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ENVIRONMENTAL CONTAMINANTS DIVISION

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CURRENT RESEARCH

MARCH 1983

Inland Waters Directorate
Direction Générale des Eaux Intérieures

ENVIRONMENTAL CONTAMINANTS DIVISION
NATIONAL WATER RESEARCH INSTITUTE

CURRENT RESEARCH
MARCH 1983

Canada Centre for Inland Waters
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Burlington, Ontario L7R 4A6

FOREWORD

Research accomplishments of the staff of the Environmental Contaminants Division, National Water Research Institute, are reported annually in Current Research. Each study is described separately by the study team. The reports complete the annual planning cycle which is initiated with the publication of Study Plans, fifteen months prior to this report. These Study Plans say what we expect to do and why during the upcoming fiscal year. During the year, six- and nine-month reports on each study are prepared internally for management control of resources. These reports are brief and include shifts in direction or problems encountered. Finally Current Research is prepared in the last month of each fiscal year and describes accomplishments only. Current Research says what we have done and includes references to all reports or publications prepared under each study since the last issue of the previous March.

R.J. Allan

R.J. Allan
Editor

CITING PROCEDURE

Articles in this report should be cited as follows:

"Oliver, B.G. and Nicol, K.D. 1983. Chlorinated hydrocarbons in sediments and biota of the Great Lakes in Current Research, Environmental Contaminants Division, NWRI, p. 20-22 ."

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ENVIRONMENTAL CONTAMINANTS DIVISION

RESEARCH PROGRAM

by

R.J. Allan

Contamination deleteriously affects many uses of Canada's freshwater resources. Action to alleviate public concern about contamination and/or to reduce or eliminate contamination is predicated by in-depth knowledge of the fate of contaminants in aquatic ecosystems. The Environmental Contaminants Division (Tables 1 and 2) investigates five groupings of contaminants - organic chemicals, usually of industrial or agricultural origin; toxic metals; organometallics; ions associated with acid rain; and radionuclides.

Division activities are carried out in four sections (Table 1) as follows:

Organics-Pathways Section

The objective is to resolve the entry, fate, distribution, and transfer of organic contaminants in aquatic ecosystems. Research is conducted primarily at specific polluted aquatic ecosystems, but also in experimental ponds, and in the laboratory. Projects include studies in large and small river-lake systems. Atmospheric input of organic contaminants to the aquatic environment is being studied in the Great Lakes drainage basin.

Organics-Properties Section

The objective is to investigate, primarily in the laboratory, the physical-chemical characteristics of organic chemicals which govern their interactions with biota and abiotic material in aquatic ecosystems. Structure-activity (property - biological effect) correlations are established for a variety of contaminants with a view to establishing general underlying

Table 1. Environmental Contaminants Division (as of April 1, 1983)[1]

Chief - Dr. R.J. Allan - applied geochemistry
Secretary - Mrs. E.M. Kerr
Administrative Officer - Miss J. Major

ORGANICS-PATHWAYS SECTION

Head - Dr. J.H. Carey	• Photodegradation of organic contaminants.

Researchers:

Mr. M.E. Fox	• Persistent organic contaminants in aquatic ecosystems.
Mrs. J.L. Metcalfe	• Biological fate of contaminants.
Dr. E. Nagy	• Fate and effects of organic contaminants in test ecosystems.
Dr. B.F. Scott	• Fate and effect of organic contaminants in test ecosystems.
Dr. W.M.J. Strachan	• Organic contaminants in aquatic ecosystems especially rain.

Technologists:

Miss L. Coletta, Mr. J.H. Hart.

ORGANICS-PROPERTIES SECTION

Head - Dr. K.L.E. Kaiser	• Structure-activity correlations of organic contaminants.

Researchers:

Dr. R.M. Baxter	• Biochemistry and degradation products of PCBs.
Mrs. K. Kwasniewska	• Biodegradation of organic contaminants and toxicity to microoganisms.
Dr. D.L.S. Liu	• Biodegradation of organic contaminants.
Dr. B.G. Oliver	• Sources of aquatic organic contaminants; water chlorination by-products.
Dr. R.F. Platford	• Physical chemistry and contaminants enhancement in water surface films.

Post Doctoral Fellow:

Dr. J.M. Ribo	• Structure-activity correlations of organic contaminants.

Technologists:

Mr. M.E. Comba, Mrs. K.D. Nicol, Mrs. K. Thomson.

INORGANICS SECTION

Head - Dr. R.J. Maguire	• Aquatic fate of organometallics.

Researchers:

Dr. Y.K. Chau	• Chemical and biological processes of organometallics in the aquatic environment; metal speciation and toxicity.
Dr. D.S. Jeffries	• Geochemical processes controlling lake acidification; metal geochemistry
Dr. K.R. Lum	• Chemical forms of trace metals and geochemistry of particulate matter.
Mrs. A. Mudroch	• Chemical forms of trace metals in suspended solids and bottom sediment of aquatic ecosystems.
Mr. R.G. Semkin	• Geochemical processes controlling lake adicification.

Technologists:

Mr. G.A. Bengert, Miss M.D. Jones, Mr. R. Neureuther, Mr. N. Seymour, Mr. R.J. Tkacz.

RADIONUCLIDES SECTION

Head - Dr. R.W. Durham	• Impact of nuclear power development on aquatic ecosystems.

Researcher:

Dr. S.R. Joshi	• Aquatic pathways of radionuclides

Technologists:

Mr. J.A. FitzGerald, Miss E. Kokotich, Miss S. Livermore.

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[1] In 1982, ECD employed 19 summer students.

Table 2. Environmental Contaminants Division Professional Staff

Dr. R.J. Allan
B.Sc. (Aberdeen); M.S. (Wisconsin); Ph.D. (Dartmouth): D.Sc. (Aberdeen).

Dr. R.M. Baxter
B.Sc. (Mt. Allison); Ph.D. (McGill).

Dr. J.H. Carey
B.Sc. (Windsor); M.Sc. (Windsor); Ph.D. (Carleton).

Dr. Y.K. Chau
B.Sc. (Lingnan); M.Sc. (Hong Kong); Ph.D. (Liverpool); D.Sc. (Liverpool).

Dr. R.W. Durham
B.Sc. (Durham); Ph.D. (Durham).

Mr. M.E. Fox
B.Sc. (Mt. Allison).

Dr. D.S. Jeffries
B.Sc. (McMaster); Ph.D. (McMaster).

Dr. S.R. Joshi
B.Sc. (Punjab); M.Sc. (Roorkee); Ph.D. (Roorkee).

Dr. K.L.E. Kaiser
B.Sc. (Munich); M.Sc. (Munich); Ph.D. (Munich).

Mrs. K. Kwasniewska
M.Sc. (Marie Curie).

Dr. D.L. Liu
B.Sc. (Chung-Hsing); M.Sc. (U.B.C.); Ph.D. (U.B.C.).

Dr. K.R. Lum
B.Sc. (Manitoba); Ph.D. (Liverpool).

Mrs. J. Metcalfe
B.Sc. (Manitoba).

Dr. R.J. Maguire
B.Sc. (Ottawa); Ph.D. (Alberta).

Mrs. A. Mudroch
Dipl. Chem. (Prague); M.Sc. (McMaster).

Dr. E. Nagy
Dipl. Chem. (Debrecen); M.Sc. (Saskatchewan); Ph.D. (Saskatchewan).

Dr. B.G. Oliver
B.Sc. (Manitoba); M.Sc. (Manitoba); Ph.D. (Manitoba).

Dr. R.F. Platford
B.A. (U.B.C.); M.Sc. (U.B.C.); Ph.D. (Saskatchewan).

Dr. B.F. Scott
B.Sc. (Toronto); M.A. (Toronto); Ph.D. (Toronto).

Mr. R.G. Semkin
B.Sc. (Toronto); M.Sc. (McMaster).

Dr. W.M.J. Strachan
B.A. (Toronto); M.A. (Toronto); Ph.D. (Queens).

principles of properties and effects. Bulk properties such as lipid-water or sediment-water partition coefficients and processes or reactions such as hydrolysis, photodegradation and bioaccumulation are measured. The toxicity of organic chemicals to bacteria and fungi is examined. The degradation of organic chemicals is determined in controlled laboratory environments.

Inorganics Section

The objective is to determine the fate of inorganic contaminants in aquatic ecosystems. Laboratory studies on properties and transformation of various organometallics, such as organolead and organotin compounds are correlated with field measurements at polluted sites in Canada. The distribution, pathways, bioavailability and processes controlling these for toxic metals in large river-lake systems are investigated. The geochemical controls of lake acidification and the response of drainage basins to airborne deposition of ions associated with acid precipitation is studied in a calibrated watershed. Emphasis is on the spring snow melt event and on the chemistry of snow packs. The influences of acid precipitation on metal availability are examined.

Radionuclides Section

The objective is to study the behaviour in aquatic ecosystems of both naturally occurring and artificial radionuclides. Studies include the determination of pathways of radionuclides discharged to rivers and lakes during nuclear fuel cycle operations; determination of concentrations of these radionuclides in water, selected biota, and sediments to assess the radiological dose to organisms; the verification of predictive models for the dispersion of radionuclides into ground and surface water; and the measurement of concentration profiles of certain radionuclides in lake sediments to provide a time-scale for detemining the lifetimes of other contaminants in aquatic ecosystems.

Although the objectives of each Section are separated above, there is overlap between Sections. Information arrived at in one Section can be valuable to the achievement of goals in another Section. No individual project can lead to a complete modelling of the fate and impact of a contaminant released to an aquatic ecosystem. Information from several projects can lead to such predictions and to the modelling of the future fate of contaminants in already polluted aquatic ecosystems.

APPROACH TO THE ISSUES

Toxic Chemicals

Toxic contaminant research is often referred to as toxic substance characteristics in the terminology of international and national agencies dealing with toxic chemicals control. The Division program determines such characteristics. The meaning of the term characteristics can best be described by dividing into two sub-categories. These are: (1) field characteristics of chemicals in actual polluted aquatic ecosystems (i.e., data describing the real fate and actual factors and processes controlling this fate in such ecosystems), and (2) laboratory characteristics such as physical-chemical properties, laboratory tests of aquatic toxicity, bioaccumulation, biodegradation and related parameters (i.e., data which may help to allow prediction of aquatic ecosystem fate of toxic chemicals).

The emphasis of the aquatic science, toxic chemical research in ECD is (1) above because most of the issues NWRI has to respond to concern how to manage already polluted river-lake ecosystems or systems with a potential for pollution. The prime example is the Great Lakes but others are the Wabigoon River System; the Churchill-Nelson Diversion; the Fraser River; the North Saskatchewan; the Shubenacadie Headwaters Lakes etc. Specific answers to chemical specific questions at these sites could never be adequately resolved by laboratory testing alone. The types of scientific questions resolved concern the effect on chemical fate of particulate-water interactions; biota-water-particulate interactions; air-water interactions and degradation processes and products. Identification of chemicals is an additional aspect of the field programs. Laboratory tests are conducted to complement or enhance conclusions arrived at by the extensive field programs necessary for resolution of specific recommendations as to control of effluents or changes in basin water management practices.

The Division is also involved in the determination of laboratory characteristics as mentioned under (2) above to: (a) help resolve conclusions arrived at from field operations as to processes controlling fate and thus exposure of chemicals; (b) help develop and standardize new techniques for laboratory testing of physical-chemical properties; (c) to provide physical-chemical and various biodegradation, bioaccumulation, aquatic toxicity parameters on high priority chemicals, where the measurements are unique and not of a routine nature.

For any specific chemical, the research results on toxic chemical characteristics in actual polluted ecosystems and the laboratory determined "properties" or "characteristics" are interpreted and published in the scientific literature where they are used to make specific recommendations on specific issues and as input to the chemical Assessment process.

ECD initiates its specific or chemical specific research on the basis of internal and external stimuli. Internally the scientific decisions are often supported by an external agency or public interest. The field sites which receive intensive investigation usually become obvious because of public concern about pollution issues such as has occurred at sites mentioned earlier. Chemical priorities usually also become rapidly evident because of the concerns about water pollution by specific chemicals. Examples are Dioxins because of the waste dumps near the Niagara River; chlorinated benzenes, for the same reason; PCB's and toxaphene because of their levels in Lake Superior fish; mercury because of its presence in the Wabigoon River and Churchill-Nelson Diversion and so on. There are thus major overlaps between basin management issues *viz* toxic chemicals and priority chemicals *per se*.

The research information produced by the Division can in itself be valuable in substantiating recommendations for water management actions in polluted river basins. These actions may involve control of effluents, banning of chemicals, guidelines for consumption of biota or water, and many other procedures which can be implemented in Canada. Data may be valuable in negotiations on water quality matters either interprovincially or internationally. Much of the published information is equally valuable as part of the total input required for toxic chemical assessments. Various actions on the control of chemicals are usually the result of extensive, iterative assessment procedures. ECD does not by any means supply all the information required. Input from many other disciplines and agencies is required, particularly those dealing with aquatic and mammalian toxicology.

Acid Rain

The Division program aims at understanding the geochemical controls or buffers to acid precipitation in stream-lake systems. For this purpose, mass balance models are based on sampling of a calibrated watershed located near Saulte Ste. Marie. The basin research is managed by a Steering Committee presently chaired by Dr. D. Jeffries of ECD. The basin contains seven lakes interconnected by streams. The work is in association with extensive programs of other agencies in uding CFS, DFO, NHRI, and Lands Directorate. The data derived from this multi-agency, multi-disciplinary research is complementary.

