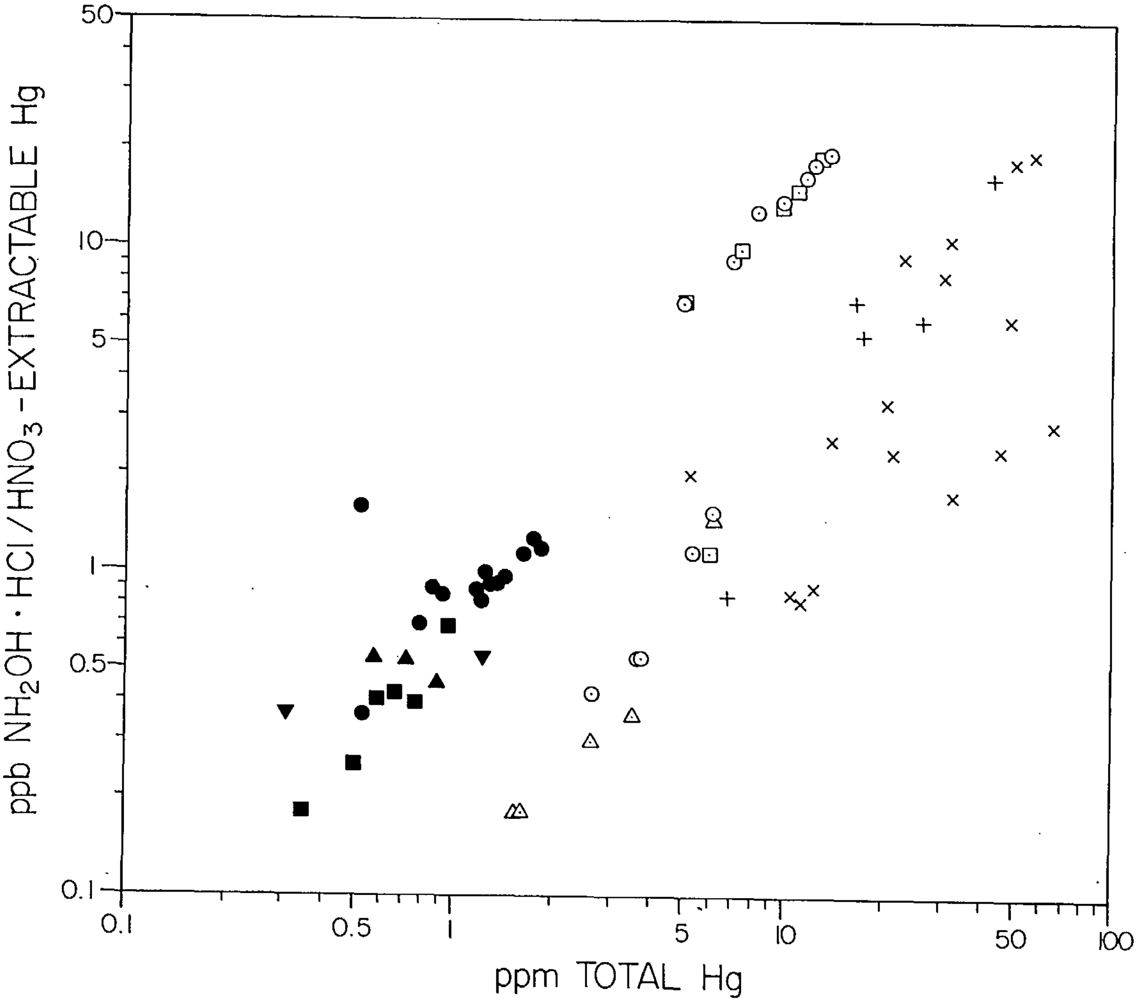


Figure 19. Variation of $NH_2OH \cdot HCl/HNO_3$-extractable Hg with total Hg in sediment samples from Wainwright Reservoir (wood chips, X ; clay ▼), the Wabigoon River upstream from the reservoir (wood chips, + ; clay, ▲), Clay Lake (east basin, ○ ; west basin, □), the Wabigoon River downstream from Clay Lake (△), and Ball Lake (south basin, ● ; north basin, ■).

methylation and bio-accumulation -- rather than the more strongly fixed forms.

In this sense, the Hg dissolved or dispersed in the pore water of the sediments behaved like the strongly bound Hg. The mean Hg concentrations of interstitial water from different depositional basins correlated almost perfectly with the mean total Hg content of the sediment (Fig. 20), and there is no discontinuity between Clay Lake and Ball Lake. Therefore, interstitial Hg, like total Hg, may to a large extent be irrelevant to the problem of Hg methylation and bio-availability, possibly because it is in the form of stable complexes.

The downstream gradient in the binding characteristics of Hg may have important implications for the biogeochemistry of CH_3Hg^+. Thus, the bottom sediments of Clay Lake, Ball Lake, and the stretch of river connecting the two lakes gave a strong positive correlation between mean CH_3Hg^+ content and the mean ratio of Ca acetate-extractable Hg to $NH_2OH{\cdot}HCl/HNO_3$-extractable Hg (Fig. 21). This relationship suggests two hypothetical explanations for the downstream increase in the proportion of CH_3Hg^+ to total Hg: (1) The sediments further away from Dryden have a higher sorption capacity for CH_3Hg^+, possibly because they are finer-grained and have a larger number of cation exchange sites; and (2) the process of methylation is more efficient in the natural sediments, because a higher proportion of the Hg bound to these sediments is readily solubilized. Considering that the absolute concentration of Ca acetate-soluble Hg was consistently one or two orders of magnitude less than the concentration of Hg in the form of CH_3Hg^+ (Table 4), the correlation cannot be ascribed to displacement of adsorbed CH_3Hg^+ from the exchange sites by the Ca acetate treatment. A more plausible alternative interpretation would be that the exchange sites play a catalytic role whereby the rate of CH_3Hg^+ synthesis is enhanced -- perhaps by an intermediate reaction involving adsorption of Hg^{2+} ions.

Now let us briefly compare the relative quantities of Hg solubilized by the different extraction procedures, using mean

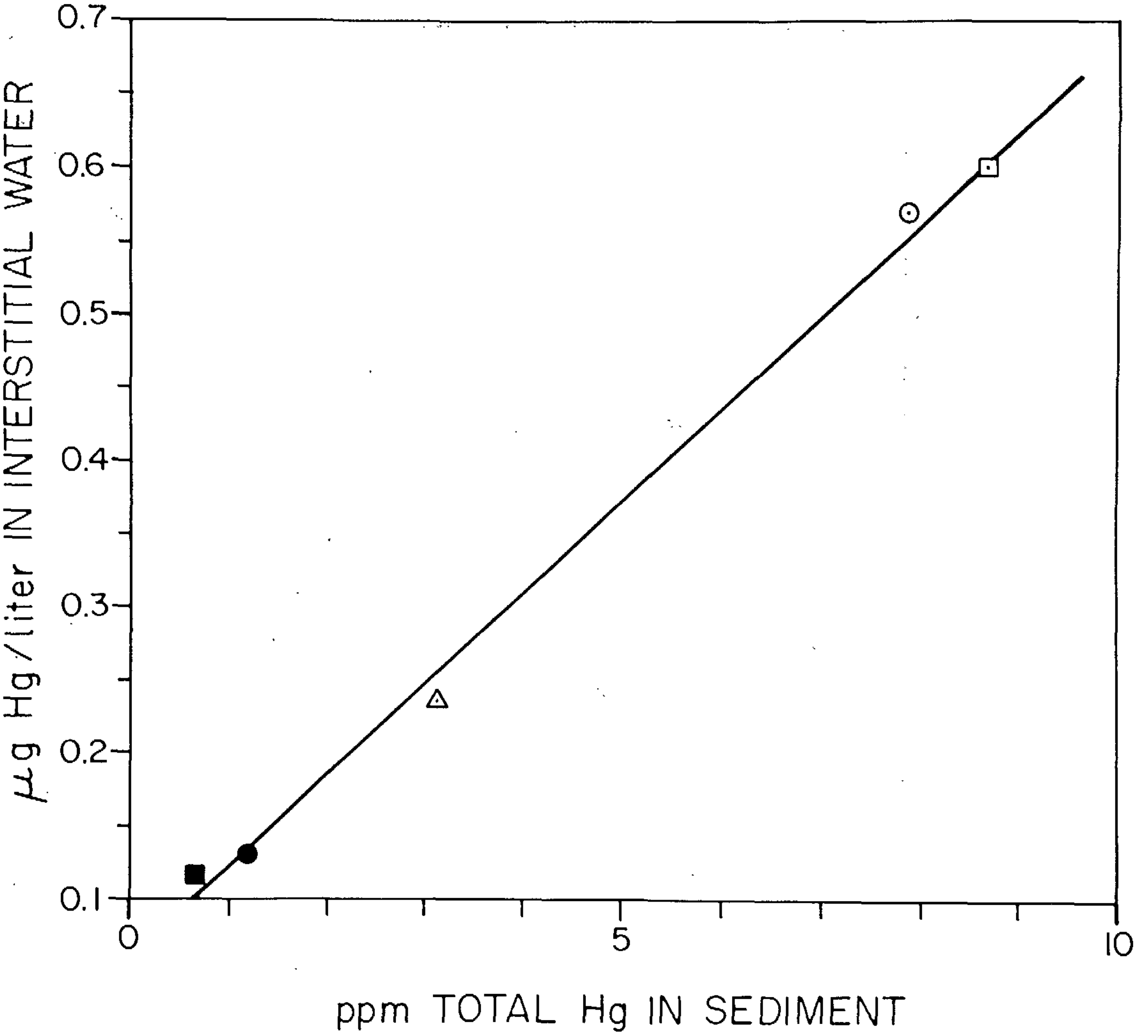


Figure 20. Relationship between mean Hg content of interstitial water and mean Hg content of sediment in Clay Lake (east basin, ○ ; west basin, □), the Wabigoon River downstream from Clay Lake (△), and Ball Lake (south basin, ● ; north basin, ■).

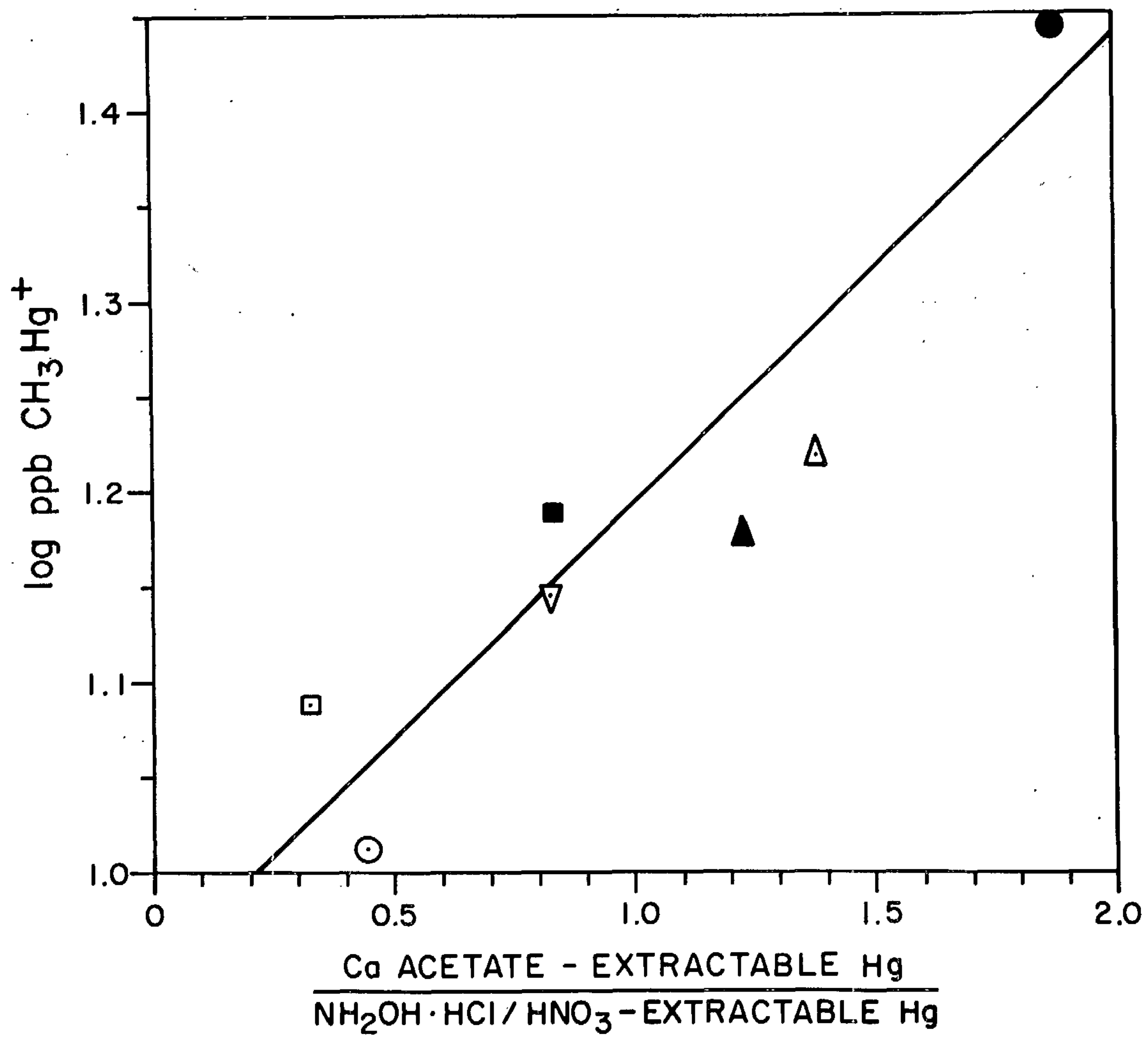


Figure 21. Relationship between mean CH_3Hg^+ concentration and the mean ratio of Ca acetate-extractable Hg to $NH_2OH \cdot HCl/HNO_3$-extractable Hg in bottom sediments of Clay Lake (east basin, ○ ; west basin, □), the Wabigoon River downstream from Clay Lake (△), and Ball Lake (south basin, ● ; north basin, ■) ($r = 0.917$; $p = 0.001$-0.01).

Table 4. Mean concentrations of extractable Hg species in bottom sediments from different regions of the Wabigoon River system.

	ngm Hg in fraction per gm of sediment											
						Electrodialyzable						
Sample material	NH_4 acetate	Ca acetate	Acetic acid	$CaCl_2$	$NH_2OH.$ HCl + HNO_3	Anions	Cations	NaOH	DTPA + $CaCl_2$ + TEA	Benzene/ Methanol	CH_3Hg^+	µgm Total Hg/gm
Wabigoon River cores (upstream from reservoir)												
Wood-chip layer	5.06	1.15	0.775	4.86	7.18	15.5	2.65	17.5	23.3	2.94	15.0	22.1
Clay layer	0.822	.680	0.258	0.480	0.510	0.417	0	5.12	10.8	0.663	1.1	0.729
Wainwright Reservoir cores												
Wood-chip layer	6.02	1.08	0.480	7.21	5.76	19.8	3.49	21.3	16.5	1.51	19.4	30.2
Clay layer	0.231	.563	0.316	0.456	0.288	0.250	0	1.07	10.5	0.879	1.8	0.38
Clay Lake												
east basin	1.96	1.91	1.97	2.21	9.15	53.2	0.57	67.7	0.646	2.17	12.0	7.86
west basin	1.98	1.95	1.99	2.49	10.8	62.1	0.53	80.4	1.21	2.05	12.3	8.68
Wabigoon River downstream from Clay Lake	0.512	0.510	0.296	0.336	0.497	19.4	0.11	19.6	0.502	1.27	16.5	3.12
Ball Lake												
south basin	2.66	1.48	0.501	1.02	0.951	0.780	0	14.1	0.901	0.945	20.3	1.18
north basin	1.60	0.352	0.170	0.360	0.387	0.396	0	4.62	1.25	0.673	15.4	0.637

values for the data from the major depositional environments of the Wabigoon system (Table 4). The NaOH-extractable fraction was invariably one of the most abundant Hg fractions, being as much as one or two orders of magnitude larger than the Hg fractions extracted by neutral salts, acetic acid, $NH_2OH \cdot HCl/HNO_3$, or benzene/methanol. CH_3Hg^+, too, was one of the more abundant extractable forms of Hg in most sediments. The levels of electrodialyzable anionic Hg are comparable to those of NaOH-extractable Hg (though somewhat lower) in the case of the Clay Lake muds and wood-chip sediments above Wainwright dam; but this fraction was one or two orders of magnitude lower in the case of the Ball Lake muds and the clay underlying the wood-chip layer. Anionic forms of electrodialyzable Hg greatly outweighed the cationic forms. Finally, the concentrations of DTPA/$CaCl_2$/TEA-extractable Hg were considerably greater than or nearly equal to the NaOH-extractable Hg in the case of sediments from behind the dam, but were one or two orders of magnitude less for the sediments from Clay Lake, Ball Lake, and the intervening stretch of river.

These results are provisionally interpreted as follows. The extractable Hg is largely in the form of stable complexes of humic matter and other organic substances, but the nature of the complexes varies with distance from the source of pollution, doubtless reflecting the gradation from decomposing wood to natural sedimentary organic matter. Near Dryden, Hg is mainly complexed with organic compounds generated during decomposition of wood, and is readily displaced from these complexes by DTPA/$CaCl_2$/TEA; but these reagents are relatively ineffective when competing with the sedimentary complexing agents further downstream. In Ball Lake, the extractable organic complexes are mainly of high molecular weight (non-dialyzable), but further upstream they are mainly of low molecular weight (dialyzable).

(2) Mercury in lake and river water

This topic is treated in much greater detail in the report by Parks et al. Nevertheless, it seemed worthwhile to include some of our preliminary findings, as they complement and, to some extent, confirm the results presented in the other report. Our data are strictly valid only for the few days on which the samples were collected, but they do serve to illustrate some of the processes that affect the movement of CH_3Hg^+ and total Hg through the river system.

In late April, when water levels were rising steadily owing to the spring runoff, the concentration of CH_3Hg^+ in Wabigoon River water between Dryden and Quibell showed a highly significant linear decrease with distance downstream from Reed, Ltd. (Fig. 22A). Conductivity and both dissolved and total organic matter gave similar trends (Fig. 22B). But in May, during the phase of declining water levels, CH_3Hg^+ increased with distance from the Reed plant, and then levelled off (Fig. 22C). Total Hg, however, did not correlate at all with distance from the Reed plant in April, and showed only a weak positive correlation of doubtful significance in May (Fig. 23). Nevertheless, the water samples taken at Quibell in both April and May showed a significant exponential increase in total Hg concentration with increasing discharge of water (Fig. 24A) ($r=0.807$, and $p=0.01-0.02$, for all samples combined; for the bridge [midstream] and gauge-station [near-shore] samples, $r=0.862$ and 0.933 respectively). CH_3Hg^+ showed a comparable but statistically insignificant tendency ($r=0.568$; $p>0.1$) (Fig. 24B). The distribution of CH_3Hg^+ and total Hg concentrations show no evidence of a discontinuity at Wainwright dam, which is about 4.3 km from the Reed plant (Figs. 14-16).

The behavior of the total Hg during the spring flood was probably controlled primarily by the erosion of Hg-contaminated bottom sediments by current action. The greater the current velocity (as represented by discharge), the greater the quantity of particulate Hg brought into suspension (Fig. 24A). The downstream decrease in the total Hg content of the bottom sediment (Table 1) and the dilution of suspended Hg by uncontaminated runoff and tributary water should have tended to cause a downstream decrease in the Hg content of the water; but these effects were evidently more or less counterbalanced by the downstream increase in discharge (Table 5) and concomitant increase in the intensity of bottom scour. Thus, there

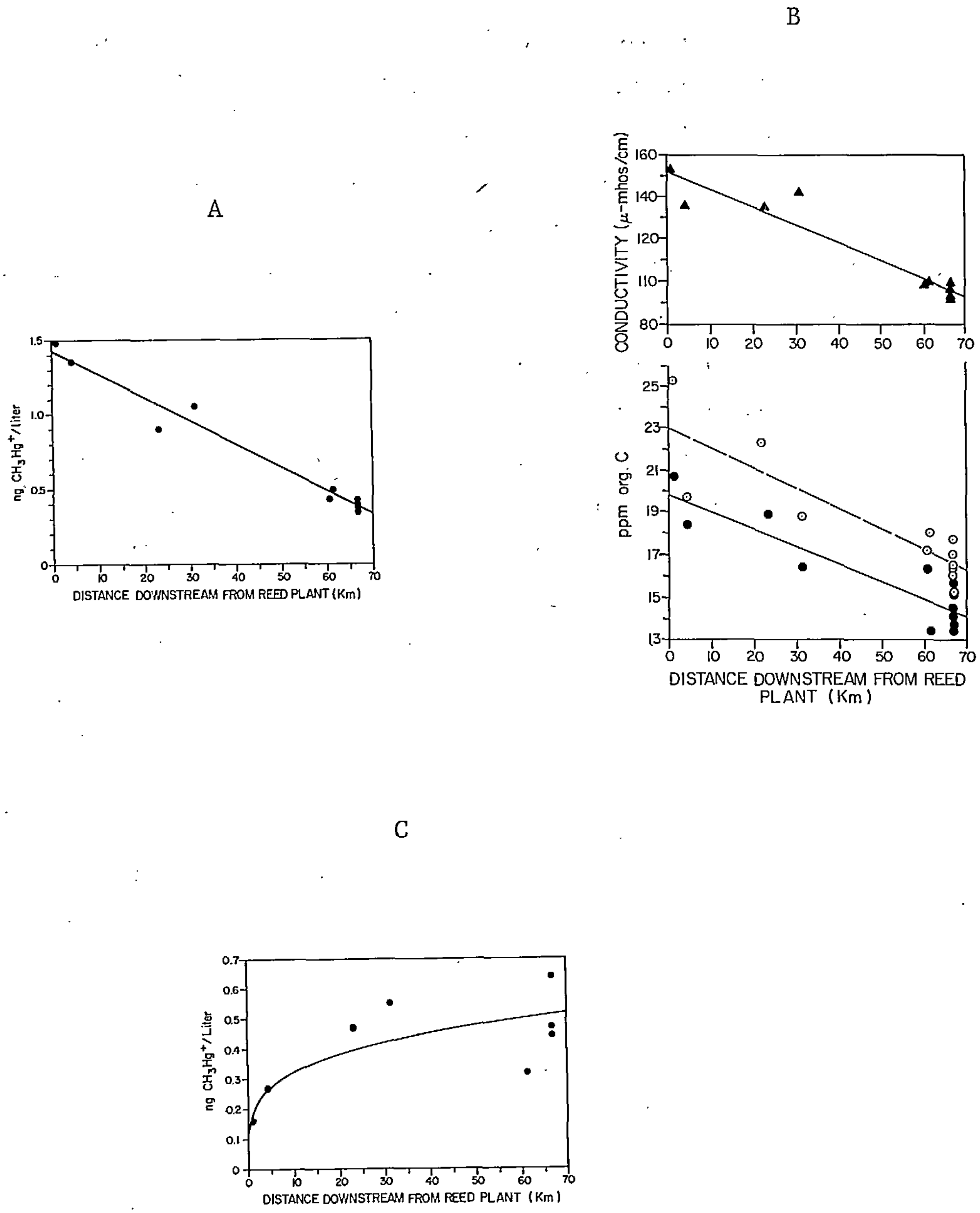


Figure 22. Variation of the (A) CH_3Hg^+ content and (B) conductivity (▲) and dissolved (●) and total (○) organic carbon content of Wabigoon River water in April [prior to peak flow of spring flood], and the (C) CH_3Hg^+ content in the water in May [after peak flow of spring flood] as functions of distance from the plant at Dryden. All correlations are significant at $p < 0.001$ or $p = 0.001-0.01$.