Most studies of acid rain deal with the effects of acid rain. The Division aim in the watershed is not to measure effects but to resolve: (a) long-term rates of acidification, and (b) buffering processes. The goal is to define how fast a river-lake system becomes acidified and what characteristics control this rate. The results are expected to lead to a better calculation of how the basin can withstand, for how long, the ionic species associated with acid rain and what parameters control this. Extrapolation to larger areas may then be feasible and airborne emission control requirements more accurately defined.

COMMITTEE INVOLVEMENT

Committee involvement by ECD personnel is listed in Table 3. Of note: Dr. R.J. Allan and Mrs. A. Mudroch continued to be involved with the Canada-U.S. Niagara Study Committee. Dr. Allan continued as Co-Chairman of the Canada-Ontario Steering Committee supervising research to ameliorate the mercury pollution problem in the English-Wabigoon River system of northwestern Ontario. Dr. D.S. Jeffries (Chairman) and Dr. R.J. Allan continued to serve on the Algoma Watershed Acid Rain Research Steering Committee. Dr. Allan and Dr. W.J.M. Strachan served on the Great Lakes Water Quality Toxics Contaminant Committee; Dr. W.J.M. Strachan continued as Chairman of the Great L kes Water Quality Agreement, Aquatic Ecosystems Objectives Committee. Dr. Strachan continued to serve on the Organization for Economic Cooperation and Development Chemical Testing Program Committee on Test Guidelines. Dr. R.J. Maguire served on the National Research Council Environmental Secretariat Panel on Aminocarb, and on the Environmental Contaminants Act Chemical Evaluation Committee. Dr. Y.K. Chau served on the Natural Sciences and Engineering Research Council of Canada, Environmental Toxicology Panel. Dr. Y.K. Chau and Dr. R.J. Maguire served on the National Research Council Committee on Scientific Criteria for Environmental Quality, dealing with organotins. Dr. J. Carey is co-leader of an internal NWRI group integrating chemical and physical data so as to model the fate of contaminants in Lake Ontario.

Table 3. ECD Committee Involvement

1.	NWRI Management Team	Allan, R.J.
2.	Canada/Ontario English-Wabigoon Mercury Study	Allan, R.J.
3.	Canada/U.S. Niagara River Study	Mudroch, A./Allan, R.J.
4.	NWRI Niagara River Study Group	
5.	GLWQA Toxic Contaminant	Allan, R.J./Strachan, W.M.J.
6.	Algoma Watershed Acid Rain Steering	Jeffries, D.S./Allan, R.J.
7.	OECD Chemical Testing Program	Strachan, W.M.J.
8.	GLWQA Aquatic Ecosystem Objectives	Strachan, W.M.J.
9.	DOE/NHW Toxic Chemical	Strachan, W.M.J.
10.	Environmental Monitoring of Forest Insect Control	Maguire, R.J.
11.	NRC Environmental Secretariat Panel on Oganotins	Maguire, R.J./Chau, Y.K.
12.	ECA Chemical Evaluation	Maguire, R./Strachan, W.M.J.
13.	GLWQA Capital Equipment	Carey, J.H.
14.	CCIW Dioxin Working Group	Carey, J.H.
15.	IJC - SAB Task Force on Non-Phosphate Detergents	Kaiser, K.L.E.
16.	Ontario Region, EARP	Durham, R.W.
17.	IJC Radioactivity Working Group GLWQA	Durham, R.W.
18.	NSERC Environmental Toxicology Panel	Chau, Y.K.
19.	Standards Council of Canada	Chau, Y.K./Liu, D.S.
20.	ASTM Oxygen Uptake Group	Liu, D.L.S.
21.	UN-FAO Marine Fouling Group	Liu, D.L.S.
22.	International Standards Organization	Scott, B.F.
23.	DOE Ontario Region - Environmental Emergency Team	Scott, B.F.
24.	AGRAD Wroking Group on Fate of Oil	Scott, B.F./Nagy, E.
25.	CCIW Open House	Platford, R.F.
26.	CCIW Capital Equipment Replacement	Lum, K.R.

Acronyms:
NWRI = National Water Research Institute;
GLWQA = Great Lakes Water Quality Agreement;
OECD = Organization for Economic Cooperation and Development;
ECA = Environmental Contaminants Act;
DOE = Department of the Environment;
NHW = National Health and Welfare Department;
NRC = National Research Council;
CCIW = Canada Centre for Inland Waters;
IJC = International Joint Commission (U.S.-Canada);
SAB = Science Advisory Board;
EARP = Environmental Assessment and Review Process;
NSERC = National Sciences Engineering and Research Council;
ASTM = Analytical Standards for Testing of Materials;
UN-FAO = United Nations - Food and Agriculture Organization.

FUTURE DIRECTIONS

The present ongoing activities of the Division and the philosophy behind them have been briefly described above. Shifts for 1983/84 and the immediate future are described below.

The Division program is an integral part of work conducted under the Great Lakes Water Quality Agreement. The major site of interest has been the Niagara River and Lake Ontario. Additional work in this area will continue but research will be initiated in 1983/84 on the contaminant problems in the Detroit River/Lake St. Clair/Lake Erie system. A study group, led by Dr. Y.K. Chau has been established to coordinate ECD projects. Research on atmospheric deposition of chemicals will continue but with the focus on toxaphene in Lake Superior.

The research on the fate of chlorophenols and other chemicals in Canagagigue Creek, Grand River Basin, will be reduced to a minimum and the conclusions arrived at will be the basis for more contaminant fate research in regions on river systems such as the Fraser in B.C.; the North Saskatchewan in Alberta; the Qu'Appelle in Saskatchewan; and the St. John in New Brunswick. Likewise, the toxic metals fate research, so far focused on the Great Lakes, will be expanded to involve the arsenic/acid mine drainage issue problem in the Schubenacadie Headwaters Lake system of Nova Scotia. The radionuclides pathways research program which has also been focused on the Great Lakes and in Ontario will be extended to include research near major uranium deposits and mining operations in northern Saskatchewan.

In terms of laboratory characteristics, emphasis on Structure-Activity Relationships will shift from toxicology using fish to the development of simpler, more rapid toxicity tests using lower organisms. Determination of specific physical-chemical properties of chemicals for assessment purposes will focus, if feasible, on those chemicals with which there are existing concerns, e.g., chlorinated di-benzo dioxins and furans; PCBs; chlorinated benzenes and phenols; toxaphene; organotins; alkyl leads; methyl-Hg; tri-aryl phosphates; Cd; As; Pb.

The acid rain program will de-emphasize the intensive sampling program because three years of data will be on file by 1984. A shift towards investigation of processes such as aging of snow packs and aluminum shock will be made. The funds saved by refining the intensive sampling operations will be used to employ

Post Doctoral Fellows with required specific expertise to resolve key process questions.

The Division will continue to actively seek external funding to support our program. There were three such sources of support in 1982/83: the Great Lakes Water Quality Toxic Contaminant Program (GLWQA); the Long-Range Transport of Atmospheric Pollutants Program (LRTAP); and the Toxic Chemicals Management Program (TCMP).

HIGHLIGHTS 1983/84

The remainder of this issue of Current Research consists of brief descriptions of the scientific advances made in each ECD project. Some figures and tables are included to give an idea of the type of information contained in the many papers and reports published by the Division and in the documents produced by committees on which Division staff serve. As an introduction to the individual reports, some highlights of and interconnections between individual reports follow:

(1) A Special Issue of the Journal of Great Lakes Research dealing with the Niagara River-Lake Ontario Pollution Problem is scheduled for publication in May 1983. Of the 23 papers in the issue, 12 are authored or co-authored by Division scientists. Many of these papers were first presented at the 1982 Conference of the Association of Great Lakes Research, held in Saulte Ste. Marie. Results are described in research reports by Kaiser and Comba, Oliver and Nicol, Fox _et al._, Lum, Maguire _et al._, Mudroch, Durham _et al._, and Joshi _et al._, and Joshi. Significant findings include the apparent recent reduction in loading to Lake Ontario of several toxic organic chemicals and toxic metals; the presence of a suspended sediment enriched Nepheloid layer extending tens of meters above the bottom of Lake Ontario and possibly of significance to chemical persistence in the lake, and the concentrations of contaminants in various lower organisms which may control chemical bioaccumulation via food webs.

(2) Organotins and other organometallics are being increasingly discovered in several Great Lakes media using newly developed analytical methods (Chau et al. and Maguire et al.). The occurrence of diethyl-, triethyl-, and tetraethyllead in fish caught in contaminated areas has been reported for the first time (Chau et al.). Laboratory tests were conducted to provide data for prediction of organometallics persistence in aquatic ecosystems.

(3) The use of complex computer programs to calculate various bond strengths of toxic organic chemicals is being correlated by Kaiser et al. with toxicity data for lower organisms (Liu et al.; Kwasniewska) to advance the use of Structure Activity Correlations as a means of assessing the dangers of specific chemicals.

(4) Physical-chemical processes such as sediment-water (Strachan) and lipid water partition (Platford) coefficients have been determined to assist in resolution of the fate of old and new chemicals in aquatic ecosystems. Biodegradation (Liu et al.) and photodegradation processes are studied in the laboratory for the same reason.

(5) Through investigations of bioaccummulation of toxic organic chemicals, leeches (Metcalfe et al.) which are common in Canadian rivers, have been shown as potential biomonitors. Sampling has been conducted in WNR, OR and Atlantic Region.

(6) A sampler has been designed and tested (Strachan) for use in measurement of toxic organics in precipitation. The potential is for this or a more advanced model to provide more accurate measurements of the role of the atmosphere in the fate of contaminants loaded to or volatilized from aquatic ecosystems.

(7) The degradation of 2,4-D (Scott et al.) has been resolved in experimental ponds and found to be primarily photochemically induced and that disappearance is relatively rapid.

(8) The bacterial biodegradation steps for PCB are shown to be complex, involving sequential separate processes and resulting in an as yet identified as a yellow substance (Baxter and Sutherland).

(9) A Report Series on research results from the Turkey Lakes, acid rain, calibrated watershed has been launched by the Steering Committee (Jeffries). The release of acidifying ions from the snowpack is dependent on the amount of rain and the rate of snowmelt (Jeffries _et al_.; Jeffries and Semkin).

(10) Studies of bioaccumulation and bioavailability have been conducted at polluted sites and in the laboratory. At the Niagara River inflow area of Lake Ontario, amphipods have been shown to be active bioaccumulators (Fox _et al_.). In the laboratory, tests of organic chemical bioaccumulation by oligochaetes have begun (Oliver and Matteliano). In Hamilton Harbour, iron oxides have been found to control the bioavailability of lead, zinc and chromium in sediments (Lum).

(11) Radionuclide trends in the Great Lakes continue to show decline (Durham _et al_.) but point sources may still cause input from groundwater leaching of landfills (Durham, Bobba and Fitzgerald).

(12) The effects of dredging and dredge disposal were assessed by examining harbour and lake sediment from the Great Lakes for contents of hydrocarbons (Nagy) and toxic metals (Mudroch; Lum).

(13) The factor controlling accumulation of chlorophenols in freshwater biota has been identified as water concentrations rather than the food chain (Carey _et al_.).

(14) The photochemical degradation of the lampricide TFM, which was predicted from previous laboratory studies, was confirmed both in a field test pond (Scott _et al_.) and in sampling of a stream during treatment (Carey _et al_.).

A. PRIMARILY FIELD PROJECTS DEALING WITH THE NIAGARA RIVER POLLUTION PROBLEM AND FATE IN POLLUTED AQUATIC ECOSYSTEMS OF CHLOROPHENOLS, CHLOROBENZENES, VOLATILE ORGANICS, TOXIC METALS AND RADIONUCLIDES

ROLE OF SUSPENDED SOLIDS IN BENTHOS UPTAKE OF ORGANICS, NIAGARA RIVER MOUTH

by

M.E. Fox, J.H. Carey, B.G. Oliver, D.M. Whittle,
J.L. Metcalfe, H. Huneault, L. Coletta and K.D. Nicol

INTRODUCTION

In the first year of this study 1981/1982 the role of suspended solids in organochlorine compound loading from the Niagara River to Lake Ontario was investigated. High levels of ten chlorobenzenes, hexachlorobutadiene and PCBs were found on suspended solids from the river, with highest levels on the larger particles. Sediments, benthic fauna and fish were collected in Lake Ontario in the vicinity of the Niagara River. A relationship was found to exist between river suspended solids, Lake Ontario surficial sediments and some benthos (amphipods) for the compounds studied. A trend toward greater bioaccumulation for compounds having higher octanol-water partition coefficients was observed at all trophic levels.

In 1982/83 the study was divided into two parts:

(1) A surficial sediment, benthos and fish study as in 1981/82 designed to investigate the fate of two different classes of organochlorine compounds in the receiving zone, namely chlorobenzenes and chlorophenols (CB's and CP's). Preliminary results and theoretical considerations indicate that their uptake into benthos and fish from sediments and water should be very different with consequent insights into the processes of bioaccumulation.

(2) An attempt to determine the fate of dissolved organochlorine compounds in Lake Ontario from the Niagara River. Previous analysis of filtered and unfiltered water from the Niagara River have shown that most of the CB's are in the dissolved form.

This part of the study consisted of intensive sampling of filtered and unfiltered water on a fixed grid in the region of the Niagara River plume in Lake Ontario while APSD staff, as part of a complementary study, concurrently followed and plotted the course of the plume by the use of drogues.

It was expected that a comparison of the spatial distribution of dissolved CB's with the corresponding physical dimensions of the plume would reveal typical solution loading profiles of Lake Ontario from the Niagara River.

RESEARCH RESULTS

Surficial sediment, interface water, benthos and fish were collected from five sites in Lake Ontario near Niagara River mouth and a reference site in the western basin in July 1982 and again in September 1982 with the addition of an extra site further east of the Niagara River mouth.

Amphipods and oligochaetes were sorted from the benthos in sufficient quantity for chlorobenzene and chlorophenol analysis. The surficial sediments were collected in quadruplicate at each site in September in order to investigate homogeneity.

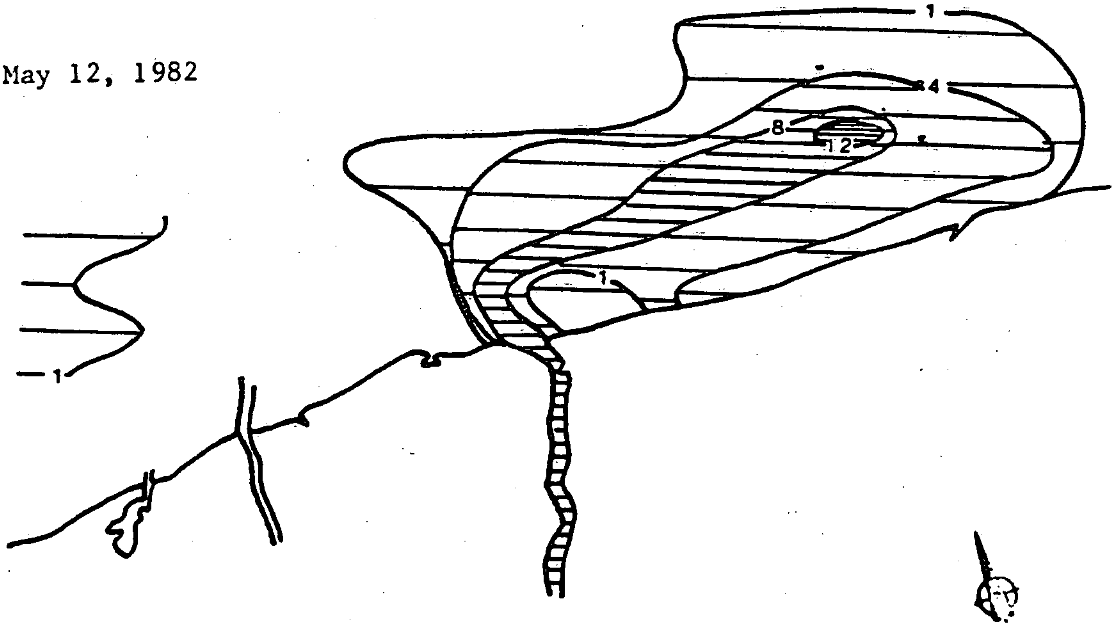
Chlorobenzene levels were higher in amphipods than in oligochaetes and poorly correlated with sediment CB levels as found in 1981/82 whereas chlorophenols exhibited a very different pattern with much higher levels in oligochaetes than amphipods (2 ppm for 2,4,6-triochlorophenol) and little correlation between these high level and sediment levels.

The relationship between bioaccummulation of these two classes of compounds in the Niagara River plume will be examined in detail when all the analyses are completed.

Filtered and unfiltered water (1 L) was collected at 37 sites on a fixed grid covering much of the predicted path of the Niagara River plume on seven occasions between April and November 1982. The water was sampled at 1 m on all occasions and below the thermocline, when it existed. The samples were extracted <u>in situ</u> and subsequently analyzed for chlorobenzenes. EBT and transmissometer profiles were obtained at each site and samples were also collected for Cl^- and SO_4^{--} analysis. Plume tracking by means of drogues was carried out concurrently by APSD staff who also made continuous weather observations.

Although most CB's were detected, the 1 L sample size dictated by logistical considerations made plume concentration

May 12, 1982



October 4-5, 1982

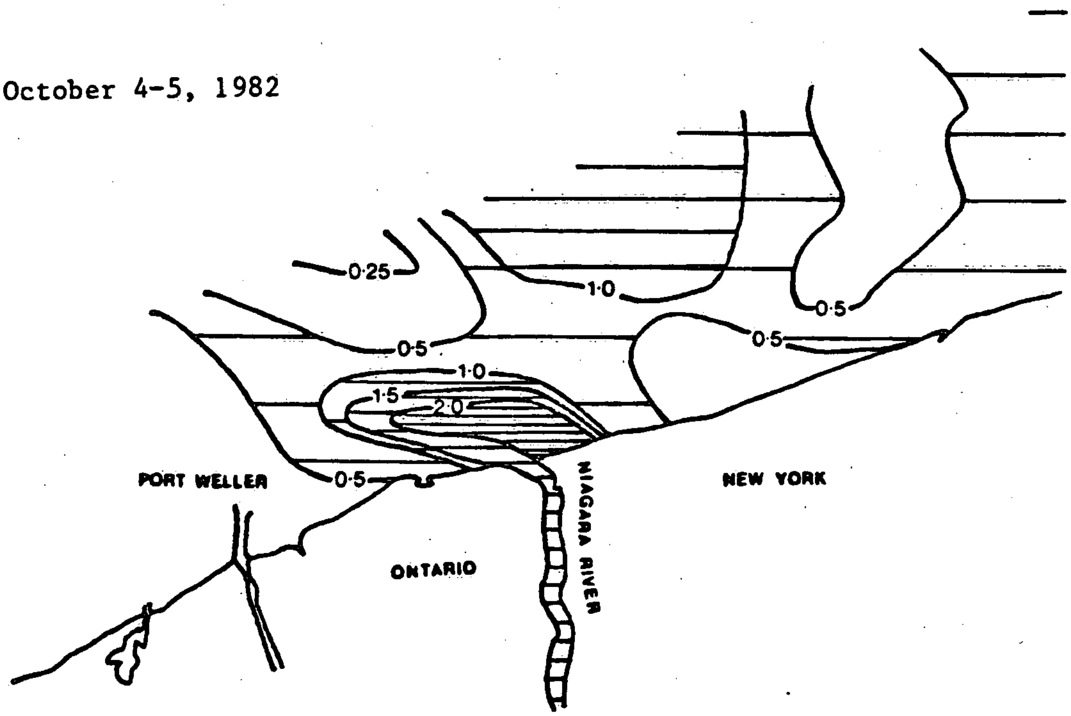


Figure 1. 1,2,3,4-TETRACHLOROBENZENE ng/L in the Niagara River plume (unfiltered, 1m)

profiles difficult to construct for several CB's. 1,2,3-TCB and 1,2,3,4-TTCB were selected to illustrate transport of CB's in solution by the plume. Figure 1 shows the 1 m profiles of 1,2,3,4-tetrachlorobenzene in the plume under westerly and easterly wind conditions in May and October 1982. Drogue tracking and transmissometer data showed essentially the same pattern. The similarity of concentration in filtered versus unfiltered water indicated that most of the CB's were present in the dissolved phase.

In 1983/84 larger samples of water (~10 L) will be processed by gas stripping and sorption onto traps in situ. A finer scale grid will be sampled also. These refinements in addition to monitoring the Niagara River mouth for short term variability of CB levels are expected to produce useful information on the loading profiles of Lake Ontario from dissolved contaminants in the Niagara River.

PUBLICATIONS

1. Fox, M.E., Carey, J.H. and Oliver, B.G. Compartmental distribution of organochlorine contaminants in the Niagara River and the Western Basin of Lake Ontario. J. Great Lakes Res. (In Press).

2. Fox, M.E. and Joshi, S.R. The Fate of Pentachlorophenol in the Bay of Quinte, Lake Ontario. To be submitted to J. Great Lakes Res.

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ORGANIC CONTAMINANT SOURCES AND SINKS IN THE NIAGARA RIVER AND IN LAKE ONTARIO

by

K.L.E. Kaiser and M.E. Comba

INTRODUCTION

A large number of potentially harmful toxic substances has been identified in water, sediments, and biota of the Great Lakes. In particular, the Niagara River contains high levels of many of such compounds and it is important both to determine their sources and pathways in the aquatic system. This study is part of the effort to address these questions.

RESEARCH RESULTS

In collaboration with scientists at the University of Illinois, Drs. R. Kaminsky and R. Hites, sediment samples from Lake Ontario were analyzed by gas chromatographic-mass spectrometric methods. A number of highly chlorinated derivatives of benzene, styrene, anthracene, phenanthrene and pyrene (aromatic hydrocarbons) were identified as well as trifluoromethyl-substituted benzene derivatives. The origin of the former remains to be determined - some are not commercially produced - while the latter have previously been identified in waste dumps near the Niagara River and are thought to originate there (1).

A survey of volatile contaminants in Lake Ontario was completed during the fall of 1982. The results show several areas of elevated levels of certain volatile chlorocarbon compounds (Fig. 1). The data have been combined with those previously obtained from the Niagara River and are showing the influence of the Niagara River and other tributaries on Lake Ontario (2).

Because of the high sensitivity and simplicity of the headspace analytical technique (3) it has been found useful to determine contaminant concentrations also in different water layers in other lake and river water studies. At present, results are being analyzed of a study of the Niagara river plume in Lake Ontario (4).

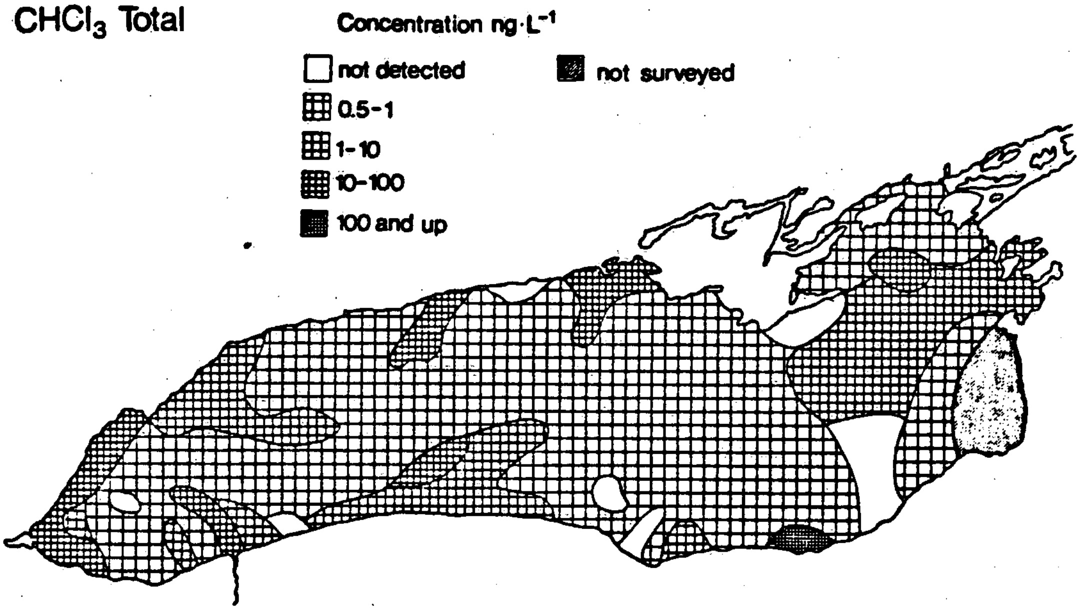

Figure 1. Distribution of total chloroform in Lake Ontario water (from Ref. 2).

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CHLORINATED HYDROCARBONS IN SEDIMENTS AND BIOTA OF THE GREAT LAKES

by

B.G. Oliver and K.D. Nicol

INTRODUCTION

The study of environmental contaminants in transboundary waters is one of the priorities of Environment Canada. We have done a considerable amount of work in the Niagara River/Lake Ontario vicinity, a location where there has been considerable public concern in recent years. Our studies have focused on current and historic loading patterns, and on bioconcentration by fish and benthic invertebrates of chlorinated hydrocarbons. Most of the compounds under study are by-products of chemical manufacturing along the river.

RESEARCH RESULTS

After method development[2,3] we studied the history of contaminant loadings to Lake Ontario by sediment core analysis[6] (see Durham _et al_. for this report) and the compartmental distribution of these contaminants[5] (see project 220 for detailed results). Over the past year and a half we have analyzed weekly, 16 liter, water samples from the Niagara River at Niagara-on-the-Lake for approximately 25 chlorinated compounds. In addition, contaminants on settling particles (collected in sediment traps in Lake Ontario ≈10 km from the river mouth) and in surficial sediments from throughout Lake Ontario have been analyzed. The results of these studies will be the subject of future reports.

The uptake of ten chlorobenzenes, hexachlorobutadiene, and hexachloroethane by rainbow trout from water at environmental levels (ppt) has been studied with A. Niimi (Great Lakes Fisheries Research Branch)[7]. The uptake of the chemicals by the fish is strongly correlated with the chemical's octanol-water partition coefficient - the higher the partition coefficient the higher the exception of hexachlorobenzene (HCB) reached a constant equilibrium value in the fish within a few weeks. Using the BCF's from the lab experiments and measured concentrations of the chemicals in Lake Ontario we attempted to predict the chemical concentrations in field rainbow trout from Lake Ontario (see Table). An excellent agreement between predicted and measured environnental residues is obtained for all compounds except HCB. This prediction does not work for HCB because the chemical has a long half-life in the fish and thus never reaches equilibrium with the surrounding water.

Table: Use of laboratory BCF's and chemical concentrations in Lake Ontario waters to predict residue levels in Lake Ontario rainbow trout.

Compound	Concentration Lake Ontario Waters* (ng/L)	Predicted Concentration in Fish (ng/g)	Mean Concentration Lake Ontario Fish (ng/g)
1,2,4-TCB	0.6	0.8	0.6 ± 0.3
1,2,4,5-TeCB	0.1	0.5	0.5 ± 0.2
1,2,3,4-TeCB	0.1	0.5	1.0 ± 0.4
QCB	0.2	2.6	3.4 ± 1.3
HCB	0.06	0.7	33 ± 15
HCBD	0.05	0.3	0.2 ± 0.08
HCE	0.2	0.01	0.03 ± 0.02

* Reference 1.