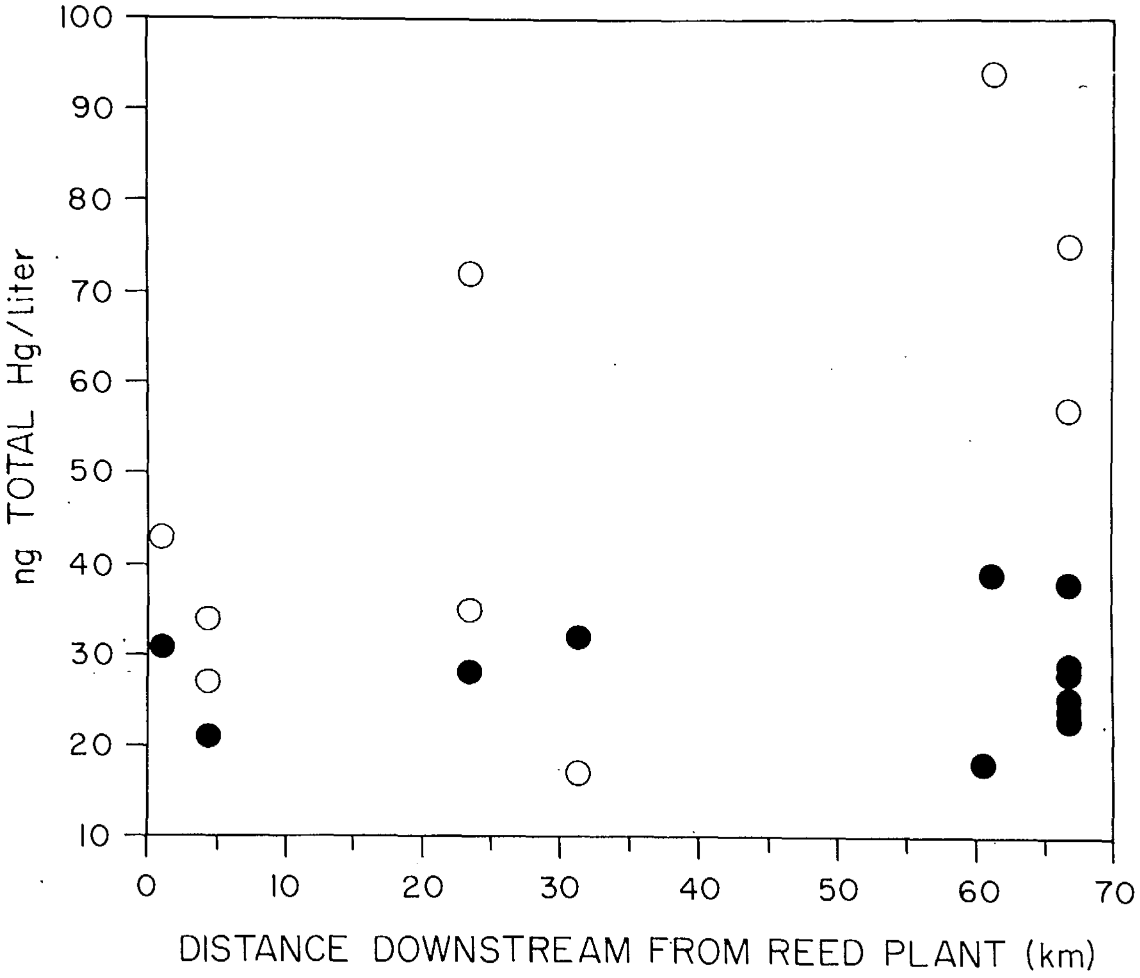


Figure 23. Variation in the total Hg content of Wabigoon River water with distance downstream from the plant at Dryden in April (●) and May (○).

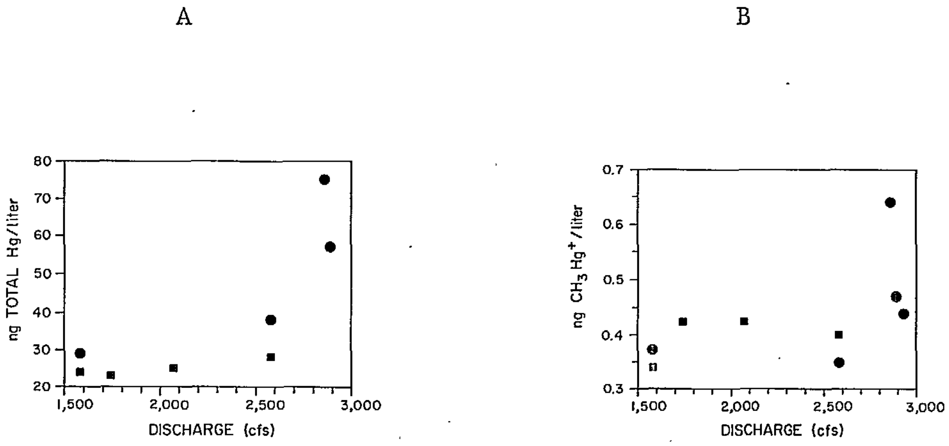


Figure 24. Variation of the (A) total Hg ($r = 0.807$; $p = 0.01-0.02$) and (B) CH_3Hg^+ ($r = 0.568$; $p > 0.1$) concentrations of Wabigoon River water as functions of discharge at the middle of the bridge (●) and at the near-shore gauge station (■) at Quibell during the spring flood. For both plots, a semi-log function gave the strongest correlation.

Table 5. Discharge rates and CH_3Hg^+ and total Hg concentrations and loadings for Wabigoon River water at different sampling sites between the Reed plant and Quibell in April and May.

	April 21-24					May 9-11				
Distance from Reed plant (km)	CH_3Hg^+ (ng/L)	Total Hg (ng/L)	Discharge (cfs)	CH_3Hg^+ loading (μg/sec)	Total Hg loading (mg/sec)	CH_3Hg^+ (ng/L)	Total Hg (ng/L)	Discharge (cfs)	CH_3Hg^+ loading (μg/sec)	Total Hg loading (mg/sec)
1.0	1.48	31	550	23.1	0.48	0.16	43	500	2.2	0.61
4.25	1.35	21	600	22.9	0.36	0.26	34	550	4.1	0.53
						0.27	27		4.2	0.42
23.25	0.900	28	900	22.9	0.71	0.47	35	1,200	16	1.2
						0.46	72		16	2.4
31.25	1.05	32	1,200	35.7	1.1	0.55	17	1,750	27	0.84
60.6	0.425	18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
61.25	0.49	39	1,550	21	1.7	0.32	94	2,780	25	7.4
66.75 (Quibell, at bridge)	0.375	29	1,580	17	1.3	0.44	>920	2,930	36.5	>76
	0.35	38	2,580	26	2.8	0.47	57	2,890	38	4.7
						0.64	75	2,860	52	6.1
66.75 (Quibell, at gauge station)	0.34	24	1,580	15	1.1	-	-	-	-	-
	0.425	23	1,740	21	1.1	-	-	-	-	-
	0.425	25	2,070	25	1.5	-	-	-	-	-
	0.40	28	2,580	29	2.0	-	-	-	-	-

was little or no net change in the Hg concentration of the water with distance from the source of pollution (Fig. 23).

On the other hand, variations in the CH_3Hg^+ concentrations of the water can be ascribed only partially to erosion of CH_3Hg^+-enriched surface sediments (Fig. 24B). Other mechanisms, such as fluctuations in the CH_3Hg^+ content of the sediment or in the rate of CH_3Hg^+ production, may also be suspected. The downstream decline in CH_3Hg^+ concentrations during the phase of rising water levels (Fig. 22A) suggests the release of a relatively large mass of CH_3Hg^+ into the water near Dryden followed by progressive dilution of the CH_3Hg^+ during its downstream journey owing to the influx of uncontaminated water from runoff and tributaries. During the stage of declining water levels (Fig. 22C) there seems to have been a decline in the release of CH_3Hg^+ near Dryden, the higher levels further downstream representing, perhaps, the "tail end" of the large mass of CH_3Hg^+ generated earlier near Dryden. The relatively high CH_3Hg^+ levels observed in the water near Dryden early in the spring flood episode could have been due to erosion of the loosely packed, CH_3Hg^+-enriched surface zone of the woodchip sediments, resulting in rapid release of CH_3Hg^+ which had accumulated there during the winter months owing to bacterial activity. By the time the spring flood had passed its peak, this short-term pulse must have been largely dissipitated. This interpretation is consistent with the fact that CH_3Hg^+, org. C, and conductivity gave similar patterns of variation during the period of rising water levels. The org. C and conductivity probably represent organic matter and interstitial salts displaced from the surface sediments along with the CH_3Hg^+. On the other hand, the weak tendency of total Hg to parallel the downstream increase in CH_3Hg^+ concentration in May (Fig. 23) suggests the possibility that part of the CH_3Hg^+ was generated in the water column upon resuspension of particulate Hg.

The spring-flood results appear to support the conclusion that the Wainwright Reservoir had no marked net effect on the flux of CH_3Hg^+ and total Hg. Over the years, however, the Wainwright dam has trapped a considerable amount of particulate Hg, as will be discussed below.

The spring-flood data also demonstrate that the Wabigoon River can discharge appreciable quantities of CH_3Hg^+ as well as total Hg into Clay Lake (Table 5). The spot-check of CH_3Hg^+ distribution in the water of Clay Lake and Ball Lake in mid-July (Table 6; Fig. 25A) confirmed this observation. In July, CH_3Hg^+ concentrations in surface water decreased progressively from the east end of Clay Lake (near the mouth of the river) to the south basin of Ball Lake, presumably indicating release and downstream transport of CH_3Hg^+ from surface sediments above the inflow to Clay Lake accompanied by progressive attenuation due to dilution and removal processes.

In contrast, CH_3Hg^+ concentrations in deeper waters <u>increased</u> from Clay Lake to Ball Lake, being almost as high in the hypolimnion of Ball Lake as in the Wabigoon River water flowing into the east end of Clay Lake (Table 6; Fig. 25A); this pattern of variation probably reflects the comparable tendency observed in the mean CH_3Hg^+ concentrations of the bottom sediments (Table 1; Fig. 25A).

These data, though preliminary and not necessarily representative of the entire year, are consistent with the rather logical hypothesis that CH_3Hg^+ in the surface waters of Clay Lake and Ball Lake is largely derived (in the summer, at least) from the Wabigoon River upstream from Clay Lake, whereas much of the CH_3Hg^+ which accumulates in the deeper lake waters is generated in the bottom sediments of the lakes.

(3) <u>Mercury in aquatic animals</u>

What is the ecological importance of allochthonous riverborne CH_3Hg^+ discharged into Clay Lake and Ball Lake compared with autochthonous CH_3Hg^+ generated in the bottom sediments of the lakes? Without more information, this crucial question cannot be answered unequivocally. Nonetheless, other workers' estimates of Hg concentrations in fish and crayfish from 1970 to 1977 (Fig. 25B) together with the geochemical data presented here (Fig. 25A) provide some interesting clues. Mean Hg concentrations in different species of pelagic fish (including walleye, pike, cisco, whitefish, and sauger) decreased from Clay Lake to Ball Lake, whereas the mean Hg concentrations of bottom-feeding animals either increased (as in the case of suckers) or showed no significant change (as in the case of crayfish). The decrease

Table 6. CH_3Hg^+ content, pH, and conductivity of Clay Lake and Ball Lake water samples collected in July. Notation: Number of samples: N; Median: M_d; Mean: $\bar{X}$; Standard deviation: Stand. dev.

Sampling site	Total depth of water (m)	Depth of sample (m)	N	ng CH_3Hg^+/L				pH	Conductivity (µmhos/cm)
				M_d	$\bar{X}$	range	Stand. dev.	M_d	M_d
Clay Lake, near mouth of Wabigoon River	1.8	1	3	2.8	2.8	2.6-3.0	0.20	7.30	162
Clay Lake, center of east basin	7.0	1	3	2.3	2.5	2.3-3.0	0.40	7.48	151
		6	3	1.2	1.5	1.0-2.2	0.64	7.50	122
Clay Lake, center of west basin	18.5	1	3	1.6	1.6	1.5-1.8	0.15	7.50	152
		16	3	1.2	1.3	1.0-1.6	0.31	6.73	149
Ball Lake, south basin	32.0	1	3	0.8	0.8	0.7-0.9	0.10	7.57	132
		28	3	2.1	2.2	1.8-2.8	0.51	7.35	129

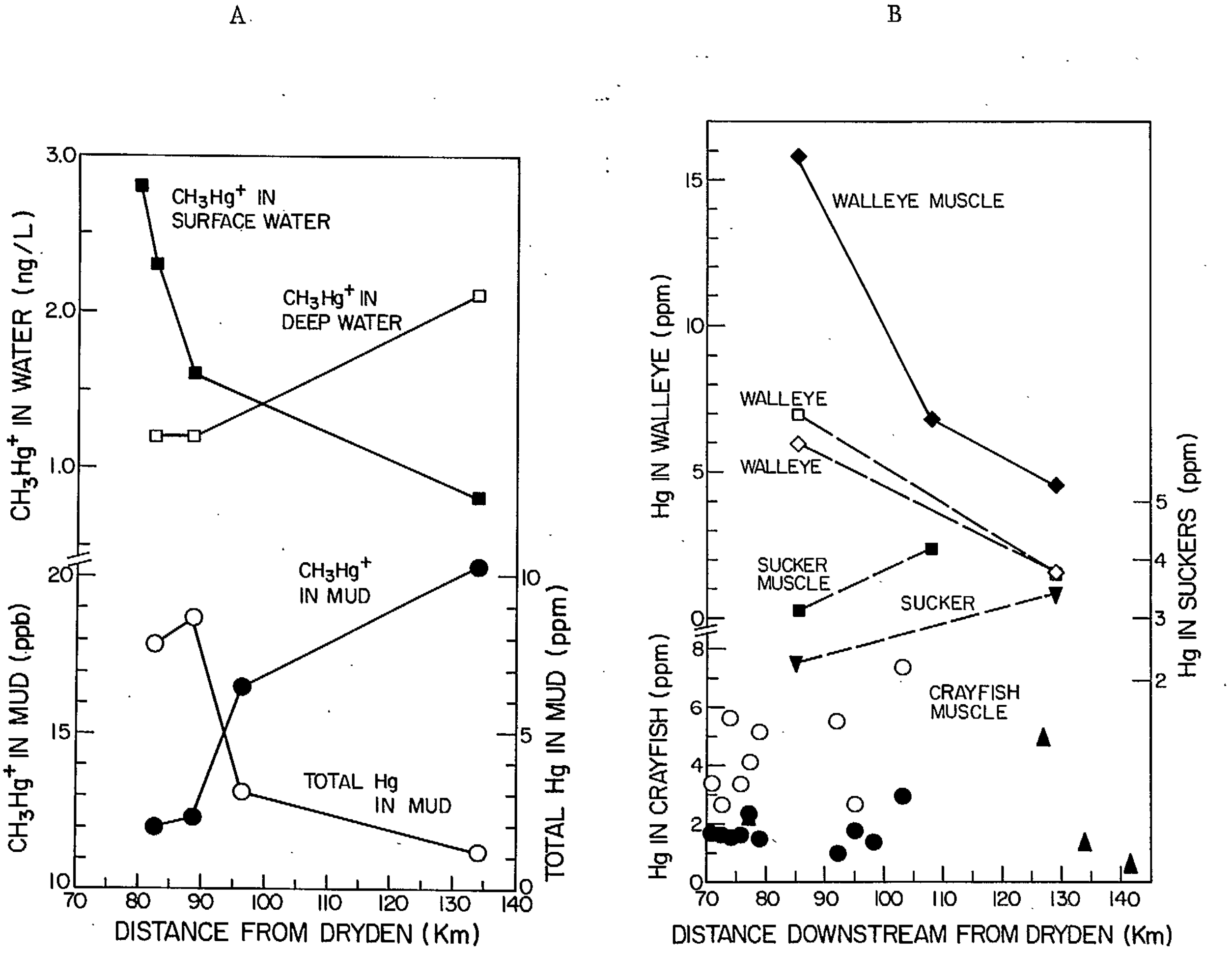


Figure 25. Variation of (A) CH_3Hg^+ and total Hg in water and sediments, and (B) Hg in fish and crayfish, as functions of distance from Dryden. Each point on each graph represents the mean of multiple replicate samples. Sediment and water data came from the present study; fish and crayfish data were furnished by Fimreite and Reynolds (1973), Bishop and Neary (1976), B. P. Neary (unpublished data, personal communication), Armstrong and Hamilton (1973), and G. McRae and A. Hamilton (unpublished data, personal communication).

Symbols in Figure 25B indicate year of sample collection:

Walleye: ◆, 1970; ◇, 1975; □, 1977.

Suckers: ■, 1970; ▼, 1972.

Crayfish: ○, 1971; ●, 1974; ▲, 1976.

in the Hg levels of pelagic species with distance from Dryden continued at least as far downstream as Tetu Lake near the Manitoba border (Fimreite and Reynolds, 1973), although the concentrations remained well above background levels and were too high for human consumption (Bishop and Neary, 1976). Comparison of the observed variations in the composition of the sediments, water, and biota (Fig. 25, A & B) suggests that the Hg contamination of pelagic fish is due primarily to CH_3Hg^+ loadings from the river, while fish and other creatures which feed on the bottom are contaminated to an equal or greater extent by CH_3Hg^+ generated in bottom sediments.

This tentative conclusion, if substantiated, may have an important bearing on the problem of selecting suitable methods for restoring the Wabigoon-English-Winnipeg River system. It implies that removal or immobilization of the mercury in the contaminated riverbed sediments upstream from Clay Lake might bring about a rapid and substantial reduction in the mean mercury levels of pelagic fish throughout the system.

(4) Retention of contaminated sediments by Wainwright dam

Figure 26 shows a longitudinal section of Wainwright Reservoir drawn in accordance with the available data. The thickness of the sediment wedge was computed to be no more than ~3 meters right behind the dam, but Parks (1976) states that these sediments reach a maximum thickness of 12 meters. The mean thickness probably lies between these two extremes, though a reliable estimate of it is lacking. Therefore, the approximate Hg content of the wood-chip layer is best expressed in terms of a probable upper and lower limit.

The total absolute quantity of anthropogenic Hg bound to the river and reservoir sediments between Dryden and Clay Lake is estimated to range from about 1.2 to 3.9 metric tons (the mean value being ~2.6 tons), 80-94% of which is trapped behind Wainwright dam (Table 7). If this estimate is reasonably accurate, and if the total discharge of Hg at Dryden was 9-11 tons, as officially admitted (Armstrong and Hamilton, 1973), then 67-87% of the Hg discharged has been removed to Clay Lake or beyond. However, a more detailed study would be required to confirm this preliminary estimate, which is based

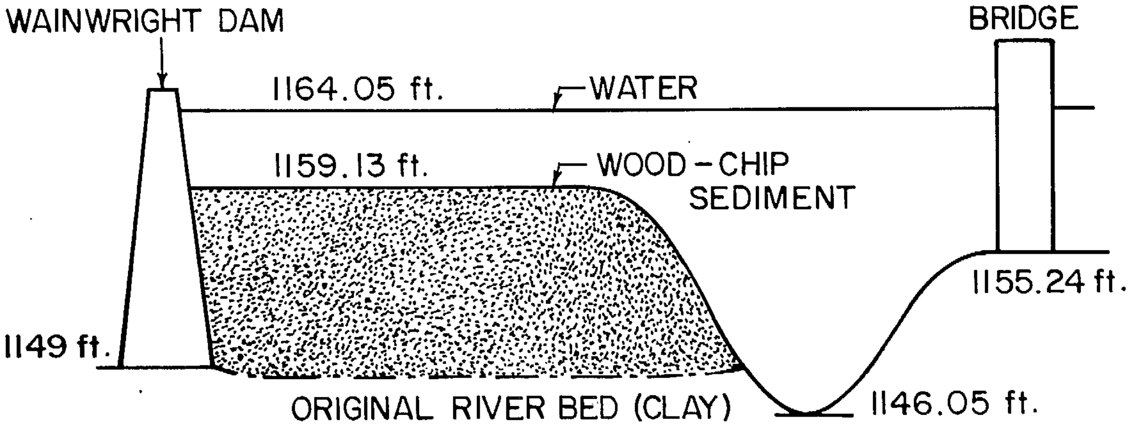


Figure 26. Schematic longitudinal section of Wainwright Reservoir, based on available information.

Table 7. Estimates of the total sedimentary Hg burden of different subdivisions of the Wabigoon River between Dryden and Clay Lake.

Compartment	Total metric tons of Hg
Wabigoon River between Reed plant and Wainwright Reservoir	0.13
Wainwright Reservoir	0.86-3.52
Wabigoon River between Wainwright Reservoir and Clay Lake	0.24

on extrapolation from cores collected near the shore.

(5) Technical note on the determination of total Hg in sediments

Consistently higher total Hg concentrations were recorded for sediment samples digested with HNO_3/H_2SO_4 at 80°C. or 160°C. than for replicate portions of the same samples digested with HNO_3/HCl (Table 8).

For two Clay Lake samples and a sample of Lake Ontario sediment, the results obtained with HNO_3/H_2SO_4 were only 1.27-1.41 times the results obtained with HNO_3/HCl, but for a Ball Lake sample the HNO_3/H_2SO_4 data were 5.60 times as great. This disparity could reflect differences in the chemical species of Hg in the Clay Lake and Ball Lake mud. Further research is planned to check the results.

The results of the experiment suggest that Clay Lake sediments contain 2.7 metric tons of anthropogenic Hg instead of the 2 tons estimated by Armstrong and Hamilton (1973).

Further experiments on analytical methodology are being conducted in collaboration with A. Lutz of the Freshwater Institute, and interlaboratory comparisons are underway.

DISCUSSION: IMPLICATIONS FOR LAKE/RIVER RESTORATION

The results demonstrate that CH_3Hg^+ is currently being generated in the Hg-contaminated surficial sediments of the Wabigoon River and its associated lakes and is being released into the overlying water. The kinetics of these processes evidently depend on environmental variables rather than total Hg supply. The surface waters of the lakes are being contaminated by CH_3Hg^+ and other forms of Hg leached or eroded from bottom sediments in the riverbed between Dryden and Clay Lake and subsequently transported downstream by river water. Hg accumulations in the pelagic fish of the lakes are probably due principally to this riverborne "allochthonous" CH_3Hg^+, whereas bottom-feeding species are affected more strongly, or to an equal extent, by "autochthonous" CH_3Hg^+ generated in local bottom sediments.

Table 8. Total Hg data obtained for replicate sediment samples after wet-ashing by the HNO_3/H_2SO_4 method of Hendzel and Jamieson (1976) and the HNO_3/HCl method of the Dow Chemical Co.

Notation: Mean: $\bar{X}$; Standard deviation: Stand dev.

		ppm Hg					
		HNO_3/H_2SO_4 digestion (Hendzel & Jamieson, 1976)			HNO_3/HCl digestion (Dow Chemical Co.)		
Sample	No. of replicates	$\bar{X}$	range	Stand. dev.	$\bar{X}$	range	Stand. dev.
Clay L. mud (east basin, 1978)	5	7.62	7.24-7.88	0.238	6.02	5.58-6.24	0.259
Clay L. mud (east basin, 1979)	5	3.56	3.47-3.61	0.0541	2.53	2.39-2.59	0.0817
Ball L. mud (south basin, 1978)	5	1.17	1.07-1.31	0.110	0.209	0.123-0.323	0.0855
L. Ontario mud (interlab. quality control sample #22)*	3	1.36	1.28-1.50	0.119	0.987	0.84-1.10	0.133

*Supposedly 1.00 ppm Hg according to Canada Centre for Inland Waters, Burlington, Ontario

The large accumulation of Hg and nutrients in the riverbed upstream from Clay Lake, and the fact that methylation is most intense at the sediment-water interface regardless of total Hg distribution, would seem to imply that contamination of the waters and fish populations of the lakes by allochthonous CH_3Hg^+ and other riverborne Hg species will persist far into the future unless remedial measures are taken.

These conclusions have the following implications for the problem of restoring the Wabigoon-English-Winnipeg River system:

(1) No scheme for lake restoration is likely to succeed unless it includes an efficient procedure for halting the release and downstream transport of CH_3Hg^+ and other forms of Hg from the riverbed between Dryden and Clay Lake.

(2) There are grounds for believing that removal or immobilization of the Hg accumulations in the sediments between Dryden and Clay Lake would be the most effective way to restore the river-lake system -- at least, from the standpoint of reducing Hg levels in the fish species which are of greatest importance to the human communities in the region.

(3) Without implementation of a suitable plan for restoration of the river system, the Hg concentrations in the fish are expected to exceed the accepted level for human consumption for an indefinitely long time.