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HYDROCARBONS IN LOWER GREAT LAKES SEDIMENTS

by

E. Nagy

INTRODUCTION

Surficial sediment samples from lakes St. Clair, Erie and Ontario, and from small-craft harbours on the Canadian shores of these lakes were analysed for hydrocarbon contents. The work was part of a larger survey of various contaminants in these sediments which may affect dredging and dredge disposal in the area (Thomas, Mudroch, 1979).

Hydrocarbon distributions in the lake sediments were similar to the patterns shown by other contaminants. Generally, low concentrations were found in the high energy inshore zones, while the distributions in the lakes followed the outlines of the sedimentary basins. Hydrocarbon concentrations were found to be low in Lake St. Clair, intermediate in Lake Ontario, and highest in Lake Erie. The heaviest contamination for the whole region was shown in the western end of Lake Erie, where even the shallow inshore zone contained high hydrocarbon levels. The distribution for Lake Erie, shown in Figure 1, indicates major inputs from the Detrot River.

The UV and IR spectra of the sediment extracts indicated petroleum-type hydrocarbons in the majority of the samples. More complex mixures were shown in a few areas, such as a dumping site in Lake Erie.

The survey of the small-craft harbours showed hydrocarbon concentrations exceeding 1000 $\mu g\ g^{-1}$ in the sediments of only two: Wheatley in Lake Erie and Portsmouth in Lake Ontario. Even in these harbours, hydrocarbons were found to be highly localized in well protected mooring areas.

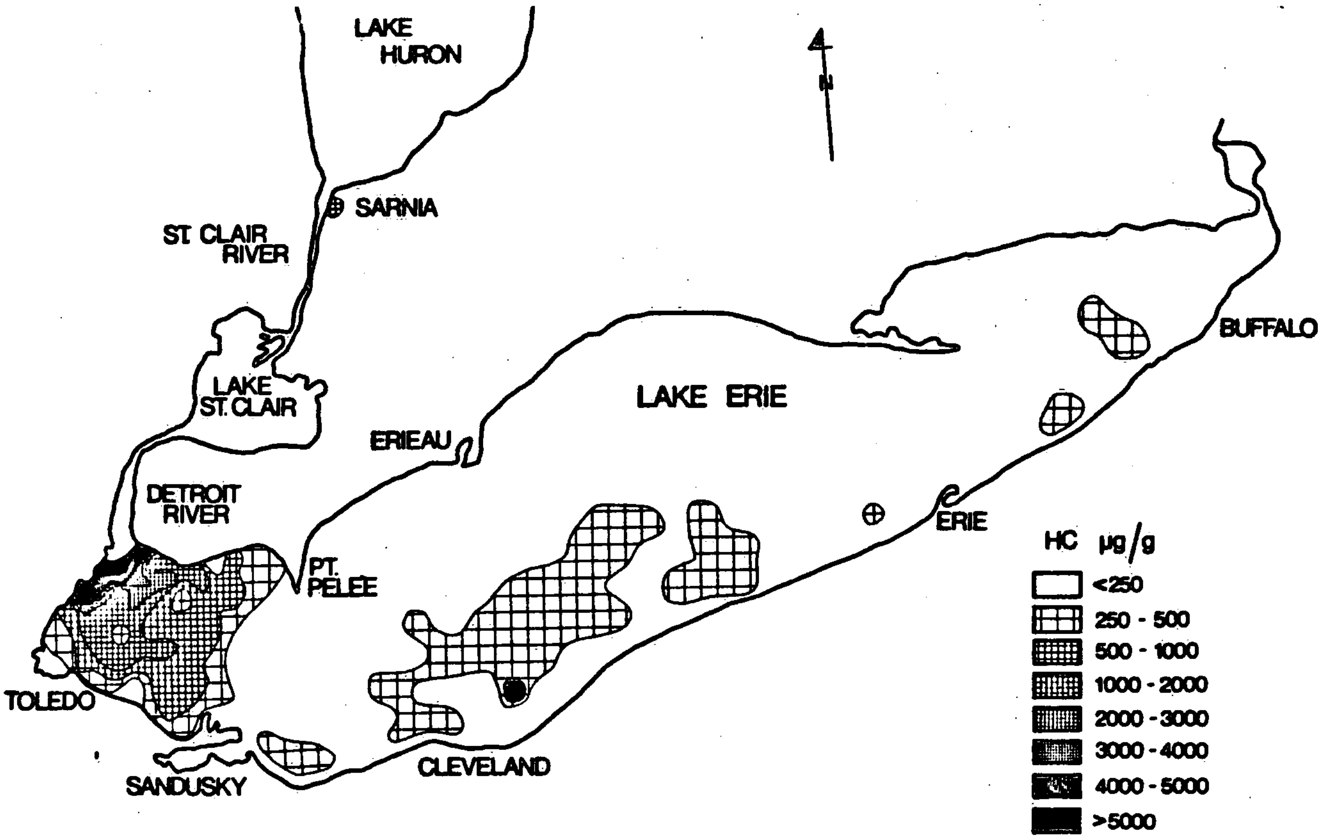

Figure 1. Hydrocarbons in Lake Erie sediments

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HEAVY METAL CHEMODYNAMICS IN THE NIAGARA RIVER PLUME

by

A. Mudroch

INTRODUCTION

A comprehensive investigation of toxic chemicals in the Niagara River began in 1981. This included identification of direct municipal and industrial discharges to the river and those from major toxic waste disposal sites. Earlier pollution concerns in the river included bacterial contamination, phenol problems, and elevated concentrations of Fe, P and Hg. Present investigations are focused on organic toxic substances and metals in the Niagara River and in Lake Ontario, in particular in the Western Basin, their pathways and effects on the ecosystem (1).

Studies carried out in 1982/83 on metal concentrations and characteristics of sediment in the Western Basin of Lake Ontario indicated a major transport of metals originating from the Niagara River and associated with clay- and silt-size particles, towards the north-east-north and east of the river mouth (2). Determination of organic compounds in sediment in the Western Basin of Lake Ontario revealed the presence of various organic contaminants such as aromatics, polynuclear aromatics, alkylated polynuclear aromatics, alkylated benzenes, phthalates, methyl esters, olefines, aldehydes, chlorobenzenes, benzyl esters and benzoates (3). A presence of a nepheloid layer in Lake Ontario was demonstrated (4). By vertical mixing of the Lake and upwelling particles, the nepheloid layer may play an important role in the transport of contaminants across the entire lake.

Based on information obtained during 1982/83 on sediment contamination in the Niagara River and at the river mouth, a study was carried out on the affect and availability of sediment associated contaminants from the Niagara River mouth area on Lake Ontario natural phytoplankton population.

Further investigation was carried out on the relationship between contaminants and various properties of sediments from the Niagara River to identify the best procedure for standardizing contaminant concentrations for comparative purposes.

RESEARCH RESULTS

Bioassays were carried out with the liquid phase of the standard elutriate test performed on freshly collected sediment. The impact of elutriated sediment-associated contaminants from the Niagara River mouth and from a mid-lake station in Lake Ontario on various size assemblages of natural plytoplankton was determined (5). The C^{14} fractionation bioassays indicated that the addition of Niagara River mouth elutriate from which dissolved metals were removed enhanced the C^{14} uptake when compared to the elutriate containing dissolved metals (Figure 1). On the other hand elutriate obtained from a mid-lake sediment containing dissolved metals induced higher C^{14} uptake than that without dissolved metals (Figure 2). A number of past studies showed that the form of metals play a significant role in the growth rates of phytoplankton, for example, that ionic Cu is more toxic than organically-bound Cu or stable Cu complexes. With the exception of Mn, all dissolved metals concentrations were higher in the elutriate from the Niagara River mouth. Although the concentration of organic contaminants in the elutriates was not determined, it is known that sediment at the Niagara River mouth contains a number of organic contaminants and the possibility of their elutriation has to be considered. It was concluded that at least two types of synergistic effects such as nutrients/metals and metals/organics interaction affected the C^{14} uptake. The inhibition of photosynthesis indicated community stress due to pollutants; however, some species were more affected than others. These changes of the phytoplankton community induced by the sediment-associated contaminants are not desirable in an ecologically balanced ecosystem and may alter the sensitive equilibrium of the food-chain dynamics.

A data set obtained by determination of about 50 contaminants in 150 Niagara River sediment samples was analyzed (6). The sediments were a heterogeneous group with a wide range of grain size distributions and other physical and chemical properties. Correlation between each individaul parameter and a) content of 63 µm particles and b) volatile solids was investigated. A regression was performed and percent variability attributable to the parameter R^2 (i.e, 63 µm particle size fraction or volatile solids) was determined. It was found that metals in the sediment were more correlated with volatile solids than the organic contaminants. The organics correlated with volatile solids were the most common contaminants (polynuclear aromatics, phthalates) found in the river sediment. The correlation between the < 63 μm particle size fraction and most of the contaminants was much poorer than that with the volatile solids. These findings indicated a different mechanism of sediment-contaminant association in the River than that found in the past in Great Lakes basins. It was proposed to carry out the standardization of the data set for the river sediment only for the parameters showing significant correlation with volatile solids. This method should improve the identification of pollution sources and processes of contaminant transport by the Niagara River.

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RADIONUCLIDE PATHWAYS IN THE NIAGARA RIVER

by

S.R. Joshi, R.W. Durham, E.A. Kokotich,
S. Livermore and J.A. FitzGerald

INTRODUCTION

Nuclear fuel reprocessing activites at NFS, Inc., located 65 km upstream of Lake Erie (in West Valley, NY, U.S.A.) started in 1966. Though the NFS ceased fuel reprocessing in 1972, storing of spent fuel continued until 1976. Evidence of former reprocessing activities at West Valley has been found in sediment and fish samples from the Cattaraugus Creek. Limited amount of available data suggests that very low levels of transuranium isotopes are reaching the receiving Lake Erie waters. The present study was initiated to determine the inputs, if any, of these radionuclides to Lake Ontario via the Niagara River. Initially it was planned to measure the ^{239,240}Pu profiles in ^{210}Pb-dated Lake Ontario sediments. Various isotopes of uranium and thorium as well as ^{241}Am and ^{244}Cm were subsequently added in the investigations.

RESEARCH RESULTS

The measurement of these radionuclides in sediment required the availability of a reliable method for their simultaneous determination at extremely low levels. A literature survey revealed that no simple method is available for this purpose. Experiments were, therefore, initiated to evaluate the existing few procedures. These experiments have resulted in the development of a method for the measurement of ^{238,239,240}Pu, ^{241}Am, ^{244}Cm, ^{210}Pb, ^{228,230,232}Th, and ^{234,235,238}U using the same subsample. The method involves the leaching of all isotopes with hot, concentrated HNO_3 following determination of ^{210}Pb and ^{228}Th by gamma-ray spectrometry. The radioisotopes are then selectively absorbed on LaF_3 from the diluted leachate. The fluoride precipitate is re-dissolved in 5 M HCl saturated with

$AlCl_3$ and, following adjustment of their oxidation states, individual isotopes are separated using a liquid ion exchanger and various strippants. The fluoride precipitate can also be dissolved in very dilute HNO_3 and radionuclides of interest can be extracted quantitatively into tri-n-octylphosphine oxide. Individual radionuclides are then separated using an anion-exchange technique. Sources suitable for alpha-particle spectrometry are then prepared by precipitating the separated radionuclides with microgram amounts of LaF_3.

The entire wet chemical procedure can be completed in about two days and yields results comparable to those involving much more complex chemical separations and time-consuming electrodepositions. The application of this technique to the determination of radionuclide levels in sediment cores collected from five locations in Lake Ontario commenced in March, 1983.

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5. Durham, R.W. and Joshi, S.R. Concentrations of Fallout Radionuclides in the Open Waters of the Great Lakes. (To be submitted to Environ. Monit. & Assessment).

B. PRIMARILY FIELD PROJECTS DEALING WITH CONTAMINANTS IN THE GREAT LAKES, INCLUDING NEARSHORE/OFFSHORE STUDIES; PRECIPITATION; GROUNDWATER; HARBOURS; FOR TOXIC METALS, ORGANOMETALLICS, AND RADIONUCLIDES

TRACE METAL BIOAVAILABILITY

by

K.R. Lum

INTRODUCTION

Current models/conceptions of the rules of trace metals in vivo indicate that nutritive and toxic effects and assimilability all depend on the chemical form and availability of the metals. From the perspective of availability, the determination of metals in a dissolved state or those metal forms which can be readily desorbed or solubilized from particulate matter are clearly important factors in assessing the impact and degree of hazard of metals in the environment. In addition, data on metal concentrations in the water column provide information on actual environmental exposure to biotic systems including man.

RESEARCH RESULTS

Eight sediment cores were obtained from Hamilton Harbour during 1982 to determine the impact of metal inputs on the distribution of their chemical forms in harbour sediments. Some of the results to date are shown in Table 1 in which the vertical distribution of nine elements at two sites is compared. The data for Windermere Basin suggests that metal inputs from the Hamilton STP and Red Hill Creek have significantly decreased, the maxima being observed between 6 to 12 cm. These results may be related to the start up of operation in 1964 of the primary treatment plant and the introduction of secondary treatment in 1973. In contrast, the sediment layers in the deepest part of the harbour reflect dumping of a significant fraction of the spoils from the harbour and the associated shipping channels prior to World War II (25 to 28 cm depth) and continuing contaminant inputs to the present. The dominant solid phase controlling the availability of Pb, Zn and Cr in the sediments at Station 258 are Fe-oxides (Table 2). The role of Fe-oxides is less important for the Windermere Basin sediments which are likely the result of higher organic loadings from the

Table 1

Vertical Distribution of Selected Elements in a Core from the Deepest Point of Hamilton Harbour (Station 258). Concentrations in μg g^{-1} or dry wt % where indicated.

Section	Co	Zn	Cd	Fe	Mn	Pb	Cu	Ni	Cr
0 – 2 cm	60	5460	21	10.8%	3760	780	220	90	370
2 – 4 cm	60	6020	27	13.9%	4770	920	210	85	430
4 – 6 cm	54	5810	22	13.2%	5160	1150	200	95	495
6 – 8 cm	40	1660	10	7.2%	2630	330	90	50	165
8 – 10 cm	30	620	7	4.4%	1530	140	55	35	80
15 – 18 cm	40	450	13	4.3%	1630	110	50	55	135
25 – 28 cm	20	245	4	2.6%	1140	65	40	245	570
45 – 50 cm	30	250	5	3.4%	1075	60	50	420	1210

Vertical Distribution of Selected Elements in a Core from Windermere Basin, Hamilton Harbour. Concentrations in μg g^{-1} or dry wt % where indicated.

Section	Co	Zn	Cd	Fe	Mn	Pb	Cu	Ni	Cr
0 – 2 cm	18	1420	9.1	3.6%	860	440	270	85	535
2 – 4 cm	37	2310	9.4	4.9%	1000	850	530	120	1045
6 – 8 cm	37	2460	33	5.6%	1120	1750	600	120	1165
9 – 12 cm	40	3220	19	4.9%	1015	1110	860	130	1690
20 – 25 cm	22	1900	12	3.4%	825	700	380	105	950
50 – 55 cm	47	3480	15	5.6%	840	860	610	150	1015

Table 2

Correlations Between Selected Elements and Iron Extracted in Fraction C

Sample Set (N)	Pb versus Fe γ^2/Slope	Zn versus Fe γ^2/Slope	Cr versus Fe γ^2/Slope
Hamilton Harbour Station 258 (8)	0.88/0.006	0.83/0.080	0.95/0.005
Windermere Basin (6)	0.77/0.017	0.94/0.036	0.90/0.018
Hamilton Harbour SPM (7)	0.99/0.035	0.84/0.039	0.79/0.011

Hamilton STP. The slopes of the linear regression lines indicate variable sorption capacities for the three elements with the Fe-oxides at station 258 having a maximum binding capacity of 8% whereas for suspended particulate material in the harbour, the capacity is, at most, 4%.

The results of a joint study with IWD-Ontario Region of contaminant dynamics in the Niagara River are being summarized in preparation for publication. Samples of suspended particulate material were collected at five stations during May, July and October (Figure 1) and subjected to a seven-step sequential chemical extraction procedure. The results show that inputs of Zn, Cd, Cr, Mn, Be, Co, Pb and Cu are introduced to the Niagara River at or below mile 20.5 (Grand Island) and mile 19.3 and that in general larger amounts of metals originate on the U.S. side of the river. In contrast, phosphorus follows the reverse pattern with highest concentrations measured at the Lake Erie end. The data for the sum of the readily available fractions and the fraction bound to Fe- and Mn-oxides generally follows the pattern for total metal concentrations.

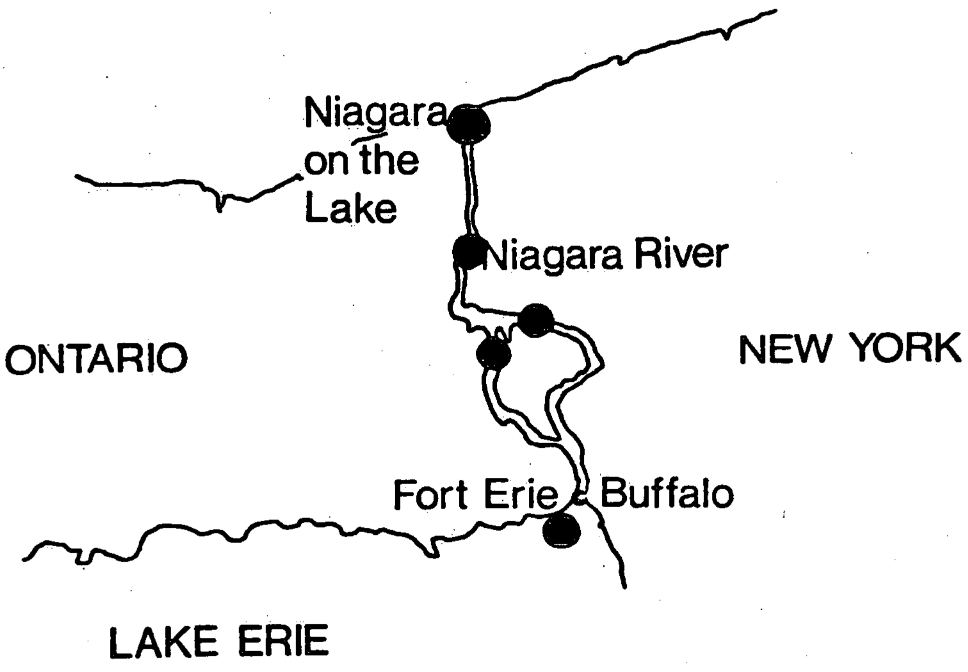

Figure 1. Niagara River Sample Sites

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RADIUM PATHWAYS FROM PORT GRANBY WASTE MANAGEMENT SITE TO LAKE ONTARIO

by

R.W. Durham, A.G. Bobba and J. FitzGerald

INTRODUCTION

Wastes from the refining of uranium at Eldorado Nuclear's Port Hope plant have been placed in landfill trenches on top of the bluffs at Port Granby for many years. Runoff from the site carried ^{226}Ra and other contaminants into Lake Ontario until 1977 when all runoff was collected behind two dams and processed to remove ^{226}Ra before being released to the lake. This study involved determining the extent of leaching of contaminants by groundwater and subsequent transport through the regional aquifer to the lake. A two-dimensional transport model has been developed to predict future leaching from the site based on measurements of groundwater flow and concentrations of contaminants.

RESEARCH RESULTS

Measurements of ^{226}Ra concentrations in shallow piezometers (2 m) along the beach in front of the bluffs continue to show very low concentrations of ^{226}Ra except near the centre of the site where seepages from above the till layer escape from the bluff face. In this area a seasonal variation in concentration has been detected with peaks occurring in both seepage and groundwater during spring runoff. Although ^{226}Ra values are now quite low, maximum to about 30 pCi/L, high concentrations of nitrate and uranium have been measured in piezometers at the east and west ends of the site. More piezometers have been installed to locate these contaminant plumes more precisely and two deep piezometers have been installed (10 m) to determine whether leachate has penetrated the till layer and contaminated the regional aquifer. Preliminary results show very low levels of ^{226}Ra in groundwater samples from these deep piezometers.

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TRENDS IN RADIOACTIVE CONTAMINANTS OF THE GREAT LAKES

by

R.W. Durham, S. Livermore, E.A. Kokotich and B.G. Oliver

INTRODUCTION

Radioactivity levels in the Great Lakes are a concern for most of the 30 million people in the Basin who get their drinking water from the Great Lakes. Inputs come from weapons testing fallout and operation of the nuclear fuel cycle in the Great Lakes Basin. Currently there is 14.8 GW of installed electrical generating capacity on the shores of Lakes Michigan, Huron, Erie and Ontario, with an equivalent amount in the construction phase. Uranium mining and milling operations are carried out at Port Hope on the north shore of Lake Ontario with wastes being landfilled at nearby Port Granby. These wastes are leached through groundwater to the lake. Water and fish samples are collected annually from the lakes and radionuclide concentrations measured in order to determine trends, radiological dose to the population and bioaccumulation factors for fish. Measurements of radionuclide concentration variations with depth in sediment cores are used to determine age profiles of the cores.

RESEARCH RESULTS

All the Great Lakes, except Michigan, were sampled during 1982 at three stations in each lake. Fifty-litre water samples were collected at the surface and near the bottom at each station and most have been analysed for ^{3}H, ^{90}Sr, ^{137}Cs, ^{125}Sb and ^{238}U. Fish samples from Lakes Huron and Ontario have been provided by Great Lakes Fisheries Research Branch and analyses of these for ^{137}Cs, ^{226}Ra and ^{238}U have started. Results of the analyses of the 1981 sampling program were published during 1982, the average values of radionuclide concentrations for each lake is given in Table 1. ^{3}H values were highest in the western basin of Lake Ontario and probably reflect the continuous input of ^{3}H from the nuclear generating station at Pickering near Toronto. Bioaccumulation of ^{137}Cs in fish was determined and the bioaccumulation factor was higher for walleye at 7500 compared with 1500 for rainbow trout although both were lower than those found in 1980.

The radiological dose to individuals drinking Great Lakes water is essentially all due to fallout ^{90}Sr. The annual dose commitments calculated from the ^{90}Sr concentration for 1981 were Lake Superior - 0.06 mrem, Lake Huron - 0.10 mrem, Lake Michigan - 0.08 mrem, Lake Erie - 0.09 mrem and Lake Ontario - 0.10 mrem. These values are all less than the 1 mrem water quality objective for radioactivity in the Great Lakes Water Quality Agreement for 1978.

Table 1. Mean Radionuclide Concentrations in the Great Lakes - 1981

Lake	^{3}H pCi L^{-1}	^{137}Cs pCi L^{-1}	^{125}Sb pCi L^{-1}	^{90}Sr pCi L^{-1}	U μg L^{-1}
Superior	168±74	0.047±0.005	0.02±0.01	0.40±0.04	0.16±0.02
Michigan	180±74	0.039±0.005	0.02±0.01	0.53±0.10	0.38±0.05
Huron	264±74	0.034±0.005	0.03±0.01	0.68±0.06	0.26±0.04
Erie	230±74	0.020±0.005	0.03±0.01	0.60±0.07	0.43±0.07
Ontario	366±76	0.026±0.005	0.02±0.01	0.69±0.18	0.50±0.08

^{210}Pb, ^{137}Cs and chlorinated hydrocarbon profiles were determined for a sediment core taken from Lake Ontario about 3 km from the mouth of the Niagara River. An age profile was constructed from the radionuclide data and used to determine historic trends of chlorinated hydrocarbon input to Lake Ontario. The sediment record of chlorobenzenes, chlorotoluenes, hexachlorobutadiene, octachlorostyrene, mirex and PCB's is in good agreement with known production and usage patterns of these chemicals. Inputs of chlorinated hydrocarbons continue but at a much lower level than in the 1960's as Figure 1 shows.

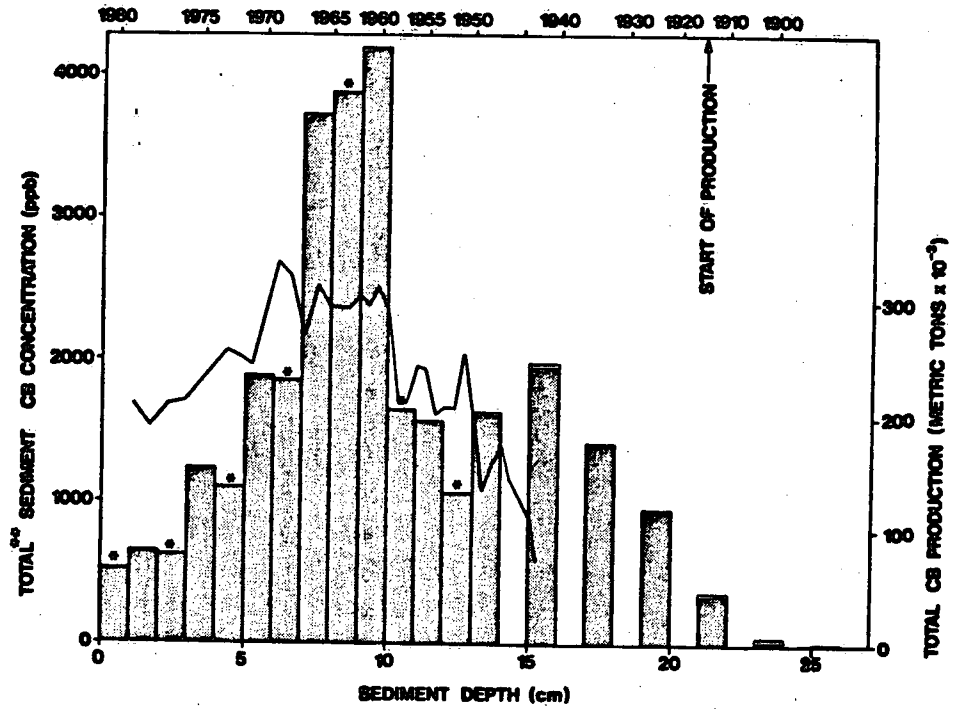

Figure 1. Historical record of chlorobenzene concentrations in Niagara River mouth sediment core

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FATE OF ORGANOTINS IN WATER

by

R.J. Maguire

INTRODUCTION

Organotins are toxic chemicals which are used extensively as polyvinylchloride heat and light stabilizers, catalysts and pesticides. Little is known of their occurrence in the environment and, in particular, their aquatic fate. For these reasons, organotins are on Canada's Environmental Contaminants Act Category III list (information required on occurrence, fate and toxicity).