Ideally, wholesale removal of polluted sediments by dredging the riverbed between Dryden and Clay Lake would probably be the most satisfactory means of dealing with the problem. Dredging and other engineering methods are treated in detail in the reports by Wilkins, and Wilkins and Irwin. If this approach were judged to be impractical owing to excessively high cost and other drawbacks, a possible alternative might be to enhance the Hg-trapping potential of this part of the river by converting it, in effect, into a chain of interconnected settling ponds which could be subjected to chemical treatments for suppression of CH_3Hg^+ production and immobilization of both CH_3Hg^+ and total Hg. One of these settling ponds would be the Wainwright Reservoir, and others could be constructed by damming the river further downstream, near Clay Lake. The chemical treatments could include liming to raise the pH, sulfide treatments, and the use of CH_3Hg^+-adsorbing substances (Muzzarelli and Isolati, 1971; Feick et al., 1972; Jernelöv, 1972; Jackson, 1978). A pilot experiment to test the possible effectiveness of this approach could be performed in Wainwright Reservoir, which is a ready-made potential settling pond of the kind envisioned, and is small enough to be manipulated at a reasonable cost. CH_3Hg^+ and total Hg inputs and outputs would be monitored before and after selected treatments. It should be borne in mind, however, that physical removal of the sediment would probably be more effective, more desirable aesthetically, and perhaps ultimately more economical than endless chemical treatments. Besides, even if chemical treatments in ponds proved to be a practicable method, dredging of sediment accumulations from these ponds might well be required eventually. Thus, physical removal of the Hg would probably be necessary sooner or later for successful restoration of the system.

In large-scale dredging operations of the type envisioned, high costs and disposal of dredge spoil present serious difficulties. Therefore, we examined the possibility of recovering elemental Hg from the dredge spoil and selling it to help defray the cost of dredging and to prevent the Hg from contaminating some other environment after disposal of the spoil. On the basis of the February, 1980, New York market price of \$390 to \$400 (U.S.) per 34.473 Kg "flask" of Hg (Northern Miner, Toronto, personal communication), the Hg in the polluted sediments between Dryden and Clay Lake (Table 7), if quantitatively salvaged, might be expected to yield between \$14,000 and \$45,000 (U.S.). This would doubtless cover only a small fraction of the cost of the dredging operation (not to mention the expense of extracting the Hg); but extraction of the Hg might be worth considering as a technique for detoxifying the dredge spoil before disposing of it so that it would not pose a threat to environments adjacent to the disposal site.

It should be pointed out, too, that removal or immobilization of the Hg upstream from Clay Lake would not solve the pollution problem completely, because the contaminated bottom sediments of the lakes (and the intervening stretches of river) are themselves sources of CH_3Hg^+. Theoretically, it might be possible to reduce the release of CH_3Hg^+ from the bottom sediments of the lakes by suitable physico-chemical treatments. However, there are grounds for doubting whether such treatments would be feasible or sufficiently effective, especially in such a large system, and some of the treatments could have harmful ecological side effects.

In conclusion, we have not been able to find an entirely satisfactory method for restoring the river-lake system, but the most promising option available would seem to be removal of contaminated sediments from the riverbed between the plant at Dryden and the inflow to Clay Lake. The rest of the system could be left alone, and eventually the polluted bottom sediments in the lakes would be covered up by layers of uncontaminated material.

ACKNOWLEDGMENTS

Although most of the technical work was done by R. N. Woychuk (biogeochemical technician, National Water Research Institute, Winnipeg), some chemical analyses were done in the laboratories of A. Lutz and M. Stainton at the Freshwater Institute, Winnipeg, and the amino acid analyses were done by P. Mills (Department of Animal Science, University of Manitoba). L. Cha and R. Hunt also provided technical assistance. In addition, we are grateful to the following: Chemists of the Fisheries and Marine Service and Environmental Protection Service for the use of their analytical equipment; R. McNeely (Water Quality Branch) and M. Mawhinney (Canada Centre for Inland Waters, Burlington, Ontario) for assisting with the field work during the summer; J. E. Slater, I. McLaurin, and others (Water Survey of Canada) for providing current-velocity records for the Wabigoon River as well as other useful facts about the river; John Barr (Ontario Ministry of the Environment) for information about the Wainwright dam and reservoir; B. Lamm for furnishing free transportation to and from Ball Lake; B. P. Neary (Ontario Ministry of the Environment) and G. McRae (Department of Fisheries and Oceans) for providing unpublished data on mercury levels in fish and crayfish, respectively; and D. P. Scott (Department of Fisheries and Oceans) for information on statistical procedures and fish biology. We also wish to thank J. W. Parks, J. W. M. Rudd, and the members of the steering committee for helpful comments on the manuscript.

REFERENCES

Armstrong, F. A. J., 1975, Spectrophotometric determination of sulfide in water: Water Quality Parameters, ASTM STP 573, American Soc. for Testing and Materials, p. 14-19.

Armstrong, F. A. J. and Hamilton, A. L., 1973, Pathways of mercury in a polluted Northwestern Ontario lake: In Singer, P. C. (ed.), Trace Metals and Metal-Organic Interactions in Natural Waters: Ann Arbor Science Publishers, Ann Arbor, Mich., p. 131-156.

Bishop, J. N. and Neary, B. P., 1976, Mercury levels in fish from Northwestern Ontario, 1970-1975: Unpubl. report, Laboratory Services Branch, Ontario Ministry of the Environment.

Fagerström, T. and Jernelöv, A., 1972, Some aspects of the quantitative ecology of mercury: Water Research 6: 1193-1202.

Feick, G., Johanson, E. E., and Yeaple, D. S., 1972, Control of mercury contamination in freshwater sediments: Report no. EPA-R2-72-077, U.S. Environmental Protection Agency.

Fimreite, N. and Reynolds, L. M., 1973, Mercury contamination of fish in Northwestern Ontario: Jour. Wildlife Management 37: 62-68.

Hendzel, M. R. and Jamieson, D. M., 1976, Determination of mercury in fish: Analyt. Chem. 48: 926-928.

Jackson, T. A., 1978, The biogeochemistry of heavy metals in polluted lakes and streams at Flin Flon, Canada, and a proposed method for limiting heavy-metal pollution of natural waters: Environmental Geology 2: 173-189.

Jackson, T. A., 1979, Sources of heavy metal contamination in a river-lake system: Environmental Pollution 18: 131-138.

Jernelöv, A., 1972, Factors in the transformation of mercury to methyl mercury: In Hartung, R. & Dinman, B. D. (ed's.), Environmental Mercury Contamination, Ann Arbor Science Publishers, Ann Arbor, Mich., p. 167-177.

Landner, L., 1971, Biochemical model for the biological methylation of mercury suggested from methylation studies in vivo with Neurospora crassa: Nature 230: 452-454.

Langley, D. G., 1973, Mercury methylation in an aquatic environment: Jour. Water Pollution Control Fed. 45: 44-51.

Muzzarelli, R. A. A. and Isolati, A., 1971, Methyl mercury acetate removal from waters by chromatography on chelating polymers: Water, Air, & Soil Pollution 1: 65-71.

Olson, B. H. and Cooper, R. C., 1976, Comparison of aerobic and anaerobic methylation of mercuric chloride by San Francisco Bay sediments: Water Research 10: 113-116.

Parks, J. W., 1976, Mercury in sediment and water in the Wabigoon-English River system: Unpubl. report, Ontario Ministry of the Environment.

Shin, E. B. and Krenkel, P. A., 1976, Mercury uptake by fish and biomethylation mechanisms: Jour. Water Pollution Control Fed. 48: 473-501.

Uthe, J. F., Solomon, J. and Grift, B., 1972, Rapid semi-micro method for the determination of methyl mercury in fish tissue: Jour. Assoc. Official Analyt. Chemists 55: 583-589.

Vonk, J. W. and Sijpesteijn, A. K., 1973, Studies on the methylation of mercuric chloride by pure cultures of bacteria and dungi: Antonie van Leeuwenhoek 39: 505-513.

Wood, J. M., 1971, Environmental pollution by mercury: In Pitts, J. N., Jr., & Metcalf, R. L. (ed's.), Advances in Environmental Science and Technology, Vol. 2, Wiley-Interscience, Toronto, New York, London, Sydney, p. 39-56.

Wood, J. M., 1974, Biological cycles for toxic elements in the environment: Science 183: 1049-1052.

MECHANISMS OF MOVEMENT OF MERCURY INTO AQUATIC BIOTA AND A PRELIMINARY EXAMINATION OF SOME AMELIORATION PROCEDURES

John W.M. Rudd
Michael A. Turner
Bruce E. Townsend
Alison Swick
Akira Furutani

Department of Fisheries and Oceans
Freshwater Institute
501 University Crescent
Winnipeg, Manitoba
R3T 2N6

TABLE OF CONTENTS

Page

RESULTS AND DISCUSSION

A. The Mechanism Tubes

B. Selenium Experiments

ACKNOWLEDGEMENTS

Principally, we would like to thank Jack Klaverkamp, who was involved in many of the endeavors described below. Perhaps more importantly, his timely support and confidence allowed this project to germinate and be functional when our funding was finally approved.

Our experimental design improved during many useful discussions with F.A.J. Armstrong, M. Giles, A. Hamilton, P. Healey, R. Hesslein, C. Kelly, A. Lutz, K. Patalas, C. Tam and the members of the steering committee R. Allan, T. Brydges, K. Shikaze, D. Dodge, R. Hamilton and G. Mills.

Ray Hesslein was invaluable in his development of the gamma analysis system. Additionally, we appreciated his patience while we learned to operate it. He also volunteered his expertise for the radioisotopic spiking of the tubes.

Mercury and selenium analytical support was provided by Andy Lutz, Chris Tam and their co-workers. Mike Stainton, Mike Capel and Ron Schade provided nutrient analyses and sediment core analyses. Also M. Stainton and C. Tam helped to devise some methodology for the mercury methylation bioassay.

Many people provided hard work and skill during tube construction and construction of fish and crayfish cages. We thank P. Campbell, R. Corbett, D. Duncan, M. Giles, M. Gordon, R. Hamilton, Marilyn and Richard Petersen for their assistance.

M. Gordon provided much needed good humour during a period of hard work and tension.

The people of Quibell made us welcome and tolerated our city ways in a country setting. Gordon Clark was invaluable in helping us select, acquire and handle test organisms suitable for Clay Lake. Mr. Cole kindly allowed us access to his beach property for tube construction and storage. The staff of North Star Camps - especially Eritt Gittings and Ed Quint - facilitated our access to Clay Lake. And for enabling us literally to gain an overview of the system and its problems, we thank Barney Lamm who provided aircraft support.

Our thanks to J. Parks, D. Hollinger and P. Moore, members of the Ontario Ministry of the Environment, for their co-operation and assistance during the year.

On very short notice, F.A.J. Armstrong kindly provided a constructive criticism which notably improved this report.

This project was supported by the Federal and Ontario Governments through the Canada Water Act.

TENTATIVE CONCLUSIONS

Extrapolations of the conclusions obtained from our tube experiments must be made with caution since our data suggest that enclosing a portion of Clay Lake alters the enclosed aquatic ecosystem to some degree. However, the tubes were fully functional ecosystems and they were similar to Clay Lake in many respects. For these reasons and because the total and methyl mercury budgets for the lake are available we feel justified in making careful extrapolations of our conclusions regarding general processes. The conclusions are as follows:

1) Consideration of data from the mechanism tubes and from the budget work indicates that amelioration methods such as ploughing, dredging, covering of sediments with clean clay and sulphate addition which are dependent upon the sediments being the major mercury source, may be largely ineffective. This is because Clay Lake is presently receiving substantial total and methyl mercury loading from the Wabigoon River and because this mercury seems to be readily available for methylation and bioaccumulation from the water and surface floc sediments.

2) Results obtained from the herbicide tube can be interpreted as similar to a test of nutrient removal as an amelioration method. This tube treatment reduced the rate of ^{203}Hg bioaccumulation. However, removal of nutrients at Dryden could also reduce the rate of fish growth in Clay Lake. This could be detrimental to both sport and commercial fisheries. Also, lower fish growth would necessitate longer exposure periods to produce an equivalent sized fish. If this were so mercury concentrations in fish of comparable size might not be substantially reduced. In addition, even if nutrient removal at Dryden were economically feasible natural nutrient loading and possible light limitation in Clay Lake could nullify what would be only a partial nutrient removal effect. For these reasons nutrient removal is not likely to work as a mercury amelioration method.

3) Removal of total and methyl mercury from a point source (ie. Reed) or from the Wabigoon River water before it enters Clay Lake may be a feasible amelioration approach since new total and methyl mercury presently entering the lake is the cause of the present mercury problem. "Older" mercury deeper in the lake sediments is probably not now contributing importantly to the problem.

4) Our preliminary selenium addition results suggest that selenium could reduce the mercury problem in the system in two ways. Firstly, enhanced bioaccumulation of selenium could detoxify mercury by reducing the Hg:Se ratio in fish muscle. Secondly, the addition of selenium to the system could reduce the rates of mercury bioaccumulation. Selenium would be relatively simple and inexpensive to add to the system at a point source near Dryden. Future research is needed to verify and examine possible amelioration effects of lower selenium concentrations. At the present time toxicity of selenium in aquatic ecosystems is almost unknown. Our preliminary results suggest that aquatic toxicity could be controlled by careful application rates that would keep concentrations below established drinking water standards.

5) The most practical amelioration approach may be to carry out a combination of two amelioration procedures. At this point the two most likely candidates may be removal of point source discharges of mercury to the system followed by a gradual increase of selenium concentrations in the system by careful addition of selenium.

INTRODUCTION

Research into the mercury contamination of the English-Wabigoon system by the Fisheries and Oceans group began late in the summer of 1977. At that time work was primarily concerned with preliminary examination of methodologies for large in situ enclosure experiments and development of sampling and chemical methods to obtain total and methyl mercury budgets for Clay Lake.

Sampling of Clay Lake to obtain total and methyl mercury budgets began before ice-out of 1978. This budget work was an essential part of the Freshwater Institute program since these data would be necessary to properly interpret the results of the enclosure experiments. The Freshwater Institute group continued this sampling through 1978 and 1979. Since August 1978 sampling of Clay Lake has been carried out jointly with the OME group. For the sake of clarity of data presentation all of the total and methyl mercury data are presented in the OME section of this report. These data will however be used in this section for interpretation of the enclosure experiments.

In addition to the whole lake work several enclosure experiments were carried out during the summer of 1978. For two reasons these experiments were conducted mainly with mercury and selenium isotopes: 1) the use of isotopes provided much greater sensitivity enabling the effects of the experimental treatments to be observed during the course of the experiments. 2) The simultaneous addition of isotopes and the beginning of enclosure treatments provided a definite time zero for the measurement of the treatment effects.

The enclosure experiments had two general purposes: 1) to examine some of the mechanisms of movement of mercury into aquatic biota and 2) to field test some of the proposed amelioration procedures. Research on mechanisms of mercury movement was needed before possible remedies could be intelligently designed and evaluated. It has been generally accepted but never verified in the field that sediments are the primary source of mercury bioaccumulation in contaminated aquatic systems. However there is some evidence that newly deposited sediment surface floc and the water itself or suspended matter might be important contributors of mercury to the biota (Hamilton 1972; Armstrong and Scott 1979). The hypothesis for our mechanism experiments was that mercury which had recently entered the lake and was presently in the water column or newly deposited surface floc sediments would be mainly responsible for the present elevated mercury concentration of Clay Lake biota. The large majority of mercury buried a few centimeters deep in the sediments of the lake would be essentially out of circulation. If this were so, many of the suggested amelioration methods would be ineffective.

The mechanism experiments were performed in several large enclosures in Clay Lake. One enclosure had a water-tight bottom which prevented sediment-water contact. This experiment was designed to evaluate the importance of the water column and surface floc sediment as a pathway of movement of mercury into aquatic biota. Rates of bioaccumulation of radiolabelled mercury by fish and crayfish in the enclosure with a bottom were compared to control enclosures which contained both Clay Lake water and sediments. An aquatic herbicide was added to another enclosure which was sealed to the sediments. This experiment was also designed to determine the importance of the water column and recently deposited surface floc sediments for the mobilization of radiolabelled mercury into biota. The herbicide was intended to reduce the rates of input of new photosynthetically fixed carbon into the water column and surface floc compartments. The deeper anoxic clay sediments metabolizing "older carbon" could not be affected by this treatment. The relative importance of the deeper anoxic clay sediments was examined in another enclosure in which the water column sulphate concentration was increased. This treatment was designed to affect the amount of radiolabelled mercury sequestered as mercuric sulphide in the deeper anoxic sediments.

Some of the mechanism experiments can also be interpreted as field tests of possible amelioration procedures. For instance, the addition of sulphate to one enclosure simulates the possible beneficial effect of sulphate or sulphide addition to the system. The herbicide treatment, which decreased primary productivity, simulates nutrient removal and the effects this would have on the aquatic ecosystem and on mercury bioaccumulation.

In addition to the above experiments we also carried out a clay siltation experiment which was required by the agreement. The experiment was performed in enclosures similar to the other enclosure experiments. In this case the mercury contaminated Clay Lake sediments were sealed by two thicknesses of clean clay to retard the movement of mercury into fish which were used as integrators for the experiment.

If the results of the mechanism experiments and mercury budget work indicate that incoming mercury is presently an important contributor of mercury to aquatic biota of the lake, then many of the previously suggested amelioration methods such as plowing, siltation of clean clay or dredging will be ineffective since they are dependent on the "deep" sediments being a major source of mercury. One possible amelioration procedure that circumvents the problems of the other proposed methods is the addition of selenium to the system. Selenium has been shown to reduce the toxicity of mercury and methyl mercury administered to mice, rats, quail, (e.g. Ganther _et_ _al_.1972, Sumino _et_ _al_. 1977, Potter and Matrone 1973). The presence of approximately equimolar concentrations of mercury and selenium in swordfish and tuna have been shown to have a marked beneficial effect in the reduction of lethal and neurotoxic effects of mercury compounds. This work is reviewed by NRC (1978). During the summer of 1978 we did enclosure experiments to investigate the efficacy of Se as a mercury ameliorating agent. Two hypotheses were tested: 1) that the Hg:Se ratio in freshwater aquatic biota could be favorably adjusted by addition of selenium to the system; 2) that the addition of selenium would reduce the ratio of bioconcentration of mercury by aquatic biota. If either or both of these hypotheses are substantiated cautious use of selenium may be an acceptable antidote for this and other mercury pollution problems.

METHODS AND MATERIALS

Tube construction

The experiments were conducted in 10 meter diameter cross-laminated polyethylene enclosures (tubes) (Schindler et al., 1977), which were emplaced in a sheltered bay of an island in Clay Lake, Ontario. Modifications of the tube design for this work included strengthening the frame of the tube ring and providing additional flotation to help withstand the anticipated severe wave action. The bottom of five of the tubes were sealed into the grey clay sediments of the experimental bay at a depth of approximately 2 meters. The remaining tube (the bottom-sealed tube) had a water tight cross-laminated polyethylene bottom which eliminated sediment water contact.

Tube additions

Tube leakage was monitored throughout the experiments by adding NaCl to double the natural sodium concentration inside the tubes and following sodium concentration. No tube leakage was detected. The clay sediments below the tubes contained approximately 2 mg/Kg mercury to a depth of approximately 5 cm. No stable mercury was added during these experiments.

Approximately 5 mCi $^{203}Hg(NO_3)_2$ and 2 mCi $Na_2{}^{75}SeO_3$ were added by subsurface injection into the wake of an electric outboard motor in each tube to ensure that the label was quickly mixed into the tube water column. Two of the tubes were controls and received no other chemical additions. The bottom-sealed tube received weekly additions of nitrogen and phosphorus to replace nutrient regeneration from the sediments. The N and P fertilization rate was halved 30 days after spike day to reduce primary productivity to the level of the other tubes. The sulphate tube, received two additions of Na_2SO_4. The first increased sulphate concentrations from 10 to 46 mg $SO_4^=$/L two days before the isotope spike. The second increased $SO_4^=$ concentration to 77.5 mg/L 32 days after spike day. The herbicide tube received periodic herbicide additions to control phytoplankton and periphyton primary productivity. Sufficient stable Na_2SeO_3 was added to another tube to increase the selenium concentration in the water column from undetectable concentrations (0.2 ug Se/L) to 0.1 mg Se/L. Chemical additions were carried out in the same manner as described for radioisotope additions. A summary and schedule of tube additions is given in Table 1.

TABLE 1. Chronology of major tube events

Date	Days After Isotope Addition	Event
Jul. 10-12	-3 to -4	Tubes sealed to sediment; and bottom-sealed tube filled.
Jul. 12	-3	Velpar ® herbicide added. Terbutryne ® was added on Aug. 8, and Sept. 11.
Jul. 13	-2	Na_2SO_4 added to sulphate tube
Jul. 13	-2	NaCl added to all tubes.
Jul. 15	0	$Na_2 SeO_3$ and $Na_2\ {}^{75}SeO_3$ added to the selenium tube.
Jul. 15	0	$Na_2\ {}^{75}SeO_3\ {}^{203}Hg\ (NO_3)_2\ {}^{65}ZnCl_2$ added to all tubes.
Jul. 18	3	Batch 1 pearl dace added (free and caged) to all tubes.
Jul. 31	16	Caged crayfish added to all tubes.
Aug. 6	22	Large white sucker removed from Control 2.
Aug. 16	32	Second Na_2SO_4 addition to the sulphate tube.
Aug. 22	38	Na_2SeO_3 added to increase tube C-2 to 1.0 mg/l Se.
Aug. 23	39	Batch 2 pearl dace (free and caged) added to all tubes.
Sept. 11-14	58-60	end of experiment.

Radioactive Sample Analyses

One liter samples integrated through the water column were obtained for radioisotopic analyses and returned to the field lab in linear polyethylene containers. Labels associated with particulate matter were removed by filtering through GFC glass fiber filters followed by passage through 0.45 µ Millipore ® membrane filters. Some very fine clay is known to have passed through the 0.45 µ filters. However, these fine particles were operationally defined as "dissolved" since they probably remain suspended by Brownian motion. Partitioning of the labels within the filtrate was assayed according to the method of Hesslein et al. (1979). The filtrate was passed through columns of Fisher activated coconut charcoal, (50-200 mesh) followed by an anion exchange resin (Bio Rad) and finally a cation exchange resin (Bio Rad). These columns were intended to remove mercury and selenium associated with organic material or remove mercury and selenium present as negatively or positively charged material. Since it was known that a significant fraction of the mercury would be unassociated with any of the above fractions, the extract was hot digested with potassium persulphate and sulphuric acid. The mercuric ion was then precipitated as HgS.

The various fractions of the water samples were assayed for ^{203}Hg and ^{75}Se content by gamma spectroscopy using a germanium-lithium detector (Ortec) connected to a computer based Ultima II multichannel analyzer (Ino-tech). The filters, charcoal, resins and precipitate were counted in small petri dishes (50 mm diameter, 9 mm height) which provided an ideal counting geometry (Hesslein et al., 1979).

The main test organisms for these experiments were adult pearl dace (Semotilus margarita) from a non mercury-polluted head water lake. They were released into tubes, in two batches. Batch 1 was introduced into the tube three days after the ^{203}Hg spike. After approximately four weeks those remaining from batch 1 were removed. Batch 2 fish were put in one week later. Stocking density of the fish was about 50 Kg/Hectare to ensure that ample natural food would be present in the tubes. Whole body isotope content of the pearl dace was assayed by cutting each fish posterior to the anus and the operculum enabling entire fish to be counted in a petri dish. The fish were frozen within an hour of capture and remained frozen throughout the counting period. Skeletal muscle was then removed from the dace while they were frozen and counted in small petri dishes. It was unnecessary to correct the pearl dace data for growth since the dace were adult fish and growth was negligible during the period of the experiments.

Crayfish (Orconectes virilis) were captured in Clay Lake and were kept in individual wire mesh cages which were set on the sediments of the tubes until sampling. Crayfish samples were handled in a similar manner to those of pearl dace except that the abdominal muscle was removed and counted separately from the remainder of the carcass. The two counts were then combined to yield an estimate of the whole body count rate.

All radioactive samples were corrected for isotopic decay by normalizing the counts to spike day. ^{203}Mercury and ^{75}Se were detected at 280 and 135 KeV, respectively. ^{75}Se interference with ^{203}Hg at 280 KeV was corrected for using the known relationship between the 135 and 280 ^{75}Se KeV peaks.

Primary production pontential in the water column of the tubes was estimated according to the $^{14}HCO_3^-$ incubator method of Fee (1973).

Sediment sulphide concentrations were analyzed according to the acid extraction method of Kolthoff and Sandell (1952).

RESULTS AND DISCUSSION

A. THE MECHANISM TUBES

Results

Geochemistry of $^{203-}$mercury

Radiolabelled mercury decreased exponentially in the water column in all the tubes (Figure 1). Half times of disappearance for the first and second control tubes, and the sulphur and herbicide tubes were 18, 20, 16 and 16 days respectively. The bottom-sealed tube, was the only treatment which affected the rate of movement of ^{203}Hg from the water column. In this the rate was approximately half of that of the other tubes (Figure 1).