The goal of this study is to determine the persistence and fate in aquatic ecosystems of a representative organotin biocide, bis(tri-n-butyltin) oxide (TBTO). The plan was to examine (1) hydrolysis, (2) photolysis, (3) volatilization, (4) adsorption to sediments, (5) microbial transformation, (6) accumulation in algae and fish, and to do (7) preliminary sampling of 50 sites in Ontario and Quebec (water, sediment, surface microlayer, algae and fish), and (8) based on (7), to select a specific site at which to conduct a detailed investigation of the persistence and fate of butyltins.

RESEARCH RESULTS

Studies (1) and (3) were completed last year.

TBTO in water undergoes slow ($t_{\frac{1}{2}}$ 89 d) photolytic decomposition in sunlight, at least partially by stepwise de-butylation to inorganic tin. In water, in the dark at 20°C, TBTO is chemically stable and does not volatilize over a period of at least two months. At 20°C, its aqueous solubility is 0.7 to 7 mg/L at pH 5 to 7, its log K_{OW} is 3.2 at pH 6, and its vapour pressure is estimated to be 6.4×10^{-7} mm Hg. These facts indicate that TBTO may be at least moderately persistent in water.

A method was developed for the analysis of butyltin species and inorganic tin in sediments, and the presence of these compounds in sediments in Canada was reported for the first time. The table below shows the most significant results.

Table. Butyltins in Sediment (mg/kg dry weight)

Location	$[Bu_3Sn^+]$	$[Bu_2Sn^{2+}]$	$[BuSn^{3+}]$	$[Sn^{4+}]$
Lake St Clair (Marina)	0.1	0.07	0.02	0.1
Port Dover Harbour	0.1	0.06	0.09	0.3
Grand River (Mouth)	0.03	0.01	0.1	0.2
Toronto Harbour	0.5	0.3	0.6	5.1
Whitby Harbour	0.1	0.05	0.01	0.1
Kingston Harbour	0.4	0.01	-	1.6

Toronto Harbour contained the highest concentration of tributyltin of any sediment collected, about 0.5 mg/kg. Tributyltin is the most toxic of the butyltin species to aquatic biota, with an LD_{100}^{12d} value of 5 μg/L for rainbow trout yolk sac fry. The toxicological significance of high concentrations of Bu_3Sn^+ in sediment has yet to be established; however, it is worth noting that the Bu_3Sn^+ concentration in subsurface water of Toronto Harbour was 0.8 μg/L.

Tributylmethyltin and dibutyldimethyltin were found in the sediments of some of the harbours shown in the table above. Thus it appears that (i) not only can Bu_3Sn^+ and Bu_2Sn^{2+} be methylated in aquatic environments, but that (ii) methylation may be a significant pathway of transformation for Bu_3Sn^+ and Bu_2Sn^{2+} since the concentrations of their methylated derivatives ranged from 4 to 124% of the concentrations of the parent compounds.

This report deals with studies (1), (2), (3), (7) and (8). Toronto Harbour was chosen as the detailed study site. In FY82/83, research will focus on studies (4), (5), (6) and (8).

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HEAVY METAL METHYLATION PROCESSES IN THE AQUATIC ENVIRONMENT

by

Y.K. Chau, G.A. Bengert, P.T.S. Wong and A.J. Carty

INTRODUCTION

There is a widespread usage of organolead and organotin compounds in industries, agriculture and commercial applications but very little is known of their environmental fate. Metals and organometals in the environment undergo biotic and abiotic interactions resulting in the formation of organometallic compounds. In these processes, not only the toxicological behaviours are altered (1), but the mobilization and transport patterns are also changed. To study the fate of these compounds under aquatic conditions and the mediation of biological systems are of prime importance in understanding their distributions and pathways. Recent publications (2,3) on the occurrence of organotin and organolead in environmental samples further necessitate the need to study their transport mechanisms and their speciation in the ecosystem (4,5).

RESEARCH RESULTS

1. Survey of occurrence of methyltin species in environmental samples. Two field trips were completed in June and in August 1982. About 400 samples of water, sediment, fish and aquatic weeds were collected at locations associated with organotin usage (harbours and industrial area). Analysis of these samples is in progress.

2. Studies of the chemical and biological methylation of Sn(II) and Sn(IV) compounds are in progress. Pure chemical system using carbonium and carbanion donors indicated that Sn(II) salts can be methylated by carbonium ion (CH_3^+). More biological work is underway to substantiate some early findings and to verify some inconsistent results.

3. A breakthrough has been achieved in the analysis of the highly ionic dialkyllead and trialkyllead salts in water with detection limit of 0.01 µg/L with 1 litre of water sample (6). The method involved chelation/extraction of the polar alkyllead species with NaDDTC (sodium diethyldithiocarbamate) and benzene, followed by butylation of the extract with n-butyl Grignard reagent. The butyl derivatives so formed have adequate boiling points for GC-AAS analysis. Other tetraalkyllead species and lead (II) are co-extracted and can be determined simultaneously (Fig. 1). Modifications of the technique for fish and sediment analysis have been completed. Both diethyllead and triethyllead have been found for the first time in fish caught in Maitland areas which also contained tetraethyllead (Table 1). Such findings are highly significant in the study of the metabolic pathways and toxic mechanisms of tetraethyllead in fish and in the environment. the degradation (dealkylation) of tetraethyllead in fish was not known before because of the lack of methodology for these polar alkyllead species.

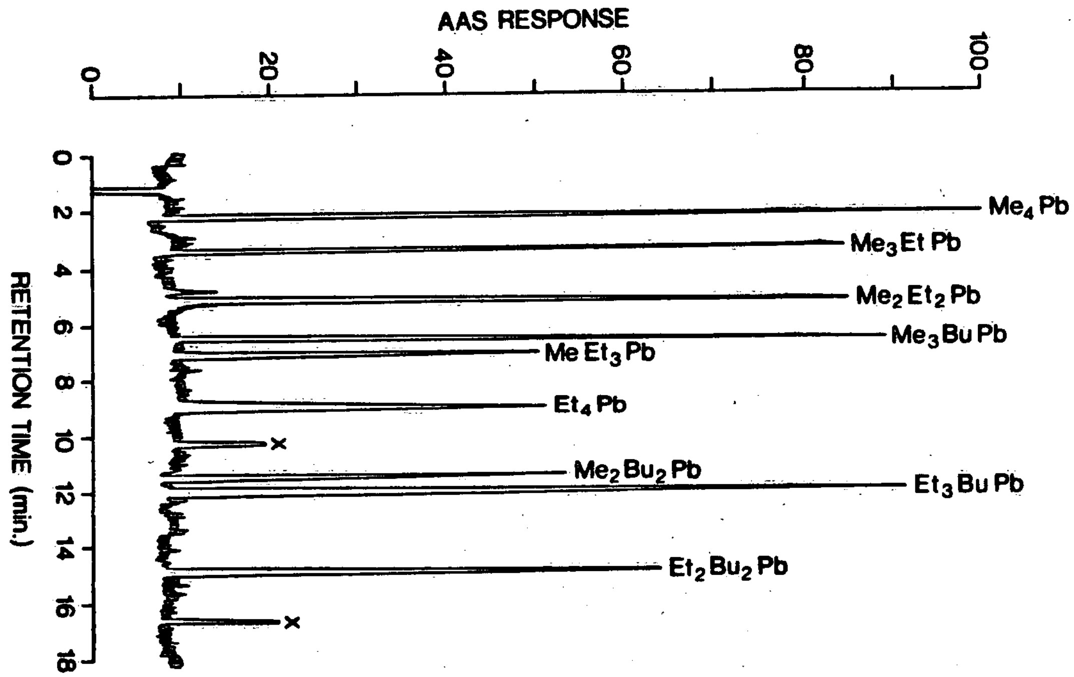

Figure 1. Gas chromatography-atomic absorption spectrometry of five tetraalkyllead compounds (10ng each); four butyl derivatives of dialkyl- and trialkyl-lead (8ng each) and Pb# (15ng) x - unidentified lead compounds (Chau _et al._, 1983.

Table 1 Organolead species in fish (Maitland, Ontario)

Fish	Me_3EtPb	Me_2Et_2Pb	$MeEt_3Pb$	Et_4Pb	Me_2Pb^+	Et_3Pb	Et_2Pb^{2+}	Total Pb wet weight	Blood Pb
Carp	33	152	1759	11299	0	5252	44	6250	15000
	0	0	508	8360	0	23300	346	7508	14000
White	0	0	7	147	0	281	0	1820	650
Sucker	0	0	27	584	0	610	0	1188	770
N. Pike	0	0	0	0	0	78	0	1477	570
	0	0	0	117	0	168	0	4200	130

Analysis was done on whole fish (less intestines); results expressed in ng/g wet weight (as Pb). Total Pb was done by acid digestion of fish followed by furnace AAS. Certain volatile lead alkyls may not be included in the results.
Blood was extracted from live fish (data source, P.V. Hodson) and determined as total lead.

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TOXIC SUBSTANCES IN PRECIPITATION

by

W.M.J. Strachan

INTRODUCTION

Atmospheric deposition of persistent organic chemicals has been identified as a major pathway for the entry of such substances to the Great Lakes system and elesewhere. PCB's and DDT are substances which have been severely limited or banned from North American usage for more than ten years and yet they continue to appear in rainfall. A need was indicated, therefore, to precisely determine the levels of such chemicals in order to provide information necessary to locate sources and determine trends.

RESEARCH RESULTS

An automated rain sampler was designed, built and evaluated as a collecting and concentrating device for persistent organic chemicals in rain. It consists of a large teflon coated funnel (0.209 m^2) with a teflon-faced, automated lid and a teflon column containing XAD-2 or 7 resin. The sampler was tested for recoveries (average 86%) and for field precision with a number of organochlorine pesticides and PCB's frequently found at the nanogram per litre level in rain. Observed levels for triplicate samples collected in the field are shown in Table 1 for two test locations - Fifty Mile Point near Hamilton, Ontario and Turkey Lakes near Sault Ste. Marie, Ontario. Samples were collected during 1981.

Other organochlorine pesticides were observed but not at levels or at frequencies of occurrence for the above substances. These others included dieldrin, γ-chlordane, pp'-DDT, endosulfan and endrin. In addition, pesticides looked for but not found included hexachlorobenzene, heptachlor epoxide, α-chlordane, pp'-DDE, pp-TDE, mirex and methoxychlor.

Table 1. **OC and PCB Concentrations in Rain Samples at 50 Mile Point (50) and Turkey Lakes (TL)**

Sample Number	Volume (litres)	α-BHC	Lindane	PCB's
		ng/L (% coef. var.)		
50-1104	0.42			61(66)
50-1404	2.1	35(49)	7(20)	9(98)
50-2404	2.1	38(15)	11(15)	11(9)
50-2804	2.2	29(29)	10(28)	22(16)
50-0505	1.0	10(31)	5(35)	32(45)
TL-0206	18.	5(3)	1(4)	1(36)
TL-0406	3.2	28(31)	7(60)	8(28)
TL-0906	4.2	48(14)	11(47)	3(20)
TL-1806	22.	19(39)	7(51)	1(65)
TL-1007	15.	32(31)	9(14)	2(33)
Average coeff. Var. %		(27)	(30)	(42)

During FY 1983-4 the samplers are being deployed on two islands in Lake Superior with the intent of evaluating the rainfall deposition of toxaphene and other organochlorines which have been implicated there as atmospheric transport polluants.

C. PROJECTS DEALING PRIMARILY WITH THE FATE OF ORGANIC CHEMICALS IN FLUVIAL SYSTEMS OTHER THAN THE GREAT LAKES

ACCUMULATION/DEGRADATION OF ORGANIC CONTAMINANTS IN FLUVIAL SYSTEMS

by

J.H. Carey, M.E. Fox, J.L. Metcalfe,
H. Huneault and L. Coletta

INTRODUCTION

In order to assess the risks posed by contaminants in the aquatic environment, there is a need for more detailed information concerning the pathways of accumulation and degradation of thse compounds. While much useful knowledge can be learned through laboratory research in this area, complementary studies of the behaviour of contaminants in real situations are also necessary.

In this study, laboratory investigations of specific modes of degradation (e.g., photochemical) are coupled with field work both at the Canagagigue Creek site and at other locations across Canada.

RESEARCH RESULTS

At Canagagigue Creek, work was concentrated upon identification of the routes of chlorophenol bio-accumulation and disappearance as well as benzothiazole disappearance from the stream. With regard to chlorophenol bio-accumulation, it now appears that food-chains are unimportant in determining the levels of chlorophenols in an organism, and that concentrations in most aquatic organisms are in equilibrium directly with water concentrations. Such factors as organ weight and outer covering appear to be controlling the extent of accumulation. Investigations of the disappearance of chlorophenols from the stream reveal only a weak seasonal fluctuation in rate although levels vary occasionally by more than two orders of magnitude. Accumulation of chlorophenols in macrophytes revealed that despite the fact that most chlorophenols appear to be dissolved and do not accumulate in the sediment, rooted plants contained higher levels than algae, periphyton, moss and duckweed. This will be investigated further in greater detail in the coming year prior to the writing of the second Canagagigue report which will be concerned exclusively with chlorophenols.

The disappearance rates of substituted benzothiazoles were much more variable than those of the chlorophenols. The results may indicate that MMBT and its oxygen containing derivatives are produced in the stream by non-chromatographable precursors. The route of formation of the oxygen containing MMBT derivatives is still unknown. Degradation studies of benzothiozole sulfenamides and of MMBT failed to produce these compounds. Further work will concentrate on identifying the source of these compounds.

Samples from the Qu'Appelle system were analyzed for chlorophenols and part of this system contains significant levels of pentachloro- and related phenols. This system may form a useful western complement to Canagagigue in the future.