Partitioning of the label into particulate, charcoal, cation and anion fractions was not significantly affected by any of the tube treatments. An example is shown for a control tube in Figure 2. The label moved into these compartments very quickly after its addition to the tube and remained there in about the same proportion for the duration of the experiment even though the total quantity of label in the water column was decreasing exponentially with time (Figure 1).

Tube variability

The two control tubes were used during these experiments to check inherent variability amongst the tubes. This was necessary to establish a threshold for discerning effects of tube treatments. The inter-comparison of the controls was probably a "worst case" comparison since a large white sucker (Catostomus commersoni) was inadvertently trapped inside control tube 2 while the tube walls were being sealed to the sediments and was not found and removed for 22 days. This roughly tripled the fish biomass within the tube and decimated haptobenthic and zooplankton populations. The tube to tube comparison was made with pearl dace (Figure 3). Despite the presence of the sucker in control tube 2 during the first 3 weeks of the experiment, there was good agreement between the concentrations of ^{203}Hg in pearl dace of the control tubes by the latter part of batch 1. We now have good reason to believe that most of the remaining variability between the tubes early in this batch can be explained by the disproportionately large number of large pearl dace which were taken from tube 3 during the first 3 sampling periods. The smaller dace accumulated Hg at a noticeably faster rate than larger dace.

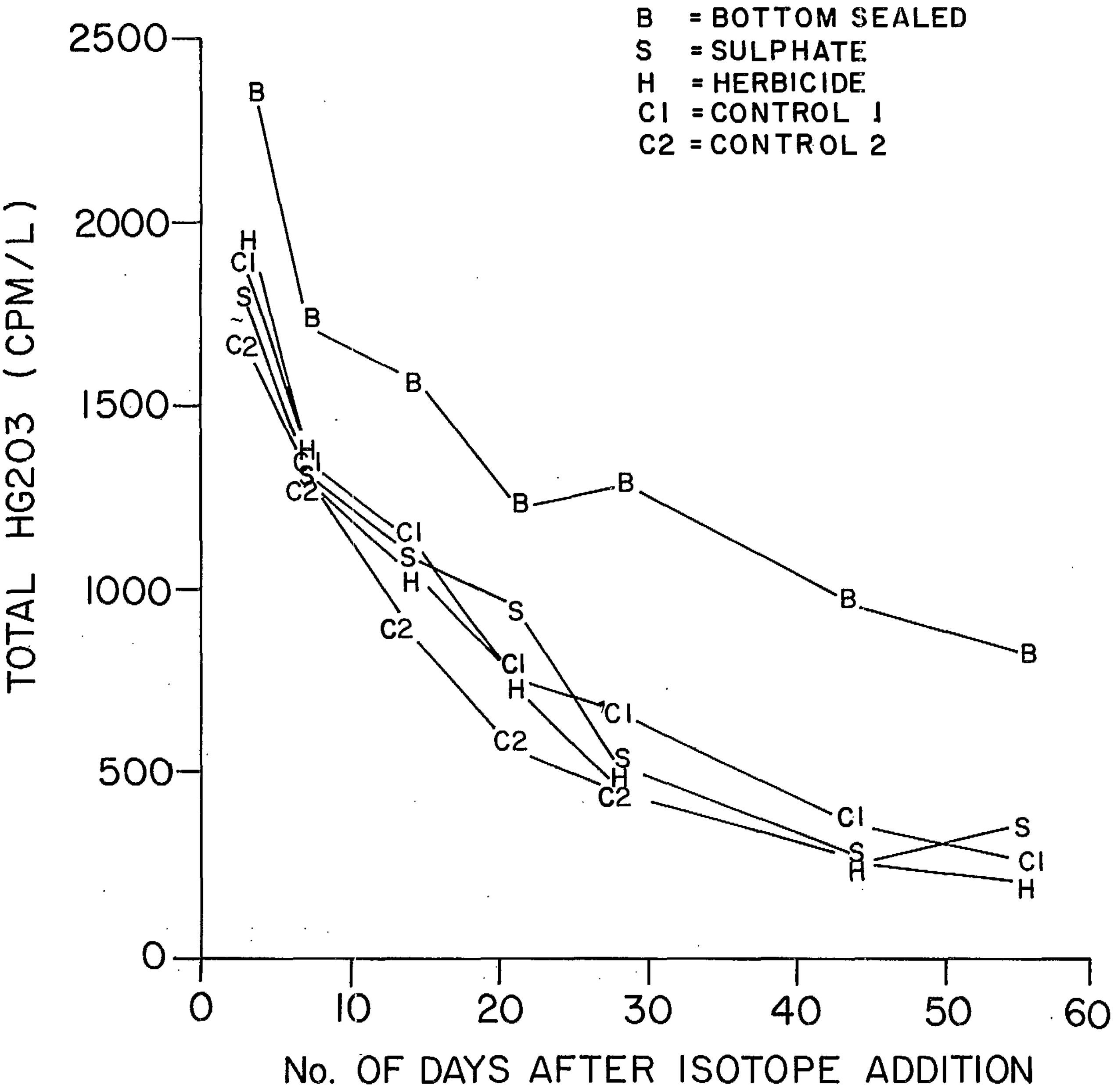


Figure 1. Total ^{203}Hg concentrations in the water columns of the control, bottom-sealed, sulphate and herbicide tubes.

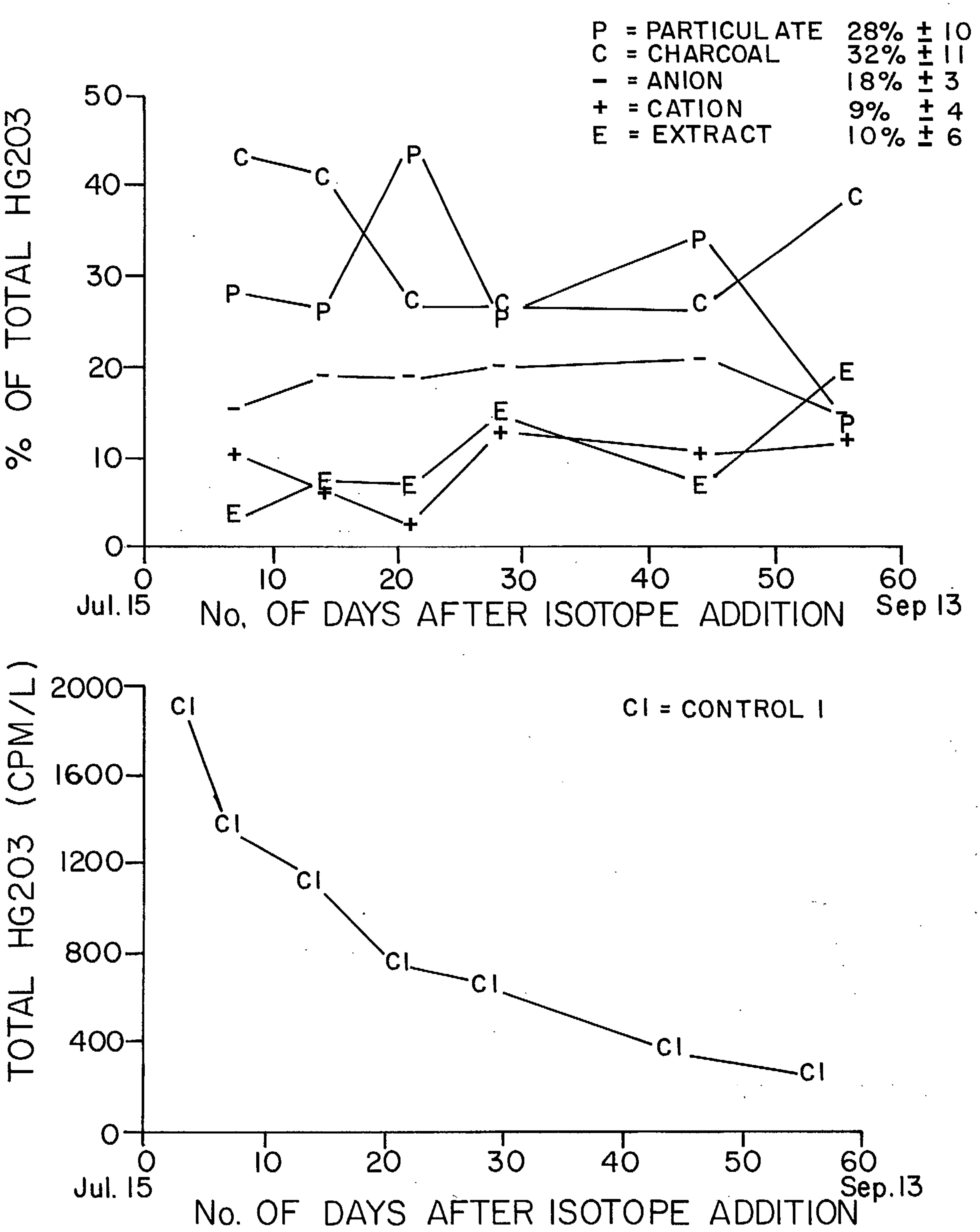


Figure 2. Upper: Fractionation of ^{203}Hg in the water column of control tube 1.

Lower: Total ^{203}Hg observed in the water column of the control tube 1.

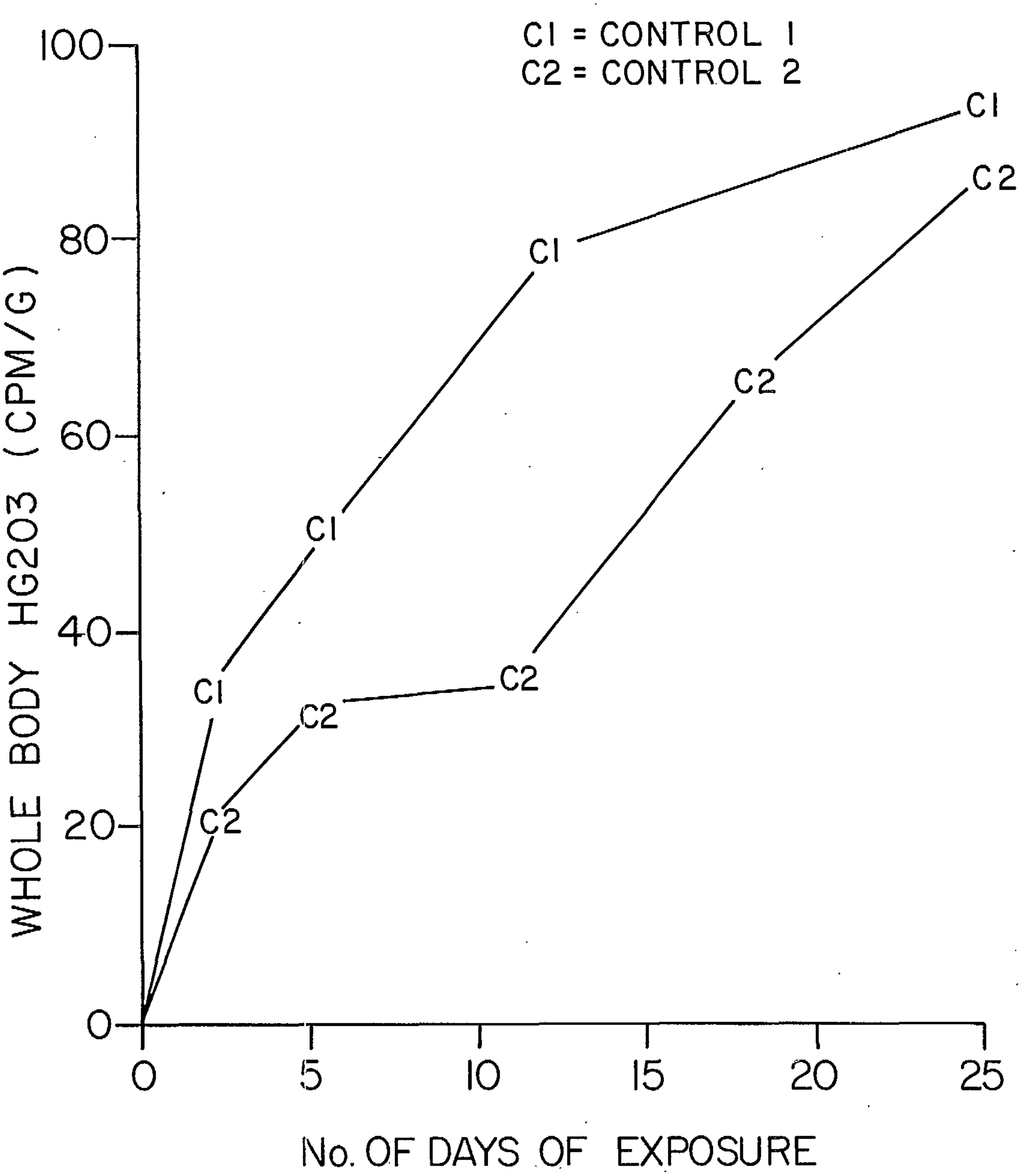


Figure 3. Total ^{203}Hg in batch 1 pearl dace retrieved from the control tubes.

Effects of tube treatments on rates of 203-mercury bioaccumulation

Whole body accumulation of ^{203}Hg by pearl dace in the control and bottom-sealed tubes is shown in Figure 4. In both batch 1 and 2 the rate of accumulation of ^{203}Hg was an order of magnitude faster in the bottom-sealed than in the control tube. This very striking effect from simply enclosing a portion of the water column occurred very rapidly. Batch 1 pearl dace removed after only 3 days and 6 days after isotope addition, contained approximately 20 times as much ^{203}Hg as the control fish. Movement of ^{203}Hg into skeletal muscle followed the same pattern as whole body accumulation (Figure 5). Preliminary analyses indicated that there was also approximately ten times as much radiolabelled methylmercury in the skeletal muscle of bottom-sealed tube fish. Bioaccumulation of ^{203}Hg by crayfish occurred in an almost identical manner. This was true for both whole body and abdominal muscle ^{203}Hg concentrations (Figures 4-6).

Rates of bioaccumulation of ^{203}Hg by pearl dace in the sulphate tube did not differ initially from the control (Figure 7). Towards the end of batch 1 there may have been a slight reduction of mercury uptake with elevated sulphate concentrations. This trend became more pronounced in the batch 2 fish with the overall uptake in the sulphate tube being halved.

Herbicide was added to the herbicide tube one week before the addition of pearl dace. During the course of the experiment the herbicide reduced the primary production potential in the water column to approximately half of that of the control. This reduction of primary productivity was successful in at least halving the rate of ^{203}Hg bioaccumulation in whole body of batch 1 and batch 2 pearl dace (Figure 7).

Discussion

All of the treatments, bottom-seal, herbicide and sulphate produced differences in the rates of bioaccumulation of mercury by pearl dace and crayfish. The immediate order-of-magnitude increase in Hg bioaccumulation caused by simply enclosing a portion of the water column in the bottom-sealed tube (Figures 4-6) clearly demonstrated the potential of mercury to move from the water column and sediment floc into aquatic biota. Because of this very large effect we feel that this tube is the most significant in terms of establishing the water column and newly deposited sediment floc as an important

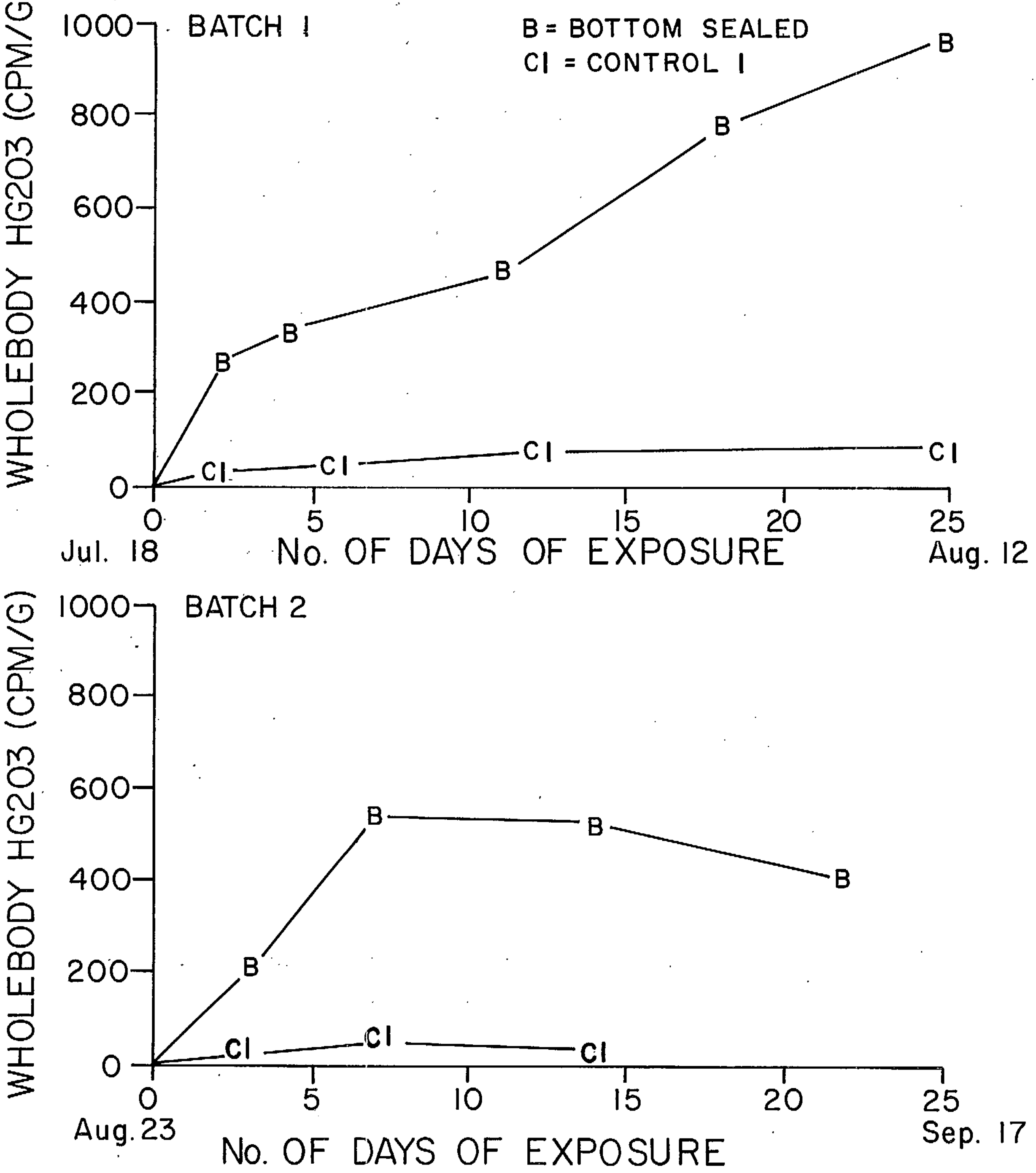


Figure 4. ^{203}Hg bioaccumulation by pearl dace in the control and bottom-sealed tubes during batch 1 (upper panel) and batch 2 (lower panel).

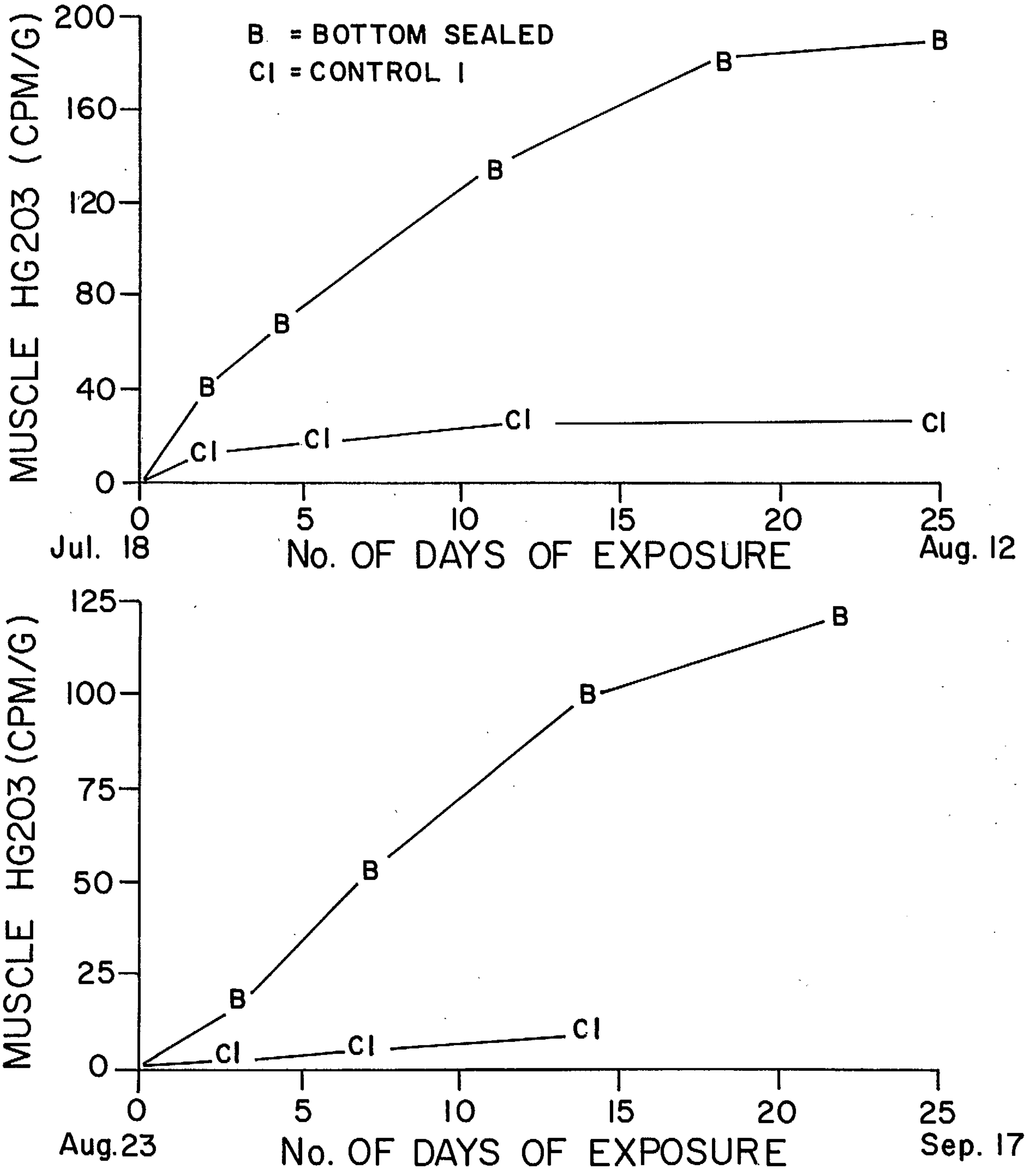


Figure 5. Total ^{203}Hg in PEARL DACE SKELETAL MUSCLE retrieved from the control and bottom-sealed tubes during batch 1 (above) and batch 2 (below).

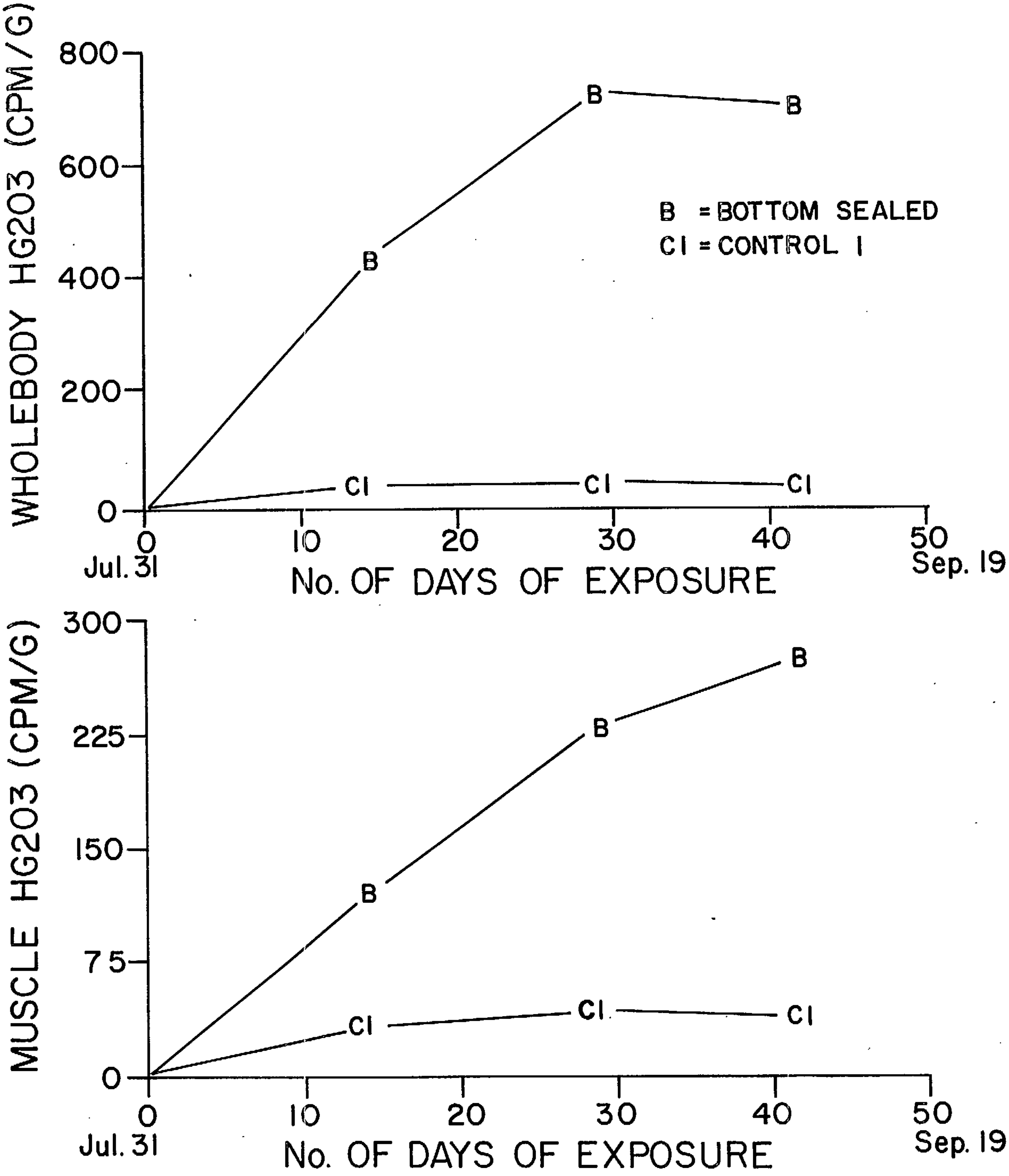


Figure 6. Total ^{203}Hg observed in CRAYFISH (upper: WHOLEBODIES; lower: ABDOMINAL MUSCLE) from the control and bottom-sealed tubes.

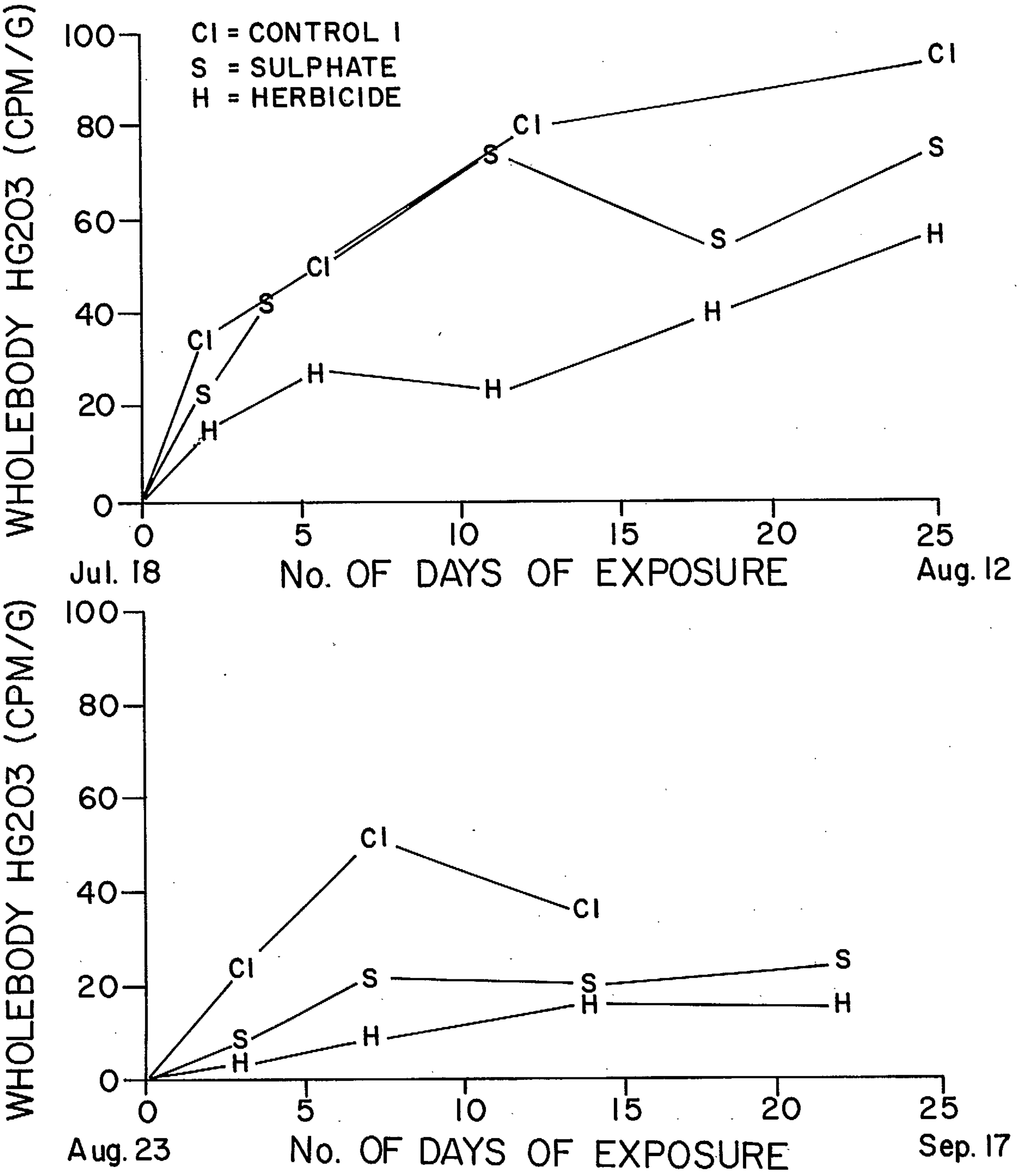


Figure 7. Total ^{203}Hg observed in PEARL DACE WHOLEBODIES (upper: batch 1; lower: batch 2) retrieved from the control, sulphate and herbicide tubes.

compartment from which mercury can be rapidly bioaccumulated. Apparently mercury entering an aquatic ecosystem does not have to be incorporated into deeper sediments before it is readily available for bioaccumulation by biota and "older" mercury deeper in the sediments is probably essentially out of circulation.

The mechanism of the effect seen in the bottom-sealed tube cannot be explained by differences in the amount of isotope added to the bottom-sealed tube since the total quantity of ^{203}Hg in the bottom-sealed tube was only 10% greater than in the control tube (Figure 1). It is also not a function of the concentration of label in the water column since the effect was immediate while isotope concentrations were very similar in both tubes. During the remainder of the experiment concentration was usually only a factor of two greater than the control tube. The two most obvious differences between the tubes were the initial high primary productivity in the bottom-sealed tube as a result of fertilization and the increased transparency of the bottom-sealed tube as a consequence of settling of suspended clay particulate material.

These hypotheses were tested in five bottom-sealed tubes during the summer of 1979. Preliminary examination of these data indicates that the lack of suspended clay particles and not the addition of nutrients to the bottom-sealed tube was responsible for the observed results during summer of 1978.

The approximately 50% reduction in the rate of ^{203}Hg bioaccumulation in the herbicide tube also demonstrated the importance of the water column and recently deposited surface floc sediments as compartments from which mercury can be readily bioaccumulated (Figure 7). It is unlikely that this effect was the result of herbicide toxicity since the herbicides used specifically inhibited the enzymes of photosystem 2 of the photosynthetic process. The concentrations used did not affect bacterial respiration in Clay Lake water samples (unpublished data) and they were one-thirtieth to one-fiftieth of the LD50 for fish (Ciba-Geigy, undated report). The herbicide reduced haptobenthic, phytoplankton and zooplankton populations so that the effect may have been partially explained as a food chain effect. The objective of this tube was not intended to differentiate between what step of the food chain was responsible for the observed data.

The sulphate addition was designed to reduce ^{203}Hg accumulation either by immobilizing the ^{203}Hg as HgS in the deeper anoxic sediments or by affecting the microbial metabolism of the anoxic sediments (Winfrey and Zeikus 1977). This treatment appeared to decrease the rate of mercury bioaccumulation by about a factor of two suggesting that the deeper anoxic sediments may contribute somewhat to mercury bioaccumulation. However sulphate concentrations in the sediments of this tube were not higher than the control tube (0.03 mg/g sulphate vs. 0.06 mg/g control) and sulphate was not significantly removed from the water column. Both of these observations suggest that sulphide production and consequently mercuric sulphide formation were not of any great significance. An alternative explanation for the results of this tube could be related to the decreased transparency of this tube as compared to the control. Because of its exposed position in the bay, clay sediments in the tube were preferentially suspended by wave action. These suspended clay particles may have bound the ^{203}Hg making it less available for bioaccumulation. Experiments were carried out during the summer of 1979 to clarify this point.

The overall conclusion from these mechanism experiments is that the water column and recently deposited surface floc appear to be very important compartments from which mercury is mobilized into aquatic biota. This conclusion is supported by several observations that very often mercury concentrations in fish are unrelated to sediment mercury (eg. Scott 1974). In addition Armstrong and Hamilton (1973) concluded that Clay Lake crayfish accumulated mercury mainly from mercury contaminated water and food rather than sediments and Armstrong and Scott (1979) have suggested that fish from the nearby Ball Lake may accumulate mercury from the water column.

This conclusion could have very serious consequences for Clay Lake if it were still receiving substantial quantities of mercury from the Wabigoon River inflow. This seems to be the case (Table 2). During the open water season of 1978 Clay Lake is estimated to have received approximately 33 kilograms of mercury and retained approximately 17 kilograms. The 17 kg mercury retained would be sufficient to raise the mercury concentration of 2 x 10^6 kg of fish flesh by 10 ug Hg/g. However, mercury concentrations in Clay Lake have been decreasing during the past few years (Armstrong and Reinke 1977) (Scott, personal communication) suggesting that the problem is improving somewhat. Also, mercury concentrations in surface sediments may have decreased since 1971, as shown by comparison of cores taken in 1971 and 1978 (Fig. 8). These core

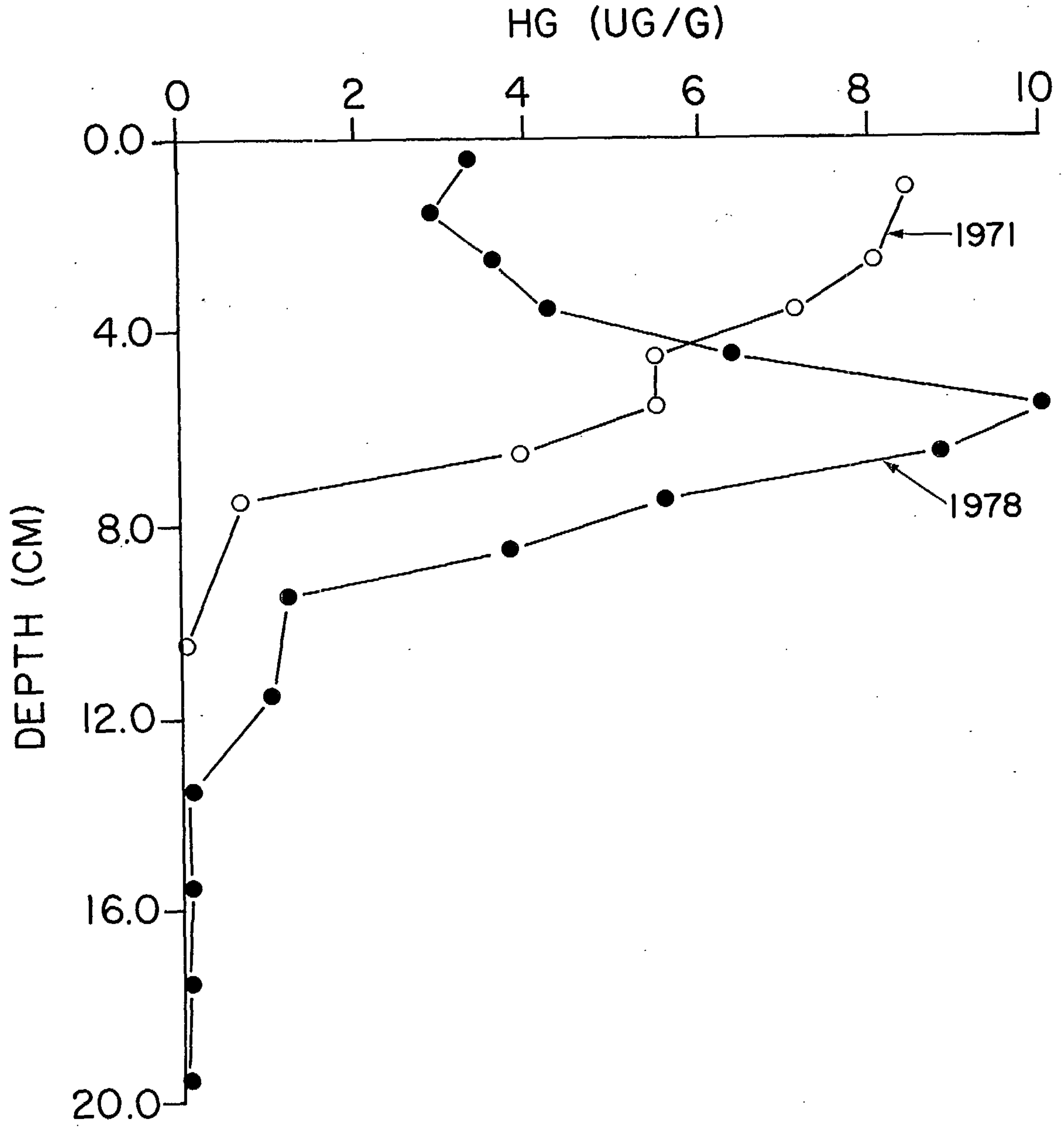


Figure 8. Sediment profiles of total mercury concentrations (ug/g, dry weight) in the eastern basin of Clay Lake. The 1971 data are taken from Armstrong and Hamilton (1973). The decrease in surface mercury concentrations may be attributed to burial or resuspension of mercury rich sediments or mixing processes.

TABLE 2. An estimate of influx and efflux of total Hg from Clay Lake during the openwater period of May to mid November 1978. Mercury sampling was carried out on a weekly basis; water flow was monitored continuously.

		INFLOW		OUTFLOW	
	Flow Rate (cfs)	Total Hg Conc'n (ng/1) $\bar{X} \pm s$	Influx (kg)	Total Hg Conc'n (ng/1) $\bar{X} \pm s$	Efflux (kg)
SPRING (60 days)	3000	33 ± 8	14.5	13 ± 5	5.7
SUMMER (140 days)	1500	36 ± 10	18.7	20 ± 7	10.4
TOTAL			33		16

data suggest two things: 1) the mercury pollution problem is receding somewhat in Clay Lake as mercury rich sediments are buried-a tentative conclusion supported by the reduced mercury concentration in fish; 2) that contrary to our overall conclusions and those of others mercury concentrations in sediments are related to and may be important contributors to mercury concentrations in aquatic biota. This seeming contradiction can be resolved by two observations of other investigators. The rate of mercury accumulation by fish per unit time exposure in Clay Lake has not decreased over a six year period (D.P. Scott personal communication), because apparently the decreased concentrations of mercury in Clay Lake fish can be attributed to an increased growth rate of the fish. Thus sediment and fish mercury concentrations are not necessarily related to sediment concentrations and our conclusion that the water column mercury concentrations are apparently an important contributor is supported. The following independent check seems to corroborate this conclusion. If the water column and surface sediments are the main contributors of mercury to aquatic biota, present water column total mercury concentrations should approximate water column concentrations in 1971 since the rate of accumulation of mercury by fish is unchanged. The early total mercury analyses available (which were obtained by the analytical methods available at that time) indicate that summer water column concentrations during 1971 were not dissimilar to those presently observed in Clay Lake (Armstrong and Hamilton 1973).

B. SELENIUM EXPERIMENTS

Results

Geochemistry of Mercury-203 and Selenium-75

In both the control and selenium tubes there was an exponential decrease in the concentration of ^{203}Hg in the water column (Figure 9). An exponential decrease explained 99% and 92% of the data variability in the control and selenium tubes, respectively. The half-time of ^{203}Hg in the water column of these tubes was 18 and 16 days respectively.

Selenium moved out of the water column of both tubes in linear fashion (Figure 9). A linear function explained 89% and 96% of the variability in control and selenium tubes respectively. Selenium half-times were 49 and 56 days. Thus the presence of 0.1 mg/l selenium did not have a large effect on either the characteristics of the movement of selenium out of the water column or the rate of movement of selenium from the water column. In the bottom sealed tube which had no clay sediments ^{75}Se concentrations did not decrease with time (Figure 9) in contrast to the exponential decrease of ^{203}Hg in the same tube.

The presence of 0.1 mg/l Se did not affect partitioning of ^{203}Hg into the particulate and dissolved fractions in the water column. In the control and selenium tubes a stable relationship was set up within seven days of spike day. During the course of the experiment this relationship was maintained even though the total amount of mercury in the water column was decreasing exponentially (Figure 10).

Even though the rate of removal of ^{75}Se was not affected by the presence of 0.1 mg/l Se (Figure 9) the stable selenite had a profound effect on the partitioning of the ^{75}Se in the particulate, charcoal, anion and cation fractions (Figure 11). In the control tube most of the ^{75}Se appeared in the charcoal fraction and was probably associated with dissolved organic matter. Most of the remainder was probably present as selenite or possible selenate, (anion fraction) while only a small portion (less than 15%) appeared in the particulate and cation fractions. In the selenium tube the ^{75}Se associated with the charcoal fraction amounted to only 10 to 15% of the total label in the water column through the entire experiment suggesting that the dissolved organic matter fraction was rapidly saturated with selenite. In this case the remainder of the ^{75}Se was in the anion fraction. During the

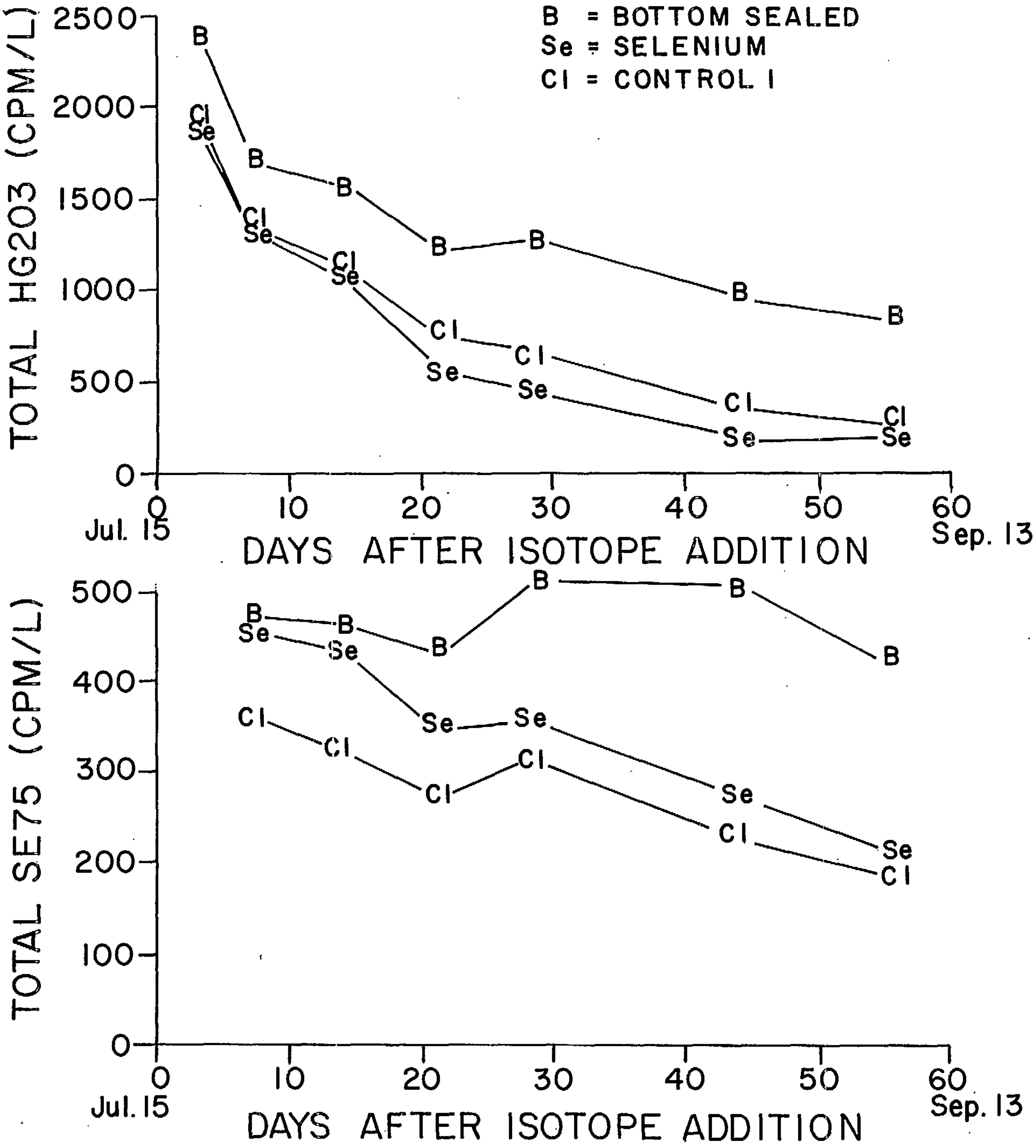


Figure 9. Total ^{203}Hg concentrations (upper panel) and total ^{75}Se concentrations (lower panel) in the water column of the control, selenium and bottom-sealed tubes.

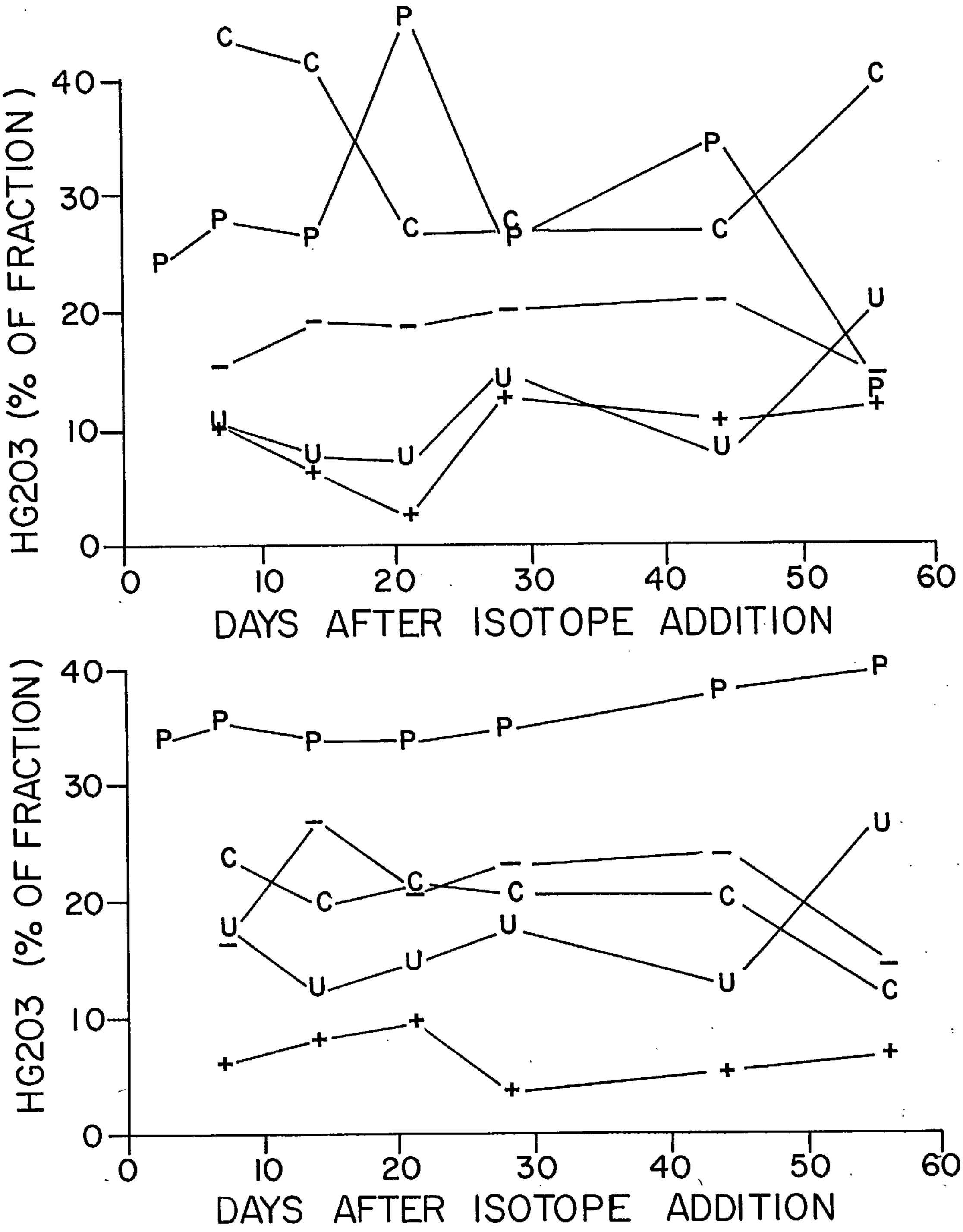


Figure 10. Partitioning of total ^{203}Hg in the control (upper panel) and selenium (lower panel) tubes into particulate (P), charcoal (C), anion (–), cation (+) and unassociated (U) fractions.