In addition to photolysis of benzothiazoles, photodegradation studies of dissolved humics were carried out. In this latter study, superoxide was found to be a product of the photolysis of aquatic humus. This species may be responsible for a variety of indirect photoreductions of contaminants in natural waters.

Finally, studies of the fate of TFM were continued. Several large ponds, treated with this chemical, as part of study 82-223 confirmed the predicted degradability of this compound. The identification of the impurities of this compound is nearly finished. When the studies of the indirect photolysis are finished in the coming year, our degradation studies of this compound will be complete. An invited presentation was made to the Great Lakes Fishery Commission concerning our work on this compound.

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ACCUMULATION AND EFFECTS OF CONTAMINANTS IN AQUATIC BIOTA

by

J.L. Metcalfe, J.H. Carey, M.E. Fox, P.A. Coletta,
D.R. Barton and J. Madill

INTRODUCTION

Toxic substances have been identified as a top priority national problem. IWD research needs related to the behaviour of toxic substances in the environment have been addressed by this project in three areas: Measurement - the development of biological indicators for monitoring water quality; Dynamics - the bioaccumulation pathways for toxics; and Effects - the impact of toxic substances in biological components of the ecosystem.

This new study is a part of Canagagigue Creek Project in which the fate and effects of organic contaminants, particularly chlorophenols, are under investigation. A 1981 survey of chlorophenol residues in the benthic community revealed that leeches had a high bioaccumulation potential for these compounds. Research goals in 1982-83 were to define the bioconcentration curves for the various species, to identify the factors responsible for this high bioconcentration capacity, and most importantly to evaluate the potential of using leeches as biological indicators or "sentry" organisms.

A 1980 fish census of the creek revealed that most species avoided the highly contaminated areas, and that specimens of at least one species (rock bass) caught in these areas tended to be in poor condition. These findings suggested that chronic effects of contaminants on the fish population might be occurring. As tests with the sensitive early life stages of fish are known to provide good estimates of potential long-term hazards of chemicals to fish, such tests were conducted with an indigenous species.

The routes of accumulation of contaminants are of considerable interest. Using a common test organism, the rainbow trout, the uptake of chlorophenols from water into fish was investigated. The distribution of chlorophenols among the various organs was also examined.

RESEARCH RESULTS

Freshwater leeches from Canagagigue Creek were found to contain residues of chlorophenols one to two orders of magnitude higher than most other benthic invertebrates (Table 1).

Table 1. Chlorophenol levels in biota and water from CN-3 and CN-5 on Canagagigue Creek.

	Chlorophenol concentration (ppb)			
Sample	2,4,6-TCP	2,4,5-TCP	2,3,4,6-TTCP	PCP
CN-3; Sept. 30/81				
Leech (*Dina dubia*)	2201	10262	508	188
Leech (*Glossiphonia complanata*)	639	1688	100	19
Leech (*Helobdella stagnalis*)	371	2461	140	72
Snails (*Physa* sp.)	25	27	7	21
Damselfly larvae (*Enallagma* sp.)	116	169	58	54
Cranefly larvae (Tipulidae)	83	9	9	23
Water	0.065	0.083	0.007	0.005
CN-5; Nov. 4/81				
Leech (*Dina dubia*)	1529	4917	119	35
Leech (*Glossiphonia complanata*)	221	640	21	1
Worms (Oligochaeta)	1128	894	124	180
Mayfly larvae (Ephemeroptera)	23	27	4	12
Dragonfly larvae (Anisoptera)	ND	2	ND	64
Damselfly larvae (*Enallagma* sp.).	24	46	24	3
Damselfly larvae (*Calopteryx* sp.)	7	4	8	1
Caddisfly larvae (Hydropsychidae)	22	26	3	4
Water pennies (Psephenidae)	ND	1	ND	10
Cranefly larvae (Tipulidae)	ND	1	1	1
Water	0.014	0.015	0.003	0.003

Only aquatic oligochaetes, which are a class of annelids closely related to leeches, had comparable residues. Annelids are primitive organisms and may be incapable of metabolizing and/or excreting these compounds. In preliminary laboratory tests, we found that specimens of the leech *Dina dubia* collected from site CN-3 did not eliminate any of their body burden of chlorophenols within a two-week period in clean water. There is evidence from the literature that leeches have a considerable bioaccumulation potential for other synthetic organic compounds, including DDT and mirex. Leeches are ubiquitous and easy to sample. As they are not easily damaged during handling, they are ideal for laboratory uptake and depuration experiments. In comparison with fish and most aquatic insects they are relatively sedentary and therefore representative of their immediate environment. These findings prompted further studies aimed at determining the potential of leeches as biological indicators of aquatic contamination.

Four species of leeches are present in abundance in Canagagigue Creek: *Dina dubia*, *Erpobdella punctata*, *Glossiphonia complanta*, and *Helobdella stagnalis*. Specimens of all species were collected from two sites on three occasions in 1982. They will be analyzed individually for chlorophenol residues. The data will be used to compare the bioaccumulation potentials of the various species and to determine whether animal size is an important parameter in uptake. Preliminary results suggest that *Dina dubia* has the highest body burden of chlorophenols.

An organism's capacity for bioaccumulating contaminants depends on many factors, including trophic level and longevity. As the life histories of Canadian leech species are very poorly known, a study on the age structure and food habits of three of our species was conducted. A paper on this subject will be prepared shortly. G. *complanata* was found to live up to two years with reproduction in May of both years. It feeds on snails, particularly the genus *Physa*. D. *dubia*, seems to have a one-year cycle, with a few individuals living up to 17 months. It feeds primarly on oligochaetes and chironomid larvae and pupae. E. *punctata* lives up to three years and grows to the largest size. It feeds primarily on tubificid worms, although chironomid and blackfly larvae are also taken. Once the contaminant analyses of our specimens have been completed, the importance of the various life history factors will be evaluated.

We have shown that several species of leeches accumulate high levels of chlorophenols. Whether this phenomenon is peculiar to these few species and/or this particular class of compounds is not known. In order to expand the range of contaminants and leech species under investigation, studies of the Grand River Watershed in Ontario and selected sites in New Brunswick were initiated. Thirteen sites along the Grand River and its tributaries were sampled in the spring, summer, and fall of 1982. A total of 805 specimens representing fourteen species were collected. Of the dominant species, H. *stagnalis* was found at all 13 sites, E. *punctata* at 11, G. *complanata* and *Nephelopsis obscura* (standard variety) at nine sites each, D. *dubia* and *Dina parva* at seven, and *Nephelopsis obscura* (new variety) at five. The new variety of N. *obscura* displays a new colour variation which has not been previously described. Studies are underway to determine whether this variety represents a new species of *Nephelopsis*. Once the analyses of water and leeches for chlorophenols and neutral organochlorines have been completed, a report on this survey will be prepared. Five sites in New Brunswick were also surveyed. Site selection was based on proximity to a source of pollution and/or a NAQUADAT Station. They included one site on the St. Croix River, one on the North Branch of the Oromocto River, and three on the Saint John River. Seven species were encountered, and again the dominant species were E. *punctata*, H. *stagnalis*, and G. *complanata*. The contaminant analyses of water and leeches are forthcoming.

In the coming year, comparative studies with leeches and other previously accepted sentry organisms, such as molluscs, will be conducted.

Two studies with fish were carried out in 1982. Survival of the early life stages of the Common Shiner (*Notropis cornutus*) at CN-3, 1.7 km below the Elmira WPCP was compared with survival at a clean site 2.3 km above the outfall. We had hoped to use rock bass for this study, but they cannot be artificially spawned. Survival to hatch was high at both sites: 82% upstream and 86% downstream. However, survival to the critical swim-up stage was reduced from 69% upstream to 49% downstream. This evidence suggests that conditions downstream of the WPCP may reduce the reproductive success of some fish species. Common shiners are widespread, easy to rear and make excellent test organisms. However, their normal early development has not been adequately described in the literature. This task will be undertaken in 1983.

Rainbow trout fingerlings were reared for six weeks at the two sites described above. No differences in mortality or growth rates between sites were noted. The uptake rates of chlorophenols by trout will be described once contaminant analyses are complete. Levels of chlorophenols in trout and their various organs will be compared with those of indigenous fish species.

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CONTAMINANT STUDIES IN MESO-ECOSYSTEMS

by

B.F. Scott, E. Nagy, J.H. Carey, M.E. Fox, J.H. Hart, S. Painter,
J. Wood, M. Charlton, M. Dickman, J. Mackie, M. Stephenson,
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INTRODUCTION

The study of the pathways and persistence of toxic chemicals in the aquatic environment is a Departmental priority. To examine the chemical and biological parameters, including the impact of the chemical on the biota (1), a series of polyethylene-lined, sediment-overlaid ponds were constructed. Chemicals of concern can be added at known dosages. The disappearance from the water column of the chemical, its build-up in the sediment and selected biological species, as well as the appearance of breakdown products can be monitored over an extended period of time, facilitating mass-balance calculations. Also by monitoring the biota, primary and secondary effects on the biota, both short- and long-term, can be ascertained (3,4,5).

RESEARCH RESULTS

The 2,4,-D was first added to four of the ponds in 1980 and the 1980 control ponds were treated in 1981. Both the N,N-dimethylamine formulations of the 2,4-D best followed first-order kinetics with a rate constant of 0.039 mg L^{-1} day^{-1} in 1980. The plot for the concentration of 2,4-D for the ester formulation exhibited two distinct patterns, the first resulting from the dissolution of the 2,4-D from the clay pellets into the water column. This was followed by a gradual decrease in the 2,4-D concentration. This decrease followed first-order kinetics, with a rate constant of 0.041 mg L^{-1} day^{-1}. For the 1981 treatments, the N,N-dimethylamine formulation had a rate constant of 0.0197 mg L^{-1} day^{-1} and the ester was 0.0198 mg L^{-1} day^{-1}. The major chemical difference between the ponds in the two successive years was the pH. In 1980 the pH of the ponds was 7.3 and in 1981, 9.5. As the disappearance of 2,4-D is photochemically induced, the influence of pH on the photodecomposition of 2,4-D will be investigated.

Analysis of clams exposed to treatment in both 1980 and 1981, indicate that there was an initial uptake by the clams of 2,4-D and some 2,4-dichlorophenol (DCP), but these compounds were eliminated within six weeks from the clam tissues. There was no mortality to the clams caused by the application of either formulation of 2,4-D at pH's 7.0 and 9.0. As the pK_a of 2,4-DCP is 7.8, using the two solutions will provide a medium where the phenol is essentially undissociated and one where the phenolate ion dominates. At the lower pH, only 18 ppm of the 2,4-DCP was needed to produce 50% mortality to the clams, and at the higher pH, 65 ppm were needed. More than 250 ppm of the parent acid was needed to produce the same result. Similar trends were noted for the fish fingerlings in the ponds about the time of treatment. Fish collected from the ponds nine months after treatment contained varying amounts of 2,4-D and traces of 2,4-DCP.

The concentrations of 2,4-D in the sediment following the 1980 treatments are shown in Fig. 1. The shape of the curves in the figure do not reflect the diminishing concentrations of the chemical in the water column at the time. It is suggested that the increases in the sediment concentrations result from the release of the chemical from the decaying plant material. Although not shown, the 2,4-DCP concentrations in the sediment follow similar patterns.

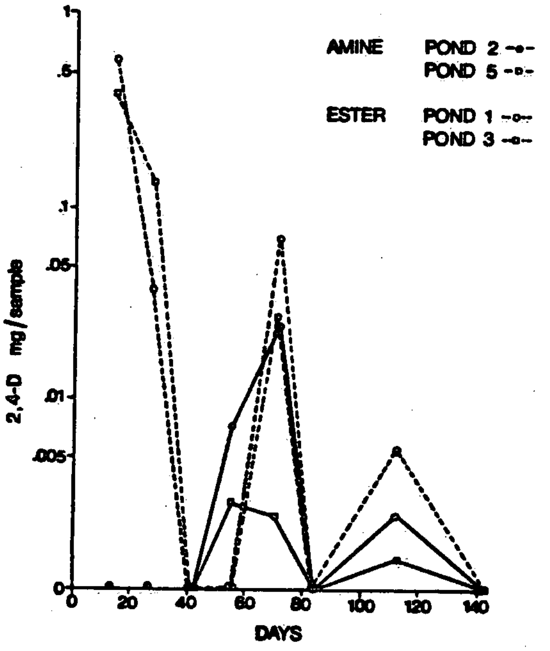

Figure 1. Concentrations of 2,4-D in sediment following treatments

The disappearance of 3-trifluoromethyl-4-nitrophenol (TFM) - a lampricide - in quiescent waters was investigated using the ponds in 1982. In two of the ponds, technical grade lampricide was used and the third pond was treated with TFM recrystallized from the commercial formulation. The chemicals were introduced under the water surface, but four days were required for the TFM to be uniformly distributed throughout the water column. The disappearance of the TFM followed first-order kinetics with respect to the TFM and the rate constants averaged 0.070 mgL^{-1} day^{-1}. Small amounts of the TFM were found in the sediment and few breakdown products were detected.

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D. PRIMARILY LABORATORY STUDIES AIMED AT MEASURING PROPERTIES AND EFFECTS OF CHEMICALS SO AS TO DEVELOP PREDICTIVE MODELS FOR THEIR FATE IN AQUATIC ECOSYSTEMS

PREDICTION OF CONTAMINANT HAZARD BY QSAR

by

K.L.E. Kaiser, M.E. Comba, J. Cullen and J.M. Ribo

INTRODUCTION

Structure-activity correlations are used as an important tool for the identification and prediction of biologically-active compounds in the development of medicinal compounds. In order to assess the environmental hazard potential of new contaminants and materials in a time and cost saving fashion, available biochemical data are correlated with the physical and chemical characteristics and properties to arrive at the structure activity correlations for the compounds to be determined. the necessity for such a program has also been recognized by the Integrated Planning and Management Activity (goal 5, A-Base Review), is a mandate arising out of the great Lakes Water Quality Agreement of 1978 (Annex 12) and has also been documented by the Great Lakes Science Advisory Board (1982 Annual Report).