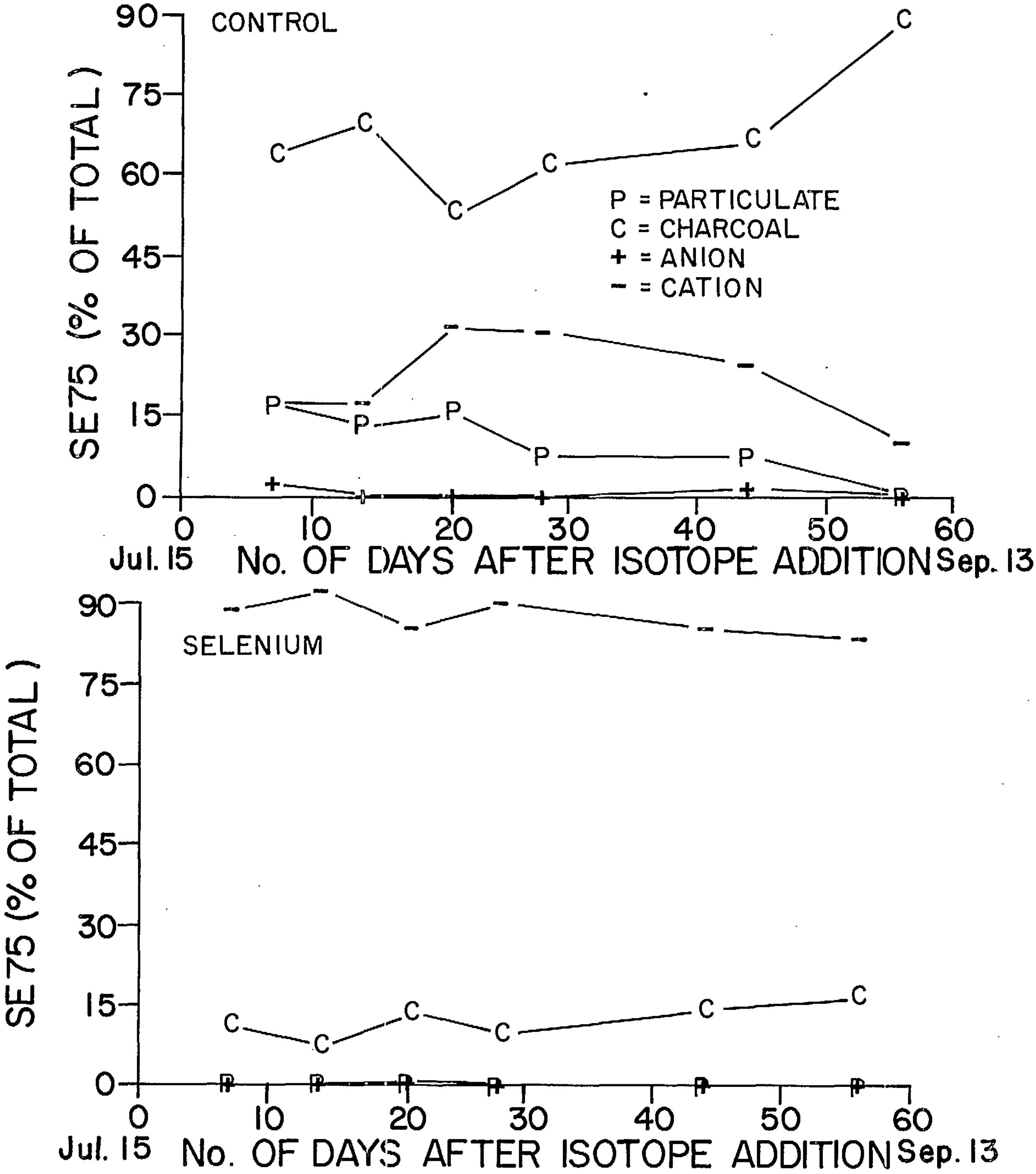


Figure 11. Partitioning of total ^{75}Se in the control and selenium tubes into particulate, charcoal, anion and cation fractions.

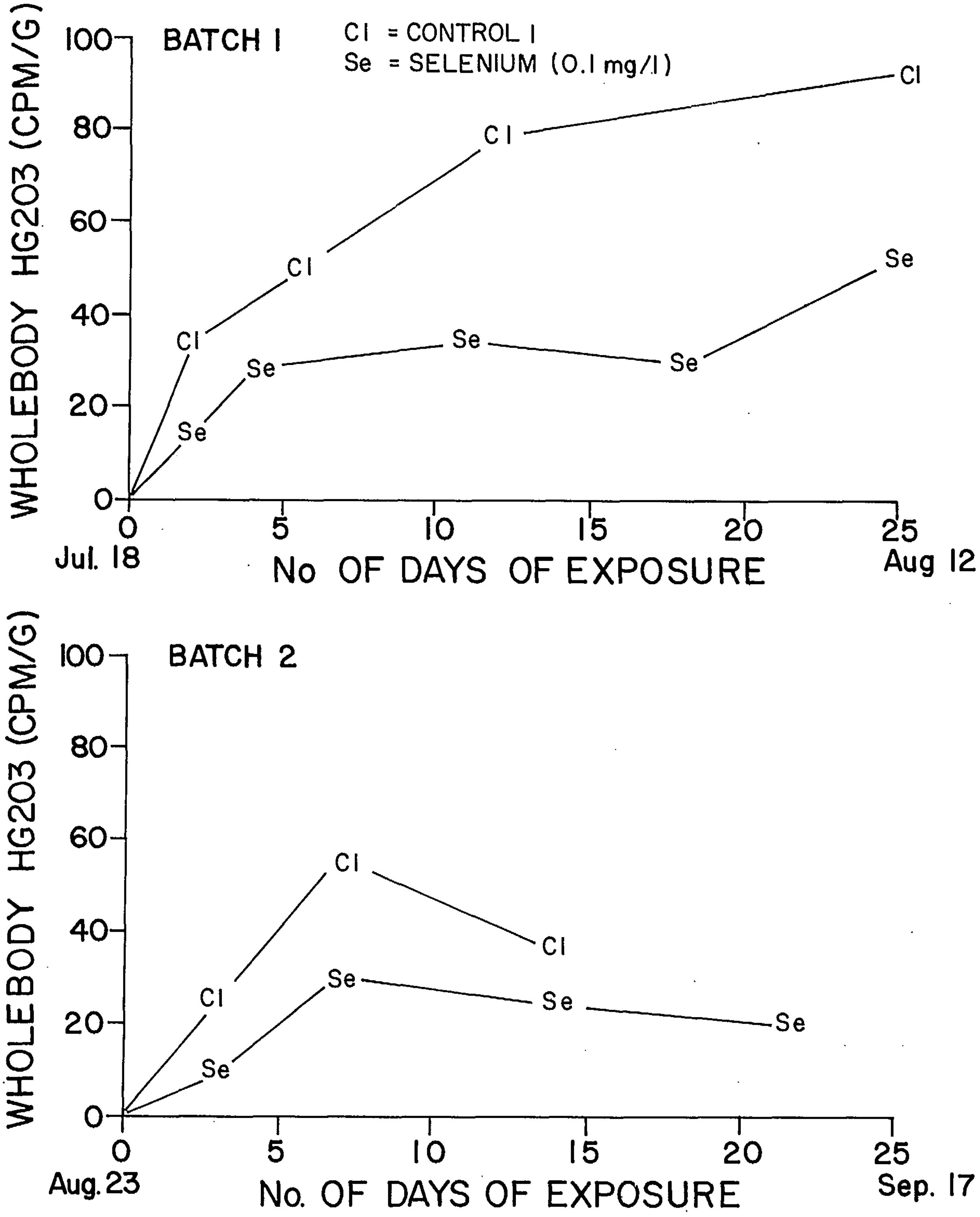


Figure 12. Total ^{203}Hg (cpm/g) observed in PEARL DACE WHOLEBODIES in the control and selenium tubes in batches 1 and 2.

course of the experiment .057 mg/l Se moved into the sediments. Of this approximately .055 mg/l left the anion fraction while approximately 0.003 mg/l left the water column from the charcoal fraction.

Bioaccumulation of 203-Mercury in the control and selenium tubes

Whole body accumulation of ^{203}Hg for Batch 1 and 2 pearl dace is shown in Figure 12. In both batches the presence of 0.1 mg/l Se appears to have decreased the rate of bioaccumulation of ^{203}Hg to about half. When the batch 2 dace were introduced to the tubes (39 days after spike day) approximately 75% of the ^{203}Hg had left the water column (Figure 9). Therefore, whether or not most of the labelled mercury was in the water column or sediments did not change the apparent selenium effect. A discussion of the relative importance of effects in water column or in sediments on movement of ^{203}Hg into aquatic biota is given in the previous section. Accumulation of ^{203}Hg in the skeletal muscle of pearl dace (Figure 13) followed the same general pattern as for the whole body measurements i.e. fish in the selenium tube accumulated mercury in the skeletal muscle at about half the rate of those in the control tube.

Crayfish were put into tubes 12 days after spike day. Again the presence of selenium reduced the rate of ^{203}Hg bioaccumulation in whole body and abdominal muscle by about a factor of two.

Bioaccumulation of Selenium

Since labelled and stable selenium were added to the selenium tube simultaneously, movement of the selenium into aquatic biota can be expressed either on a relative count per minute basis or on an absolute (concentration in ug/g) basis. In the other tubes only labelled selenium was added.

During the initial period of the experiment when ^{75}Se in the water was relatively abundant, ie. >70% of spike still in the water column (Figure 9), dace and crayfish did not accumulate selenium noticeably (Figure 14). Approximately two weeks after spike day, the animals began to accumulate selenium very rapidly. This could not have been due to the duration of exposure to selenium since the batch 2 dace rapidly accumulated selenium as soon as they were introduced to the tube (Figure 14). The selenite may have been transformed chemically or it may have moved into another compartment from

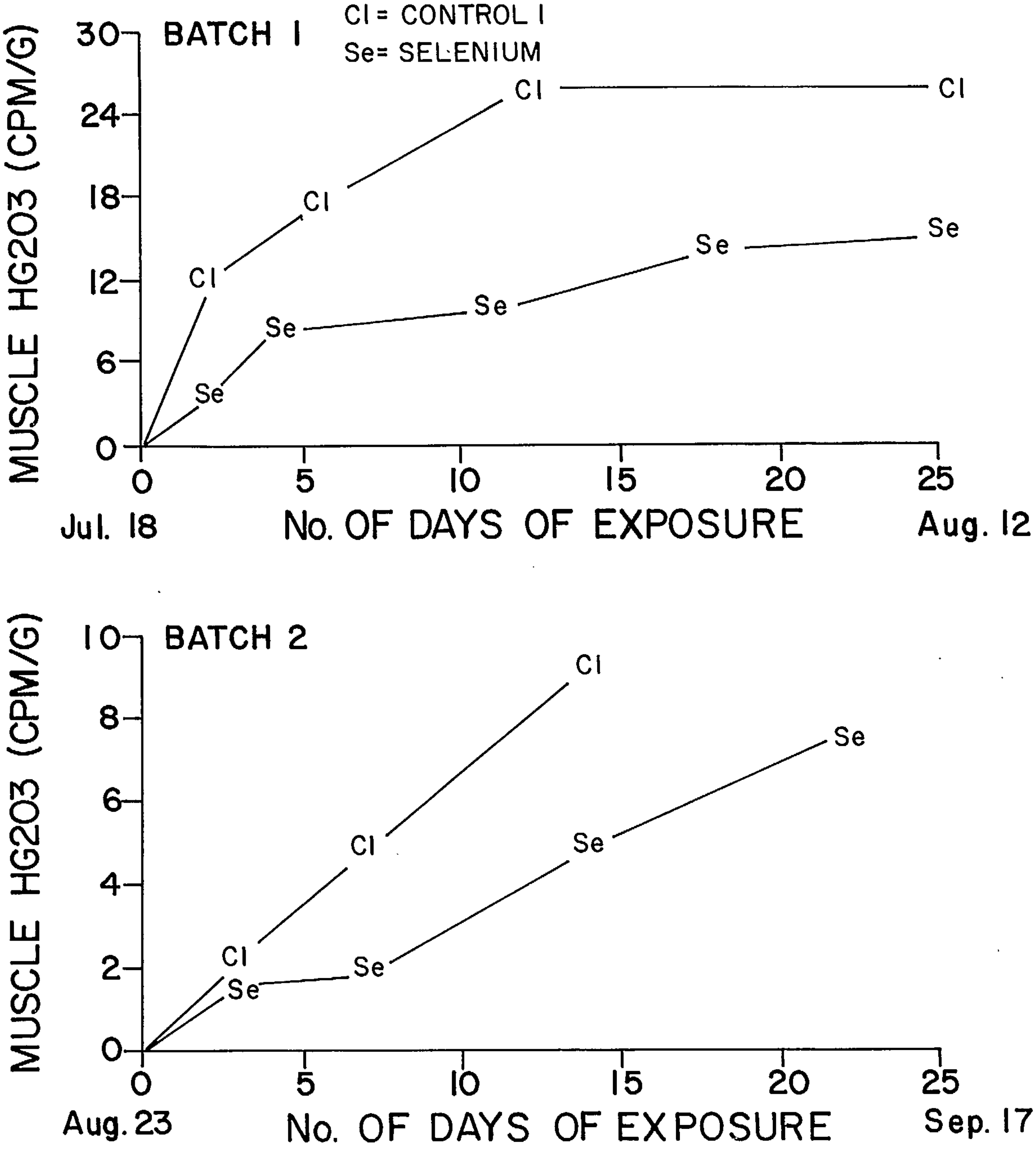


Figure 13. Total ^{203}Hg (cpm/g) observed in PEARL DACE SKELETAL MUSCLE in the control and selenium tubes in batches 1 and 2.

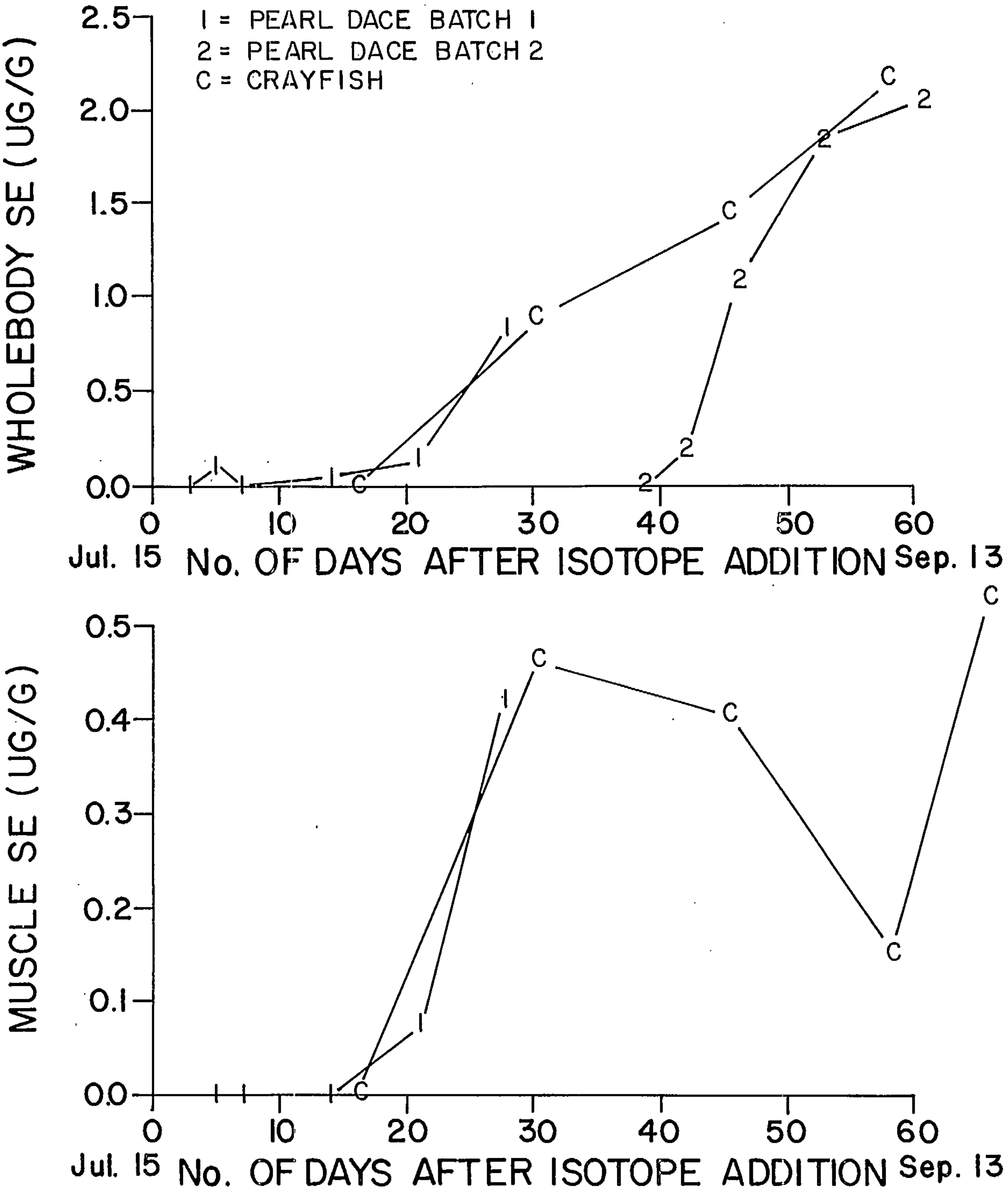


Figure 14. Bioaccumulation of selenium by crayfish and fish in the selenium tube.

which it could be readily bioaccumulated by the aquatic biota. Movement of selenium into pearl dace and crayfish muscle began at about the same time as whole body bioaccumulation commenced (Figure 14). Approximately ten days after bioaccumulation of selenium began, concentrations in crayfish and pearl dace were approximately 0.4 ug/g wet weight. Whole body concentrations were about 1.0 ug/g at that time. The rapidity with which selenium can be bioaccumulated is demonstrated by the batch two pearl dace which accumulated selenium at a rate of approximately 0.1 ug/g per day reaching a level in excess of 2 ug/g by the end of the experiment.

A similar lag before bioaccumulation of selenium commenced was also observed in the control tubes and the herbicide tube (Figure 15). Thus the mere presence of elevated concentrations of selenium does not appear to be the cause of this phenomenon.

There was no lag period for selenium bioaccumulation in the bottom-sealed tube, or in the sulphate tube (Figure 15). The very high rate of ^{75}Se uptake into tube 4 pearl dace in the bottom-sealed tube resembles the exceedingly high rates of accumulation of ^{203}Hg in this tube. Possibly a general mechanism responsible for accumulation of these two elements has been effected in this tube. Pearl dace from the sulphate tube also accumulated selenium immediately and at a high rate (Figure 15). An explanation of this may be associated with the chemical similarities of sulphur and selenium coupled with the elevated sulphate concentrations in this tube.

Discussion

There are two possible mechanisms by which added selenium could alleviate mercury pollution problems in freshwater river-lake systems. Firstly, it could decrease the rate of bioaccumulation of mercury by aquatic biota and secondly it could bring about detoxification of bioaccumulated mercury.

Decreased rates of bioaccumulation could occur either by decreasing the mercury uptake rate or by increasing the rate of mercury and methyl-mercury excretion or both. Either or both could produce the reduced rates of ^{203}Hg bioaccumulation observed in the pearl dace and crayfish of the selenium tube (Figures 12 and 13). If mercury excretion rates were increased in the presence of selenium, a first step would be the mobilization of mercury from tissues. Sumino _et al_. (1977) have found that selenite affected the tissue

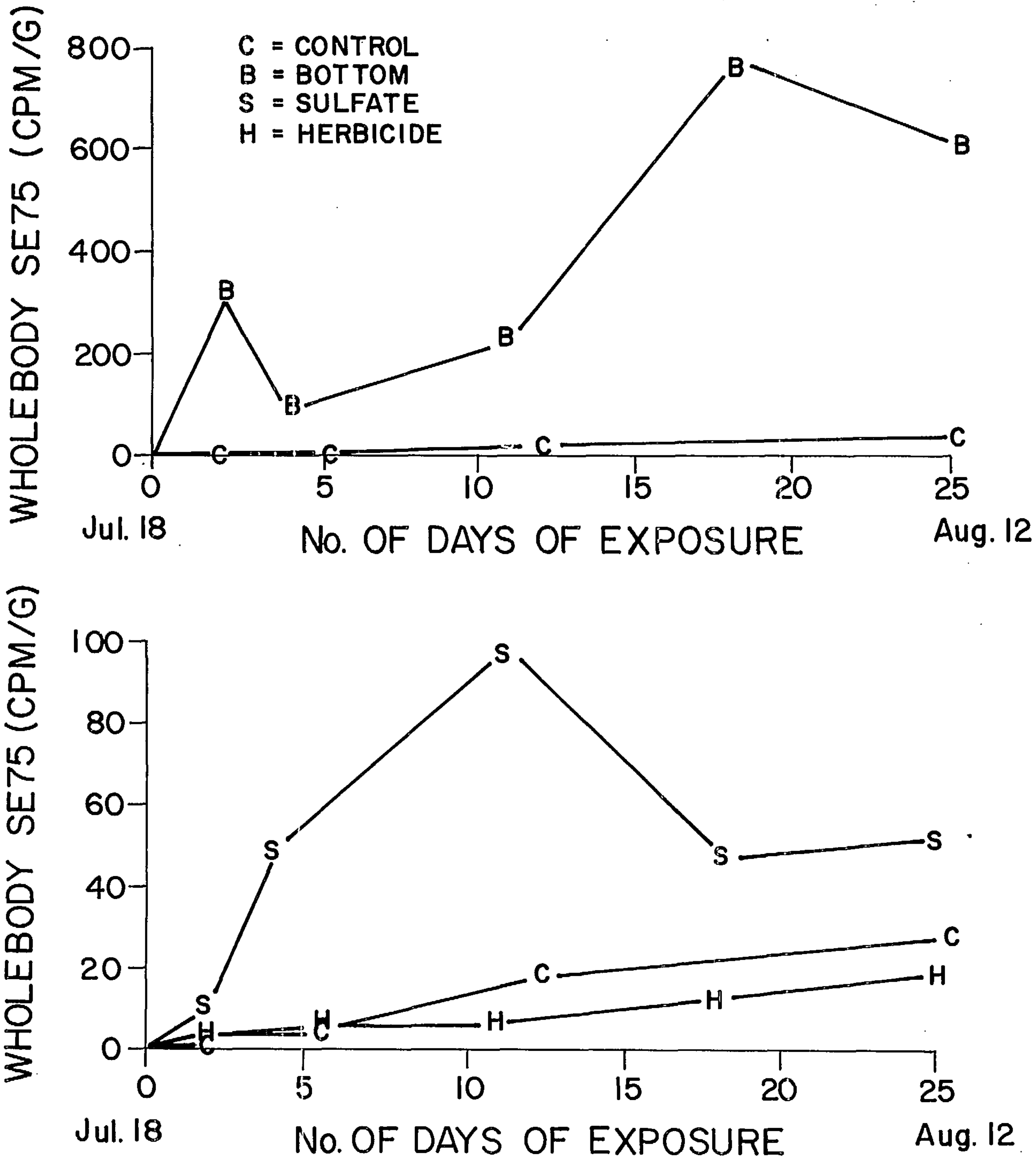


Figure 15. ^{75}Se accumulated by batch 1 pearl dace in the control, bottom sealed, sulphate and herbicide tubes.

distribution of CH_3Hg in mice and increased the percentage of unbound methylmercury in several tissues. They hypothesized that this was caused by a liberation of methylmercury from sulphydryl bonds because of the very high chemical affinity of selenium for mercury. Wood et al. (1975) have suggested that selenium may cause the demethylation of methylmercury in tissues and that methyl selenides may then be excreted. Whether or not either of these mechanisms is operative in fish and invertebrates in unknown. Another possibility which would decrease the rate of uptake of mercury by aquatic biota, is that the presence of selenium may decrease the rate of mercury methylation either in sediments, in the water column or possibly even in the intestinal contents of aquatic biota. This is not entirely speculation since we (Rudd et al. unpublished data) in preliminary experiments have found that the presence of 200 mgm/m^2 selenium in Clay Lake sediments reduced the rate of mercury methylation by a factor of ten. The selenium concentration in these experiments was the same as that to be expected if all of the selenium in the water column of the selenium tube had moved into the top 2 cm of the sediments.

A second mechanism by which selenium could reduce the affects of mercury pollution is by the detoxification of the mercury present in fish tissue. In support of this hypothesis dietary supplements of swordfish have been found to detoxify methylmercury in rats (Friedman et al. 1978) and sodium selenite was found to decrease methylmercury toxicity in Japanese quail and rats (Ganther and Sunde 1974, Ganther et al. 1972 and Ohi et al. 1976). Possible mechanisms for this detoxification effect of selenium may be similar to those discussed above. In addition Sugiura et al. (1976) have shown that a selenhydryl group binds methylmercury 100 times more tightly than the sulphydryl group. Thus selenium may detoxify methylmercury by precipitating it as a mercury selenium complex. Electron probe analyses showing dark spots in cells containing mercury and selenium tend to support this hypothesis (Frost 1972). A more complete discussion of the detoxifying capability of selenium may be found in Frost and List (1975) and in Wood et al. (1975).

If selenium is to be considered as a possible ecosystem detoxifying agent, it would be necessary to establish that it bioaccumulates either through the food chain or directly into fish tissues. In our experiments, after an initial lag period, selenium accumulated very rapidly, and to a level which could theoretically protect fish consumers from methylmercury toxicity. There are several lines of evidence which suggest that the selenium was entering the aquatic biota through the food chain. The lag times for entry of selenium into fish and crayfish (eg. Figure 14) suggest that the selenium had to enter another compartment before it was available for the fish and invertebrates. This idea is supported by the absence of lag time when the batch 2 pearl dace were added to the selenium tube (Figure 14). Similar lag times for selenium uptake were also noted for the two control tubes and the herbicide tube (Figure 15). There was also a short lag time in selenium bioaccumulation in the herbicide tube of approximately 3 days after the batch 2 fish were added though not in the other tubes. This is consistent with the food chain hypothesis since the herbicide had reduced the quantity of fixed carbon input into this ecosystem by at least 50% and had probably also reduced zooplankton populations. Conversely, in the bottom-sealed tube selenium uptake was immediate and rapid in both batches of pearl dace (Figure 15) which may be partially explained by the high productivity and plankton content of this tube. These observations are consistent with those of Sandholm _et_ _al_. (1973). They found in laboratory aquariums that fish concentrated only small amounts of selenium directly from the water. Selenium bioaccumulation occurred mainly from the zooplankton food source.

If selenium is to be considerd as a mercury amelioration agent, an important characteristic would be its capability of bioaccumulating through the food chain rather than directly from the water column. This is important because movement of selenium from the sediments up through the food web would necessitate only a single or at most a few additions of selenium to an aquatic ecosystem to effect long term mercury amelioration. Bioaccumulation by fish directly from the water column would necessitate continuous additions of selenium to a system which would be an unacceptable long-term solution.

Selenium is potentially most useful as a mercury amelioration agent if it reduces the rate of bioaccumulation of mercury in aquatic biota and itself bioaccumulates efficiently to detoxify methylmercury present in fish tissues. Our preliminary experiments suggest that it does both (Figures 12-15). There may also be a food chain enhancement effect that we did not test with this experimental design. For example, the 50%

reduction in mercury concentrations that we observed in both pearl dace and crayfish could affect higher levels of the food chain resulting in larger decreases of the mercury content in predatory fish both directly and by presenting predators with prey of lower mercury content. We are presently investigating this hypothesis.

If selenium could be proved to be an effective agent in reducing mercury pollution at the ecosystem level, a second requirement would of course be that the increase of selenium concentrations in the ecosystem and in fish would not be dangerous to either aquatic biota or to the humans who eat the fish. A detailed examination of the physiology and toxicity of selenium to humans is given by Frost (1972) and Frost and Lish (1975) and Stadtman (1974). To summarize very briefly it appears that selenium is an essential nutrient even though excessive concentrations are toxic; it appears to be an anti-cancer agent, and it has been removed from a list of carcinogens (Federal Register, 1974). It is also interesting to note that mercury has been used as an antidote to selenium poisoning (Frost 1972). One may conclude that roughly equimolar concentrations of both elements together are less toxic together than either one separately.

The toxicity of selenium in aquatic systems is almost unknown. One milligram per liter of selenium in our tube experiments results in progressive deaths of perch (Perca flavescens) over approximately a two month period. There were no deaths of pearl dace, crayfish or benthic insects during the same period at this selenium concentration. There were also no apparent deaths of any organisms at the 0.1 mg/l selenium concentration in the selenium tube. One-tenth mg/l selenium was not toxic to zooplankton communities indigenous to Clay Lake but 1 mg/l selenium was toxic to cladocerans and rotifers (S.G. Lawrence unpublished data).

Our preliminary work and that of others (Hesslein et al. 1979) indicates that the geochemistry of selenium is favorable to its being used as a mercury amelioration agent. Sediments were necessary for the removal of selenium from the water column in these experiments (Figure 9). The sediments evidently have a large capacity for selenium absorption since the rate of removal of selenium from the water column was not substantially affected by the presence of 0.1 mg/Se L (Figure 9). The 49 and 56 day half-times of selenium in the water column of the control and selenium tubes were very close to the measured 47.5 selenium half-life in Lake 224, a Canadian Shield Lake in ELA, even though sediments in Lake 224 are different, being predominantly sand overlain with coarse gravel (Hesslein et al. 1979). The affinity of selenium for both clay and sand sediments coupled with its apparent bioaccumulation through the food chain rather than directly into fish flesh are as stated, desirable characteristics of this potential mercury amelioration agent. These characteristics are important because the most convenient and efficient way to treat a system such as the English-Wabigoon River system would be to add selenium to the system at the same point that mercury entered the system. Selenium could then be distributed throughout the system in the same manner as mercury had entered the sediments where it could exert its influence over a period of years. Obviously, before any such additions could be made much more environmental information is necessary. There is need for information on selenium toxicity for a wide range of aquatic biota. There is also a possibility that selenium may be effective at concentrations lower than 0.1 mg/1. We are currently investigating both of these subjects. If selenium is safe to use in aquatic systems, it has the potential for solving a number of other aquatic heavy metal problems. In addition to mercury, selenium is known to have detoxifying effects on silver, tellurium, copper, lead and cadmium, and some forms of arsenic (Frost 1972).

In the previous section it was concluded that the water column and surficial organic sediments seem to be very important components in the movement of mercury into fish. Because of this, some of the suggested mercury amelioration measures such as plowing of sediments to reduce mercury concentrations and siltation of clean sediments over contaminated sediments would be largely ineffective if elevated mercury concentrations were still present in the water column. This was true in 1978 for Clay Lake which retained approximately one-half the mercury it received from the Wabigoon River (previous section). Since removal of mercury contaminated sediments from the Wabigoon River would be very expensive, addition of selenium to the mercury contaminated system may be a more practicable solution.

C. Clay Addition Experiment

During the summer of 1978 a clay addition experiment was carried out in 3-4 meter diameter tubes similar to those described previosuly. As required by the agreement the experiment called for measurement of rates of total cold mercury bioaccumulation from contaminated sediments which were covered by layers of clean clay 0.5 and 5.0 cm thick. Rates of bioaccumulation were compared to a control tube in which the mercury contaminated Clay Lake sediments had not been covered. The experimental effects were integrated by following total mercury bioaccumulation by pearl dace and finescale dace which were free swimming in the tubes.

The experiment was complicated by a four day storm which resuspended sediments inside the tubes resulting in increased water mercury concentrations in all of the tubes (Figure 16). These increases were above that of the lake water outside of the tube indicating that a tube effect had caused the resuspension of the underlying mercury contaminated sediments even in the tube which had a covering of 5 cm of clean clay. Despite this tube effect the bioaccumulation rates even in the control tube which had no clean clay cover were not fast enough for an increase in mercury concentration to be detected during the course of the experiment (Table 3). Because of this there were no significant differences in mercury concentration of the fish in either the controls or in the tubes with 0.5 and 5.0 cm clean cover (Table 3). Because of this methodological constraint no conclusion can be drawn as to whether or not siltation of clean clay would reduce movement of mercury into the aquatic biota of the lake.

This experiment clearly demonstrates that wet chemistry methods lack the sensitivity to detect bioaccumulation of mercury in fish in field experiments of a few weeks duration. The experiments emphasize the necessity of employing very sensitive radiochemical techniques used in the mechanism of selenium tubes.

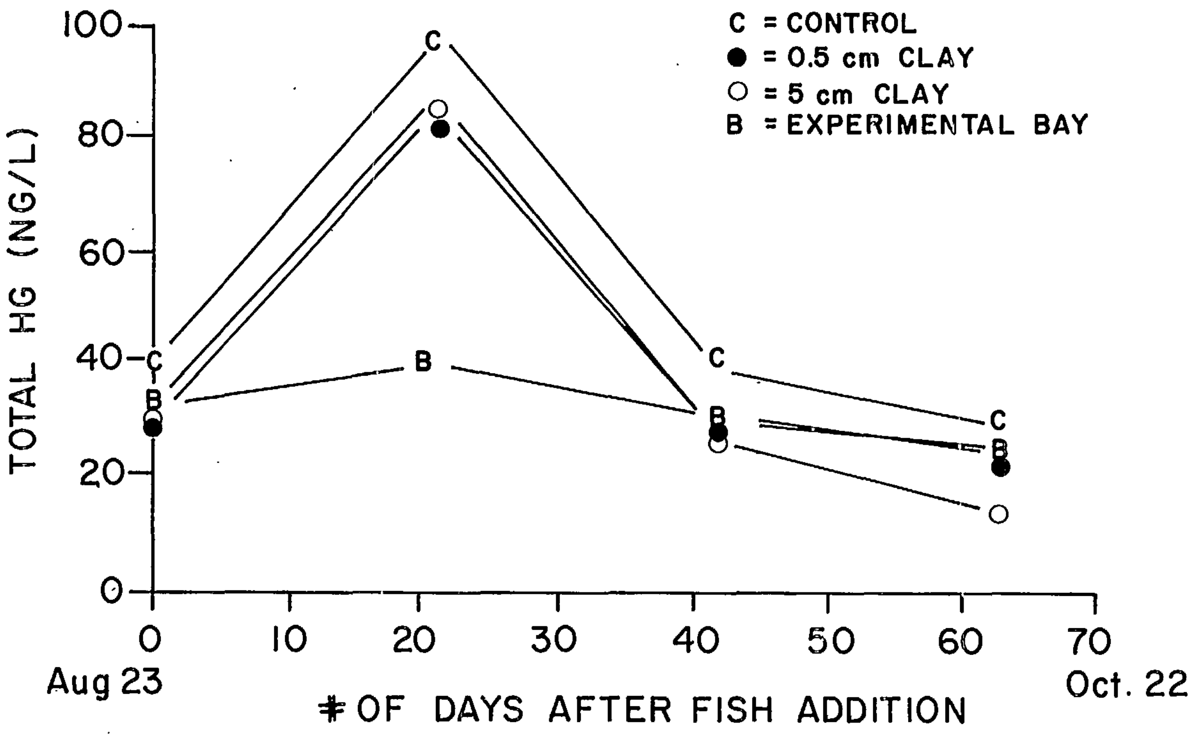


Figure 16. Total Hg in the water columns of the clay addition tubes.

TABLE 3. Mean observed total mercury concentrations (μg/g, wet weight) in Finescale and Pearl Dace wholebodies from the clay addition tubes.

Species	Tube #	# of Days after Fish Addition				
		0	14	28	42	56
Finescale Dace	Control	0.13 ± 0.03	0.14	0.13	0.15	0.14
	0.5 cm clay	"	0.17	0.12	0.18	0.15
	5.0 cm clay	"	0.13	0.13	0.15	0.13
Pearl Dace	Control	0.16 ± 0.05				0.18 ± 0.04
	0.5 cm clay	"				0.15 ± 0.04
	5.0 cm clay	"				0.14 ± 0.07

Comment: Estimates of initial concentrations were made using 10 individuals. Subsequent Finescale Dace analyses were each made upon 3 individuals pooled together. Subsequent Pearl Dace estimates were made from two analyses of 2 individuals pooled per analysis.

REFERENCES

Armstrong, F.A.J. and A.L. Hamilton. 1973. Pathways of mercury in a polluted northwestern Ontario Lake. Chapter 5. Trace metals and metal organic interaction in natural waters. P.C. Singer, ed. Ann Arbor Science Publishers, 380 pp.

Armstrong, F.A.J. and J. Reinke. 1977. Short summary, sources of information and notes on research proposed for mercury in the Wabigoon-English-Winnipeg River systems. MS Report to the English-Wabigoon Steering Committee. 14 pp.

Armstrong, F.A.J. and D.P. Scott. 1979. Decrease in mercury content of fishes in Ball Lake since imposition of controls on mercury discharges. Journal of the Fisheries Research Board of Canada. In press.

Federal register. 1974. 39: 1355-1358.

Fee, E.J. 1973. A numerical model for determining integral primary production and its application to Lake Michigan. J. Fish. Res. Board Can. 30: 1447-1468.

Friedman, M.A., L.R. Eaton and W.H. Carter. 1978. Protective effects of freeze dried swordfish on methylmercury chloride toxicity in rats. Bulletin of Environmental Contamination and Toxicology. 19: 436-442.

Frost, D.V. 1972. The two faces of selenium - can selenophobia be cured. CRC critical reviews in toxicology. 467-514.

Frost, D.V. and P.M. Lish. Selenium in biology. Annual Review of Pharmacology and Toxicology. 15: 259-284.

Ganther, H.E., C. Goudie, M.L. Sunde, M. Kopecky, P. Wagner, S.H. Oh and W.G. Hoekstra. 1972. Evidence that selenium in tuna decreases mercury toxicity. Federal Proceedings 31: 725.

Ganther, H.E. and L. Sunde. 1974. Effect of tuna fish and selenium on the toxicity of methylmercury. A progress report. Journal of Food Sciences. 39: 1-5.

Hamilton, A.L. 1972. Pond experiments on the uptake and elimination of mercury by selected freshwater organisms. In: Mercury in the aquatic environment: A summary of research carried out by the Freshwater Institute 1970-1971. ed., J.F. Uthe. Fisheries Research Board of Canada MS Report Review No. 1167. 163 pp.

Hesslein, R.H., W.S. Broecker and D.W. Schindler . 1979. The fates of metal radiotracers added to a whole lake: Sediment-water interactions. Journal of the Fisheries Research Board of Canada. In press.

Kolthoff, I.M. and Sandell, E.B. 1952. Textbook of Quantitative Inorganic Analysis. MacMillan, New York, N.Y. 159 pp.

National Research Council. 1978. An assessment of mercury in the environment. National Academy of Sciences Washington, D.C. 185 pp.

Ohi, G., S. Hishigaki, H. Seki, Y. Tamura, T. Maki, H. Konno, S. Ochiai, H. Yamada, Y. Shimamura, I. Mizoguchi and H. Yugyu. 1976. Efficacy of selenium in tuna and selenite in modifying methylmercury intoxication. Environmental Research 12: 49-58.

Potter, S.D. and G. Matrone. 1973. Effect of selenite on the toxicity and retention of dietary methylmercury and mercuric chloride. Environmental Health Perspectives. 4: 100.

Sandholm, M., H.E. Oksanen and L. Pesonen. 1973. Uptake of selenium by aquatic organisms. Limnology and Oceanography 18: 496-498.

Schindler, D.W., R. Wagemann, R.H. Hesslein. 1977. The acidification of Lake 223, Experimental Lakes Area. I. Background data the first year of acidification, 1976 and pilot experiments. AOSERP sub-project. AF 2.3.1. 84 p.

Stadtman, T.L. 1974. Selenium biochemistry. Science. 183: 915-922.

Sugiura, Y., Y. Hojo, Y. Tamai and H. Tanaka. 1976. Selenium protection against mercury toxicity: Binding of methylmercury by the selenohydryl containing ligand. Journal of the American Chemical Society. 98: 2339-2341.

Sumino, K., R. Yamanoto and S. Kitamura. 1977. A role of selenium against methylmercury toxicity. Nature. 268: 73-74.

Winfrey, M.R. and J.G. Zeikus. 1977. Effect of sulphate on carbon and electron flow during microbial methanogenesis in freshwater organisms. Applied and Environmental Microbiology. 33: 275-281.

Wood, J.M., J. Seagall, W.P. Ridely, A. Cheh, W. Chudyk and J.S. Thayer. 1975. Metabolic cycles for toxic elements in the environment. In: International Conference on heavy metals in the environment - symposium proceeding. 1: 49-68.

ENGINEERING AND ECONOMIC EVALUATION OF SELECTED REMEDIAL MEASURES

W. D. Wilkins

Chief, Environmental Impact Assessment
Water Resources Branch,
Ontario Ministry of the Environment,
1 St. Clair Avenue, West,
Toronto, Ontario.

November, 1978

Restoration procedures for the English-Wabigoon system have previously been considered by Wilkins and Irwin in 1976 (report attached). The evaluation concentrated on the Wabigoon River as far downstream as Clay Lake, and Clay Lake itself -- not because there was evidence to suggest the problem was limited to that area (evidence was in fact to the contrary) but because it was considered impractical to manipulate the vast area downstream from Clay Lake.

At this time, it is still not possible to say whether or not the mercury concentration in sediment is a key factor influencing mercury levels in fish, much less what the concentrations would have to be reduced to in each lake to achieve acceptable levels in fish. For example, are the high mercury levels in fish from Umfreville Lake 130 km (80 miles) downstream from Clay Lake (Bishop and Neary, 1976) the result of methylation in its own sediments or methyl mercury produced elsewhere -- perhaps in Clay Lake?

Wilkins and Irwin estimated that there were approximately 2,700 kg (6,000 lbs) of mercury in Wabigoon River sediments above Clay Lake, and Armstrong and Hamilton (1973) estimated that the contaminated surficial sediments of Clay Lake contain 2,000 kg (4,400 lbs) of mercury. The total quantity of mercury discharged by the chlor-alkali plant at Dryden is claimed to have been about 9,100 kg (20,000 lbs). On the basis of these estimates, about 4,400 kg (9,600 lbs) of mercury have been discharged downstream from Clay Lake (not counting the 5,000 kg (11,000 lbs) of mercury used as slimicides by Ontario Minnesota Pulp and Paper at Kenora). Sediment mercury concentrations in Ball Lake (Ontario Ministry of the Environment, unpublished data) clearly show that mercury has been transported from the Wabigoon River into the English River. Concentrations in the south basin of Ball Lake, which has the Wabigoon River input and the English River output, are an order of magnitude higher than the north basin which can be considered representative of upstream English River conditions.

Reed's pulp and paper mill at Dryden continues to discharge an estimated 45 kg (100 lbs) of mercury annually (1 ppb in 30 million gallons per day of effluent). It has not yet been determined whether this amount of mercury together with resuspended instream deposits or on its own is sufficient to maintain high mercury levels in fish (there has been no significant decline in spite of plant discharge reductions).

Even when the technical questions related to mercury transport are answered there will remain questions about the objectives of any multi-million dollar restoration program. Considering that the only fishing lodge on Clay Lake is still operating at full capacity and that even after restoration, mercury concentrations in most predator fish would not likely drop below the 0.2 ppm necessary for it to become a significant long-term food source for the Grassy Narrows and Whitedog communities (based on levels in off-system lakes in the area) what benefits would accrue from restoration and to whom?

Setting aside these reservations for the moment, restoration methods for all or parts of the system will be re-examined. Very little information is available in the technical literature on large scale restoration projects. Sweden has experimented with burying and dredging, but apparently could not justify full-scale operations after consideration of the unfavourable cost-benefit ratio and the environmental impact of the restoration operations (Jernelöv and Lann, 1973; Jernelöv et al., 1975).

Japan has been dredging for the removal of contaminated bottom sediments since 1958 and on a large scale since 1971. In 1973 Japan established a tentative criterion of 7 to 40 ppm for removing bed sediment contaminated with mercury. This criterion was exceeded at 19 rivers and ports. In 1975 a tentative criterion of 10 ppm was established for removing bed sediment contaminated with PCBs. Fifty-one locations exceeded this criterion. Dredging is proceeding at an average annual rate of 700,000 m^3 and the spoils are placed in confined disposal sites usually constructed in the sea. Where polluters can be identified, they bear a portion of the clean-up cost to the extent they are responsible and the remainder is borne equally by the central and local governments. In

1976, removal and confined disposal of 700,000 m^3 of contaminated sediment from twelve ports cost 8.2 billion yen or about $40.00 Canadian/$m^3$. In some cases special dredges have been built specifically for the removal of contaminated muds and in other cases normal production dredges doing navigation channel maintenance are utilized (Peterson and Randolph, 1977).

Closer to home, New York State has undertaken pilot dredging studies to remove PCB contaminated sediment from the Hudson River. They estimate that 75% of the PCBs in a forty mile navigable section of the river, with good access to conventional marine equipment could be removed by dredging 385,000 m^3 (500,000 cubic yards) of contaminated sediment at a cost of $25 million U.S. ($50.00/cubic yard). A total clean-up of the same reach (which contains an estimated 200,000 kg (440,000 lbs) of PCBs at sediment concentrations to 1,850 ppm) has been costed at $204 million. The project is currently stalled while the state attempts to raise funds from the federal government.

In 1976, C.K. Hurst, former Chief Engineer with the Canada Department of Public Works, was asked to review the dredging aspects of the Wilkins/Irwin Report. Mr. Hurst concurred with the dredging limitations and costs expressed in the report. Based on the Japanese and American experience however, it would appear that those costs (based on $10 (Can.)/cubic yard) may not be high enough to provide adequate disposal facilities. Application of the American estimate ($50.00/cubic yard) yields a cost of $600 million for Clay Lake alone. The cost, however, could vary from $5.00 to $50.00 per cubic yard, depending on the degree of confinement required for disposal of the dredge spoil.

A different restoration technique suggested for Clay Lake was the construction of a dam at the outlet to raise water levels and erode clay from the shoreline. The theory was that wave action would erode sufficient clay to bury the mercury contaminated sediments in place. But as will be explained below, there appears to be insufficient clay in the area for this scheme. In fact there does not even appear to be any economically exploitable upland deposits of suitable clay to cover all of the 3,000 ha

(7,400 acre) lake bottom. A combination of dredging and filling would seem to be the most appropriate technique in Clay Lake. After stripping off the surface layer of contaminated sediment from shallow water borrow areas and disposing of the spoils in confined disposal sites, the underlying material could be dredged with conventional hydraulic dredges and pumped over the deeper water sediments. The costs would be in the same order as previously estimated for dredging alone. Before this option is studied further, it would be appropriate to repeat Hamilton's 1970 survey of the surface distribution of mercury in Clay Lake sediments. In 1970 the highest concentrations were still to be found in the eastern basin rather in the deep water west of the islands. The degree of redistribution since 1970 would provide necessary information on the significance of continuing inputs to the lake, the stability of in-lake sediments and the sedimentation rate. The current distribution of surface sediment mercury concentrations would be necessary to locate borrow areas and disposal sites. Soil borings would be required to determine if the clay-silt accumulations are sufficiently deep to provide the large quantities required. One note of caution is in order: any activity which disturbs the bottom sediment is likely to increase mercury levels in overlying water. Mercury levels in fish could conceiveably increase during the construction period.

Another method which has been recommended for Clay Lake is mixing the surface sediment layer with underlying sediments by some sort of underwater "plow". This technique would be very difficult to control in a lake as irregular as Clay Lake with numerous islands of outcropping rock and varying depths to 23 m (75 feet). More information on the consistency of the deep water sediments would be required to see if they could be overturned without a great deal of resuspension. The finest materials escaping from the bottom during a plowing operation would have the highest mercury concentration and take the longest time to resettle, potentially leaving little net change in surface mercury concentrations. Plowing would probably result in the highest amount of resuspension of all the methodologies examined and hence the greatest potential to exacerbate the problem. I am of the opinion that the approach does not yet merit the considerable amount of development work that would be required.

A complete environmental impact assessment would be the best course of action to compare alternate restoration methods (including the "do-nothing" alternative) if this year's study suggests there is some hope that manipulation of a manageable part of the system might yield overall benefits.

CLAY AVAILABILITY

To explore the feasibility of burying high mercury levels in Clay Lake sediments, surficial deposits in the area were examined. For a 10 cm layer of cover material the required quantity for a 7,400 acre lake is 3,000,000 m^3. The density of existing sediment in Clay Lake is a question, but in deep water it is probably very soft. Similar materials would be required for a cover that would not displace the existing material. The cover material will have to have sufficiently large particle size that it will settle out in the lake. True clay particles 0.0001 mm in diameter require 230 days to settle one foot in still water. The best material for the project would probably be unconsolidated silts and clays with particle sizes in the range of 0.01 mm to 0.001 mm.

The Ministry of Natural Resources surficial geology map S165 shows a boundary at Clay Lake between silty to sandy tills upstream and varved clay and silt downstream.

The Dryden 52F Soil Capability for Agriculture map includes the Wabigoon River from Wabigoon Lake to Quibell. Soils in the valley, according to the map, are usually class 3 (moderately severe limitations) to class 7 (no capability for arable culture). The limitations are bedrock less than 3 feet from the surface, stoniness, adverse topography, undesirable soil structure and excess water. This area around Dryden is one of the few in northwestern Ontario which supports agriculture.

Further downstream agriculture is impractical owing to the proximity of bedrock to the surface.

The 50th annual report of the Ontario Department Mines (volume L, part 2, 1941) discusses the geology of the Dryden Wabigoon area. To quote that report,"capping the Precambrian formations is a deposit of clay which in sections around Wabigoon Lake is seen to be varved, indicating the deposition of material in a postglacial lake. North and south of this clay are morainal deposits laid down by a continental glacier. All these deposits are Pleistocene in age. The clay belt covers Van Horne, the southern part of Zealand, Southworth and Satterly Townships i.e. south and east from Dryden. In places the clay capping is thick, giving rise to gently rolling to flat country; elsewhere it is thin and numerous outcrops protrude through this cover and in places form hills. Farming is practically confined to the clay belt. North and south of the clay belt area rough rugged country prevails with local relief from 100 to 300 feet". The 48th annual report of the Ontario Department of Mines (volume XLVIII, part IV, 1939) discusses the geology of the Eagle Lake area. The most notable topographic feature is a prominent ridge of drift, which is a terminal moraine extending from Eagle River to form the north shore of Eagle Lake west of Windigo Point. Even where drift predominated bedrock was sufficiently abundant to allow accurate mapping and structural interpretation. Near the railroad farmers cultivated a stiff varved lake clay which becomes extremely hard when dry.

To support the map information the Wabigoon River was inspected by air from Dryden to the confluence of the Wabigoon and English River systems at Ball Lake. No significant exposures of overburden were noted along the river or around the shores of the lake. On the south side of the river from Dryden to the Eagle River there were patches of land in cultivation but those became rare as the plane approached Quibell. Close to Dryden some grains were being produced but downstream pasture predominates, suggesting progressively severe limitations on the soil.

The Wabigoon Valley was subsequently investigated on the ground by driving and walking to areas of exposed soil. Sand and gravel pits throughout the area confirmed the glacial-drift character of the overburden. In several locations the exposed tills contained everything from large boulders to fine silts. None of these deposits would provide suitable material for cover in Clay Lake. Most of the farms in the area appear to be located on the varved clay. Rock outcrops were numerous and exposures at road cuts showed the clay to be thin and discontinuous. The clay was very hard when dry. To be able to utilize this clay as cover material, it would have to be ground down to approximately .01 mm and smaller. To acquire sufficient quantities would necessitate a large number of small pits at prohibitively expensive distances from Clay Lake. Removal of existing or potential agricultural land may be unacceptable in an area where it is so scarce.

It had previously been suggested that clay could be obtained along the shoreline of Clay Lake. To check this assumption the entire perimeter of the shoreline was visually examined from a small boat with occasional short hikes inland. The shoreline is almost entirely bedrock with some organic soils in low marsh areas around small tributaries. An exposure of varved clay was observed near the south shore access point but the occurrence of bedrock in close proximity suggests that the deposit is small and isolated.

Information on the grain size frequency of Clay Lake surface sediments has been published by Armstrong and Hamilton (1973). Eleven samples from the east basin, which is only about 10 ft. deep, were reported to be, on the average, 37% silt (range = 14-49%) and 56% clay (range = 6-67%). Eight samples from the central basin, whose maximum depth is 75 ft., yielded average values of 22% silt (range = 16-38%) and 78% clay (range = 61-84%). Four samples from the west basin yielded values of 22% silt (range = 14-28%) and 64% clay (range = 35-76%). Core samples showed that the elevated mercury levels were limited to about the top 6 cm of sediment. Unless deep cores of the lake bottom showed only a thin accumulation of clay-silt sediment, it would appear that the only exploitable deposits of clay silt in the area are those in the lake itself. A re-evaluation of the mercury distribution across the lake and with depth in the sediment would be necessary to determine the cost associated with utilizing this resource. Even if the top 6 cm or so had to be disposed of first an in-lake borrow area would be substantially cheaper to develop than any on-land borrow sites due to the cost benefits associated with utilization of all marine equipment.

REFERENCES

Armstrong, F. A. J. and Hamilton, A. L., 1973, Pathways of mercury in a polluted Northwestern Ontario lake: In Singer, P. C. (ed.), Trace Metals and Metal-Organic Interactions in Natural Waters. Ann Arbor Science Publishers, Ann Arbor, Mich., p. 131-156.

Bishop, J. N. and Neary, B. P., 1976, Mercury levels in fish from Northwestern Ontario, 1970-1975; Unpubl. report, Laboratory Services Branch, Ontario Ministry of the Environment.

Jernelöv, A. and Lann, H., 1973, Studies in Sweden on feasibility of some methods for restoration of mercury-contaminated bodies of water: Environmental Sci. & Technol. 7: 712-718.

Jernelöv, A., Landner, L. and Larsson, T., 1975, Swedish perspectives on mercury pollution: Jour Water Pollution Control Fed., 47: 810-822.

Peterson, S. A. and Randolph, K. K. (ed's.), 1977, Management of bottom sediments containing toxic substances (Proc. U.S.-Japan Experts' Meeting (2nd), Tokyo, Oct., 1976): Environmental Protection Agency (U.S.) publication no. EPA/600/3-77/083.

COMMENTS ON THE WABIGOON RIVER DREDGING PROPOSAL

W. D. Wilkins

and

S. Irwin

Water Resources Branch,
Ontario Ministry of the Environment,
1 St. Clair Avenue, West,
Toronto, Ontario.

1976

INTRODUCTION

This report briefly investigates the feasibility of dredging or treating mercury laden deposits from the Wabigoon River downstream from the Dryden Chemicals Ltd. outfall at Dryden to the outlet in Clay Lake.

Dredging

From previous core and dredge samples obtained from this system it is believed that the bulk of mercury exists in the top two inches of sediment. This premise is substantiated in a paper by Armstrong, Metner and Capel of the Fisheries Research Board of Canada on mercury levels in the sediments of Clay Lake. They stated that 90% of the mercury was contained in the top 6 cm (172 inches) of sediment in Clay Lake.

It is, however, impossible to remove only the top 6 cm of sediment with current dredging technology so costing and volume estimates are based on at least 1 ft. of sediment being removed from the streambed. Because of the extreme heterogeneity of mercury deposits located in proximity to one another, no attempt can be made to determine where dredging would or would not be needed. Consequently it is assumed that the entire length of streambed would be dredged from shore to shore.

Volume of Sediments

For estimating the volume of sediments to be dredged, the river was divided into seven sections of either different stream width or different depths of mercury deposits. The following table summarizes the calculation of volumes of sediment required to be dredged.

1. Dryden to Hwy. 17 - 17,000 ft. x 175 ft. wide x 4 ft. depth = .44 x 10^6 cu. yds.
2. Wainwright Forebay - 2,000 ft. x 600 ft. x 15 ft. deep = .67 x 10^6 cu. yds.
3. Wainwright to Mile Six - 32,000 ft. x 175 ft. x 2 ft. = .17 x 10^6 cu. yds.

4. Mile Six to Gullwing Creek - 36,000 ft. x 175 ft. x 1 ft. = .23 x 10^6 cu. yds.

5. Gullwing Creek to Eagle River - 78,000 ft. x 164 ft. x 1 ft. = .47 x 10^6 cu. yds.

6. Eagle River to -136,000 x 315 x 1 = 1.59 x 10^6 cu. yds.

7. Clay Lake - 7,400 acres = 322 x 10^6 sq. ft. x 1 ft. = 11.93 x 10^6 cu. yds.

TOTAL - 15.5 million cu. yds.

Methods of Dredging and Disposal

Clam Shell - This type of dredging has an advantage over other types, in that not as much water is removed with sediment thus facilitating transportation and disposal. However, this system of dredging in the Wabigoon River presents many problems. Access roads must be constructed along the entire length of the river. If the river is very wide (greater than about 300 ft.) then two access roads must be constructed, one on each side of the river or the wastes must be transported to shore on barges and reloaded onto trucks.

A clamshell dredge is inefficient at taking out small layers of sediments. In deeper water, control over where the clam is operating is very poor. It is estimated that to dredge the 52 miles to the inlet of Clay Lake (3.6 million cu. yds. of sediment) under ideal conditions (good access roads, nearby dump sites, no obstructions to the movement of the dredge) the Clamshell dredge could remove about 100,000 cu. yds. per year at a cost of about $10.00/cu. yd. In addition, about one million dollars will be required for access roads construction. This project would cost about $40 million dollars and take one dredge about 35 years to complete (river alone).

This method of sediment removal from the streambed could result in much contaminated material being missed or resuspended.

Hydraulic Dredging

This method of dredging sucks up the bottom deposits and transports them via pipe to disposal areas up to 1 mile away (with no additional booster pumps). The skimming operation required however, would probably pick up only ten percent solids. When disposing of these wastes, the water picked up with this sample cannot be allowed to escape without the mercury laden solids settling out. Because of the fine clay in the river bottom this settling may take longer than one month. These large volumes of slurry (36 x 10^6 cu. yd.) will need many disposal areas along the river. The disposal areas must then be dewatered and the solids allowed to dry. If resulting mercury levels in the dry sediments are not too high (0.5 ppm mercury-Provisional Guidelines for Sewage Sludge Utilization on Agricultural Lands April 11, 1975, OMAF and MOE) then reseeding may be carried out. However, if levels are greater than 0.5 ppm in the sediment then the area must be covered with uncontaminated material. Although hydraulic dredging is cheaper than clamshell dredging because of less roads, trucks, etc., the high cost of preparing, maintaining, de-watering and covering over the disposal areas will likely raise costs to the same level as those for clamshell dredging, i.e. 40 million dollars. Because an hydraulic dredge could probably remove 200,000 cu. yds./year of sediment, the time required to carry out the dredging from Dryden to Clay Lake would be about 20 years for one dredge.

Clay Lake could probably best be dredged using a mixture of clamshell and hydraulic units. However, if the hydraulic dredge is employed the amount of slurry generated would be about equal to one half the volume of the lake. Obviously this water must be treated and returned to the lake.

The costs of removing 12 million cu. yds. of material from Clay Lake would be lower than the cost for dredging in the river. The cost may be as low as $5.00 per cu. yd. or 60 million dollars and it could possibly take as little as six years for one dredge to complete the task. It is, however, very difficult to dredge in the deeper areas of the lake (up to 75 ft. deep). Special dredges would probably have to be designed to carry out the work.

Discussion on Dredging

The total cost of dredging the Wabigoon River from Dryden to Clay Lake plus Clay Lake is estimated to be $100 million. It appears that a clamshell dredging operation would not have enough quality control to insure that the mercury laden sediments are removed, and would also release mercury in greater amounts to the water to be carried downstream to Clay Lake and undoubtedly further down the system. An access road would be required over the entire length of the stream on one side and on two sides where the river is wide to carry wastes from the clamshell operation.

An hydraulic dredge has difficulty removing a constant depth of sediment where the streambed is irregular and could consequently leave many deposits of mercury untouched in the streambed.

It appears, therefore, that neither alternative presents a good method of removing mercury laden deposits from this system.

Discussion on Burying

The literature is inconclusive about the depth of covering material required. Jernelöv reported that a covering with 10 cm of clean organic sediment appeared to be effective in limiting the production of methyl mercury. Sufficient cover would have to be added to maintain 10 cm after allowing for variations in application, scour by high water velocities and by ice. It is not possible to provide such a cover in the river or in shallow sections of the lakes subject to wave action. A cover could not be maintained over organic rich sediments which produce gas as they decay. Even if it were technically feasible to place a 10 cm thick covering layer in a lake 70 ft. deep, the quantity required for 7,400 acre Clay Lake is in the order of 6 million tons. For sediment as soft as that in Clay Lake, it would also be difficult to select a cover material that would not penetrate through the surface sediments leaving the contaminants still exposed.

Discussion on Treatment in Place

Several authors have suggested treating sediment in place to control methylation by converting mercury to a "stable" form, usually a sulphide or organic complex. While these compounds reduce methylation rates they do not completely stop it under all conditions. It is not possible to state whether the reduction would be sufficient to prevent fish from accumulating unacceptable levels. Some of the treatment methods require that the sediment be picked up and put through a processing plant before being replaced -- comparable to adding treatment costs to the dredging costs.

Diversion of River

Diversion of the river past the areas where the highest levels of mercury were found has been suggested by Acres Consulting Services (Pollution of the Wabigoon River, July 14, 1972). The longest diversion suggested by Acres involved construction of a waterway of about 5 miles in length. The costs involved in the diversion are estimated to be 17 million dollars for the construction, not counting work to be done below that 5 mile section.

The possibility was investigated of diverting the outflow from Lake Wabigoon to Eagle Lake which is drained by the Eagle River to the Wabigoon River about 28 miles downstream from Dryden. The construction costs for the 7 mile diversion are estimated to be about 20 million dollars. Although the fish, sediments and water of Lake Wabigoon contain no appreciable amount of mercury, the waters have high suspended solids and turbidity levels caused by suspended fine clay.

Eagle Lake on the other hand has very low levels of suspended solids, supports a good fishery and is aesthetically very pleasing, supporting a larger cottage population than Lake Wabigoon plus several private camps. Resistance to this diversion would be extremely high from all people who make use of Eagle Lake and Eagle River. This diversion would probably have to pass through Eagle Lake Indian Reserve No. 27.

These figures presented do not include the costs of relocating existing wastewater discharge outfalls from Reed Paper Company and the Dryden STP, the compensation to the company for loss of power generation, the costs of covering over or treating the mercury contaminated riverbed that would be exposed, or in the case of Eagle Lake diversion, the compensation to the Indians for crossing their reserve. Of course it does not include the costs and effects of all work below Eagle River as previously outlined.

Viability of Restoration Proposal

Erickson Engineering Associates and John B. Herbich reported on March 24, 1972, on the feasibility of burying or dredging mercury contaminated sediments in the St. Clair System. At that time, they concluded that burying, use of littoral traps and plowing under were impractical and that enormous costs were associated with dredging.

Does inactivating the mercury in sediments to the end of Clay Lake solve the problem of availability of mercury for uptake by fish and other members of the food chain? To answer this question a quick calculation was carried out of the amount of mercury presently contained in the sediment. It was estimated that for the purposes of the calculations most of the mercury is contained in the top one foot of the sediments to the Wainwright Dam and in the top one inch to the outlet of Clay Lake. (Although the mercury is distributed throughout the top 2-1/2 inches, the greatest concentrations are contained in the surface sediments). Using mercury sediment data collected in 1974 it was calculated that 6,200 lbs. of mercury are contained in the sediments of the river. The Fisheries Research Board calculated that 4,400 lbs. are contained in the sediments of Clay Lake. In the same report the FRB estimated the total amount of mercury discharged by Dryden Chemicals Ltd. to the system between 1962 and 1969 to be upwards of 20,000 lbs.

Therefore, downstream from Clay Lake, up to 9,400 lbs. of mercury are still in the system, available for uptake by fish and aquatic biota. A very rough estimation of sediment volumes in the English River to the Winnipeg River together with mercury data collected in 1971 indicate that about 3,200 lbs. of mercury are contained in the sediments at concentrations as high as 0.99 ppm. Data from a report prepared by the MOE on mercury in Northwestern Ontario fish (1975) show that in Umfreville Lake (on the English River about 80 miles downstream from Clay Lake) 100% of Ling (2 samples), Mooneye (4 samples), Walleye (49 samples) and 40 percent of Whitefish (5 samples) contained levels of mercury in their flesh in excess of 0.5 ppm. Since these fish are located 80 miles downstream from the proposed dredging area (separated by two waterfalls between Clay and Ball Lakes) and are unlikely to migrate that great a distance they are probably picking up the high levels of mercury from deposits in or near Umfreville Lake. Consequently, eliminating mercury laden deposits to the end of Clay Lake would not likely reduce the chance of fish flesh contamination from mercury sediment throughout the rest of the system.

A YOUNG FISH SURVEY
OF THE WABIGOON RIVER - CLAY LAKE SYSTEM

1978

C. Curry

and

K. Suns

Water Resources Branch,
Ontario Ministry of the Environment,
1 St. Clair Avenue, West,
Toronto, Ontario.

January, 1979

Fish collections were made at selected sites in the Wabigoon River System in late summer of 1978 by members of the Toxicity Unit, Ontario Ministry of the Environment. The purpose was to determine the present role of the Wabigoon River in mercury contamination of Clay Lake as an aid in the discussion of remedial measures for the system currently underway by the federal and provincial governments.

Localized fish such as yearling perch provide more useful information in a section of a system then do older ranging fish. Yearling yellow perch (Perca flavescens) have been used in previous years by the Toxicity Unit for monitoring mercury levels in Ontario inland lakes. Pearl dace (Semotilus margarita Cope) were found in the Wabigoon system under conditions not favorable for other species. The population size was adequate for our use, and the species proved to be a good monitoring organism.

Sampling sites were chosen on the basis of accessibility, compatability with water sampling stations, and the presence of suitable seining conditions and fish. Wabigoon Lake and the Eagle River were chosen for background information. The other sites were to provide data on spatial variation in mercury concentrations between Dryden and Clay Lake.

The accompanying map and table show sampling locations, fish species, sample size, age, length and mean mercury concentrations. Mercury levels in Wabigoon and Eagle River confluence are significantly ($p < 0.05$) lower than those from the other sites in the system. Mercury levels in dace at the Wabigoon and Eagle River confluence are significantly ($p < 0.05$) lower than fish further downstream. This may be the result of dilution of the contaminated Wabigoon River water by the Eagle River. Future work would require a fish sample from the Wabigoon River closer to Dryden to verify this interpretation. Fish mercury concentrations in the river and at the Clay Lake inflow and outflow are similar. To determine the zone affected beyond the outflow more fish collections must be made.

To answer the question raised by the Eagle River and its possible dilution affect and for an extension of samples in the system, we suggest the following sites for next year's work:

1) a site below Dryden but east of the Wabigoon/Eagle confluence to evaluate the possible dilution effect of the Eagle River.
2) Clay Lake inflow and outflow (for confirmation of results already obtained).
3) the Wabigoon River at Jones Road near the inflow of Ball Lake.
4) both basins of Ball Lake, the northern receives the English River, the southern basin receives and discharges the Wabigoon River.
5) a site past the outflow of Ball Lake into the Wabigoon River.
6) in the river before the Separation inflow.
7) at the outflow of Separation Lake.
8) on the river east of Umfreville Lake.
9) at the outflow of Tetu Lake (Manitoba-Ontario border).

These sites are geographically and spatially located both on the system and off, allowing the determination of variation and extent of mercury contamination affecting the fish populations in the Wabigoon system. Remedial measures may or may not be feasible depending upon the extent of the mercury problem as depicted by localized fish populations.

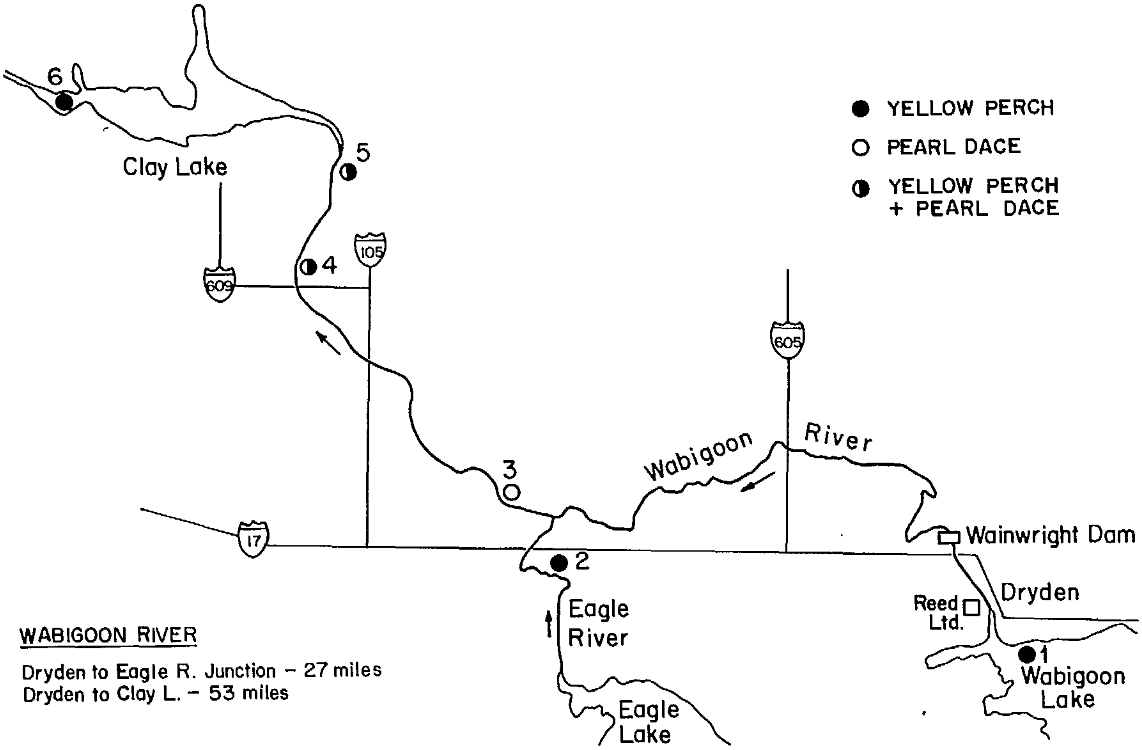
Mercury concentrations in juvenile fish
from the Wabigoon River system, 1978.

Sampling site and species*	Number** of samples	Mean Total length (mm)	Age	Mean Hg concentrations (ppm)
1) Wabigoon Lake				
yellow perch	8	56 ± 3	1+	0.03 ± 0.005
2) Eagle River				
yellow perch	7	49 ± 3	1+	0.06 ± 0.004
3) Wabigoon/Eagle				
pearl dace	7	41 ± 2	0+	0.29 ± 0.03
4) Wabigoon River (Quibell)				
yellow perch	9	56 ± 3	1+	0.43 ± 0.05
pearl dace	8	42 ± 2	0+	0.43 ± 0.04
5) Wabigoon River (1/4 mile above Clay Lake)				
yellow perch	10	56 ± 3	1+	0.41 ± 0.04
pearl dace	8	45 ± 3	0+	0.55 ± 0.08
6) Clay Lake (outflow)				
yellow perch	8	61 ± 4	1+	0.45 ± 0.1

*Scientific names:

Yellow perch = *Perca flavescens*
Pearl dace = *Margarita semotilus*

**For yellow perch, each sample was an 8 fish composite.
For pearl dace, each sample was a 10 fish composite.



Map of the Wabigoon River - Clay Lake system showing location of sampling sites and species of fish represented in the samples.