The pathways and effects, hence exposure to and hazard of toxic substances is largely controlled by their chemical and physical properties, for example, octanol/water partition coefficients. Some of these properties can be estimated from those of similar compounds, others may be calculated directly from atomic and molecular parameters.

RESEARCH RESULTS

Several independent routes are persued for the prediction of contaminant hazards. For some compounds which are extremely toxic, e.g., TCDD, even the measurement of physical constants cannot be done in our laboratory. It is therefore, of interest to be able to estimate their partition coefficients from less toxic congeners. This was achieved by development of a non-linear function for the calculation of partition coefficients of aromatic compounds with multiple chlorine substitution (1).

For nonionic compounds, the partition coefficients are independent of the pH of the aqueous phase. However, acids, such as certain phenols with a low pKa dissociate at neutral to basic pH and their partition coefficients will be quite dependent on the aqueous pH. In order to study this effect quantitatively, pentachlorophenol (PCP) was selected and its partitioning measured in the pH range 1 to 13. Our results show that the apparent octanol/water partition coefficient of PCP (Figure 1) varies in non-linear function with the pH of the aqueous solution (2).

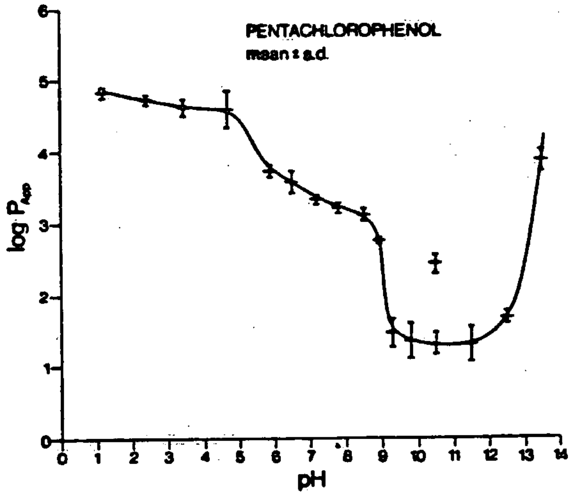

Figure 1. Variation of partition coefficient (log P_{App}) with the pH (from Ref. 2)

The project on acute and sublethal toxicity of benzene and phenol derivatives, in collaboration with P.V. Hodson (GLFRB) and D.G. Dixon (U. Waterloo) resulted in an expansion of the data base to a point where meaningful structure-activity correlations can be developed (3). In addition, the SSDH test was found to be a useful indicator of the sublethal toxicity of the compounds tested (4).

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SEDIMENT-WATER PARTITIONING OF TOXIC ORGANIC SUBSTANCES

by

W.M.J. Strachan

INTRODUCTION

Sorption on sediments is one of the major processes affecting the behaviour of chemicals in the aquatic environment. The process is characterized by a partition constant, K_d, which, in addition to laboratory or field oservations, can be calculated from K_{oc}, the comparable constant for sediments of 100% organic content. ($K_d = K_{oc}$ x fraction organic carbon.) This relationship appears to hold for a variety of sediments, soils and chemical compounds.

RESEARCH RESULTS

In an attempt to investigate sorption behaviour, a large sample of Lake Ontario sediment was fractionated using settling times to give a coarse ($\phi<4$) and fine ($\phi>8$) fractions. These were freeze-dried to provide homogeneous and reproducible substrates throughout the study. Samples of these fractions were suspended in water and equilibrated with hexachlorobenzene (HCB) and dichlorodiphenyldichloroethane (DDE) at concentrations below their saturation levels. Preliminary results are presented in Table 1.

Solubilities were also determined on a large number of replicates. HCB was 5.3 (s.d. 1.1) µg/L and DDE was 0.68 (s.d. 0.08) µg/L in reasonable agreement with literature values.

While it is too early in the progress of the study to discuss statistically significant relationships, it appears that there is an effect on Kd by the suspended load which operates in opposite directions for the two compounds. It also seems that there are no differences arising from the use of coarse or fine suspended sediments. A more precise means of sediment fractionation is being investigated as are improvements in the recovery procedures which will allow more reproducible mass balance determinations.

Table 1. Kd's for HCB and DDE

	HCB			DDE		
Sediment Size	Water (µg/L)	Sediment (µg/g)	Kd ($\times 10^3$)	Water (µg/L)	Sediment (µg/L)	Kd ($\times 10^3$)
			100 mg s.s./L			
Coarse	1.1	1.7	1.5	0.061	0.75	12.3
	1.2	2.4	2.0	0.079	1.0	12.7
	0.9	3.9	4.3	0.069	1.4	20.3
Fine	1.6	2.3	1.4	0.20	0.65	3.3
	1.2	2.8	2.3	0.03	0.68	22.7
			50 mg s.s./L			
Coarse	0.27	1.4	5.2	0.10	0.41	4.1
	0.26	1.8	6.9	0.067	0.50	7.5
	0.24	1.2	5.0	0.086	0.39	4.5
	0.26	1.6	6.2	-	-	-
	0.37	2.4	6.5	0.42	1.99	4.7
Fine	0.29	1.5	5.2	0.19	0.37	1.9
	0.24	1.7	7.1	0.11	0.37	3.4
	0.31	2.7	8.7	-	-	-
	0.30	2.5	8.3	0.14	2.24	16.4

CHEMISTRY OF CHLORINATED HYDROCARBONS AT THE AIR/WATER INTERFACE

by

R.F. Platford

INTRODUCTION

I have continued to measure the partition coefficients of solutes between model lipids and water; this last series has been on water soluble compounds rather than on the hydrophic compounds I have studied previously. This partitioning work is now more or less complete, except for the possible future investigation of a few unusual or representative compounds.

The field program consisted of preliminary sampling of Niagara River water, surface water and air, in a search for some suitable tracer which can be used to estimate water to air transport of pollutants (with R.J. Maguire). Finally, in collaboration with M. Dickman of Brock University, we have collected a string of water samples from each of two NWT hypersaline lakes.

RESEARCH RESULTS

The results of the partitioning measurements collected over the past three years are summarized in Figure 1 along with three pertinent values from the literature (compounds 9, 10 and 14). The partition coefficients in the figure cover a range of ten decades and illustrate the inverse relation between octanol-water partitioning and water solubility - a point which has been made before by others.

I have made physical chemical measurements on the hypersaline lake samples (conductivity, major ions, density and freezing points); the results are consistant with those for concentrated sea water.

The heavy metal analyses are being done by IWD and will probably not be ready until 1983, as will also probably be the case for the Niagara River samples.

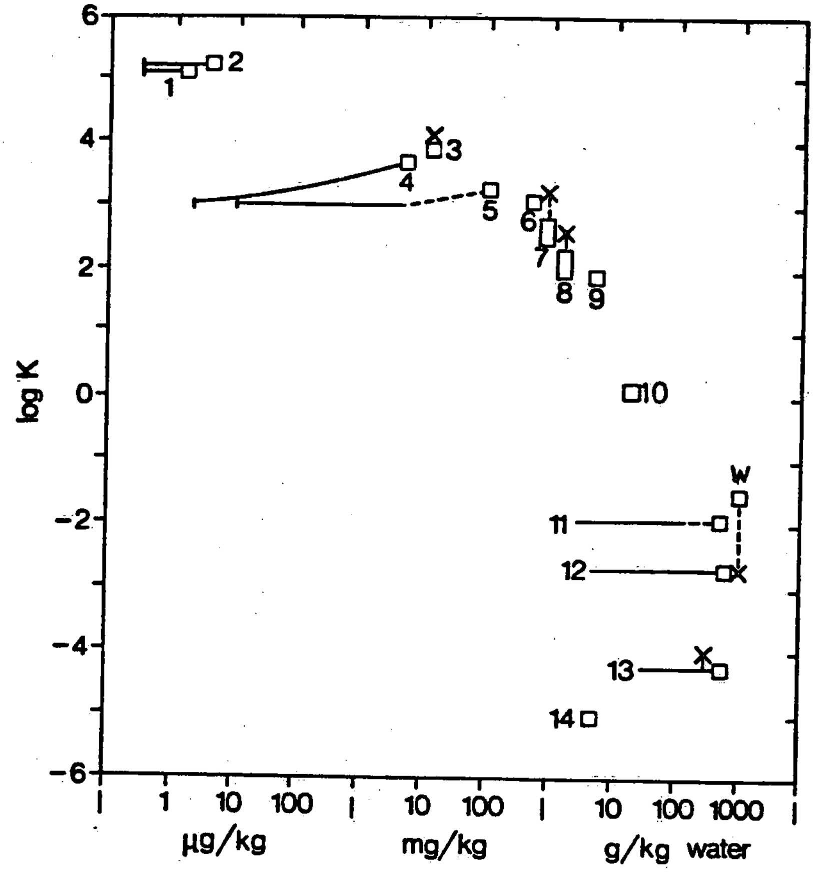

Figure 1. Octanol-water partition coefficients (—) and triolein-water partition coeffients (X). 1, DDT; 2, hexachlorobenzene; 3, n-hexane; 4, lindane; 5, methylthiobenzothiazole; 6, n-octanol; 7, carbon tetrachloride; 8, benzene; 9, benzoic acid; 10, caffeine; W, water; 11, mellitic acid; 12, silver perchlorate; 13, paraquat dichloride, pH 7.4; 14, paraquat diiodide, pH 7.4. Rectangles indicate water solubilities and all concentrations are per kilogram of solution (usually at 25°C).

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BACTERIAL DEGRADATION OF ORGANIC ENVIRONMENTAL CONTAMINANTS

by

D. Liu, K.L.E. Kaiser, K. Kwasniewska and K. Thomson

INTRODUCTION

Toxicity and biodegradability are important factors governing the fate and behaviour of an organic compound in the environment; the degree of bioaccumulation of a toxic substance in food-chain also depends heavily on these parameters. Such investigations are highly relevant to assessing hazard, an aspect important to both the Great Lakes Water Quality Agreement and the Environmental Contaminants Act. Bacterial degradation, in particular, provides a major route for the removal of such substances from the environment. Chemical toxicity, on the other hand, may affect the capability of the microbial degradation process as well as the operation of the food-chain in the aquatic ecosystem. Thus, information on toxicity and biodegradability is essential for effective management of chemical contaminants.

In addition to studying the toxicity and biodegradability of chemical contaminants, an objective of the project is intended to develop a better understanding of the quantitative relationship between structure and toxicity/degradability of toxic substances. Such information is useful in the assessment of new chemicals for their possible environmental impact.

RESEARCH RESULTS

The biodegradability of various commercial PCB formulations was assessed under the simulated wastewater treatment process conditions. The results indicate that the flow rate of the medium has a profound effect on the pattern of Arclors' degradation. The levels of dissolved oxygen, nitrogen and phosphorus encountered in most wastewater are adequate for PCB degradation. However, a high stirring rate is desirable for maintaining the optimal condition for PCB removal.

The toxicity of various halogenated phenols was quantitatively investigated and the data indicate that the positions of chlorine substituents in the chlorophenols strongly affect their toxicity potential. The toxicity of these phenols was also elucidated from the molecule electronic structure.

Table 1. IC$_{50}$ of various chlorophenols and bromophenols to the culture TL81 expressed in mg L^{-1} and as logarithms of the inverse molar concentrations C[mol L^{-1}]

Chemicals	IC$_{50}$(ppm)	log $\frac{1}{C}$	Chemicals	IC$_{50}$(ppm)	log $\frac{1}{C}$
Phenol	2300	-1.39	2,3,4-TCP	13	1.18
2-MCP	700	-0.74	2,3,5-TCP	10	1.30
3-MCP	450	-0.54	2,3,6-TCP	190	0.02
4-MCP	400	-0.49	2,4,5-TCP	12	1.22
2,3-DCP	130	0.10	2,4,6-TCP	240	-0.08
2,4-DCP	75	0.34	3,4,5-TCP	5	1.60
2,5-DCP	85	0.28	2,3,4,5-TCP	4	1.76
2,6-DCP	550	-0.53	2,3,5,6-TTP	54	0.63
3,4-DCP	52	0.50	PCP	9	1.47
3,5-DCP	25	0.81	2-MBP	550	-0.50
			3-MBP	380	-0.34
			4-MBP	400	-0.36
			2,4-DBP	60	0.62
			2,6-DBP	500	-0.30

A rapid and inexpensive screening technique has been successfully developed for the toxicity assessment of water insoluble substances. The test is based on the quantitative measurement of the interaction between toxicant and microbial dehydrogenase in a reaction mixture containing 5% DMSO. The reliability and reproducibility of this test were evaluated using eleven chlorobenzenes and eight phenols.

Long-term (four years) effect of farmland disposal of anaerobically digested sewage sludges on groundwater quality was systematically studied using the lysimeter system. The results indicate very little possibility of bacterial contamination of groundwater by the practice of sludge farmland disposal.

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BIOCHEMICAL AND PHOTOCHEMICAL PROCESSES IN THE DEGRADATION OF CHLORINATED BIPHENYLS

by

R.M. Baxter and D.A. Sutherland

INTRODUCTION

Last year's report discussed the metabolism of a number of chlorinated biphenyls by a bacterial strain isolated by Dr. D. Liu. It was mentioned that with certain compounds, a yellow intermediate accumulated, which was bleached by sunlight or artificial light.

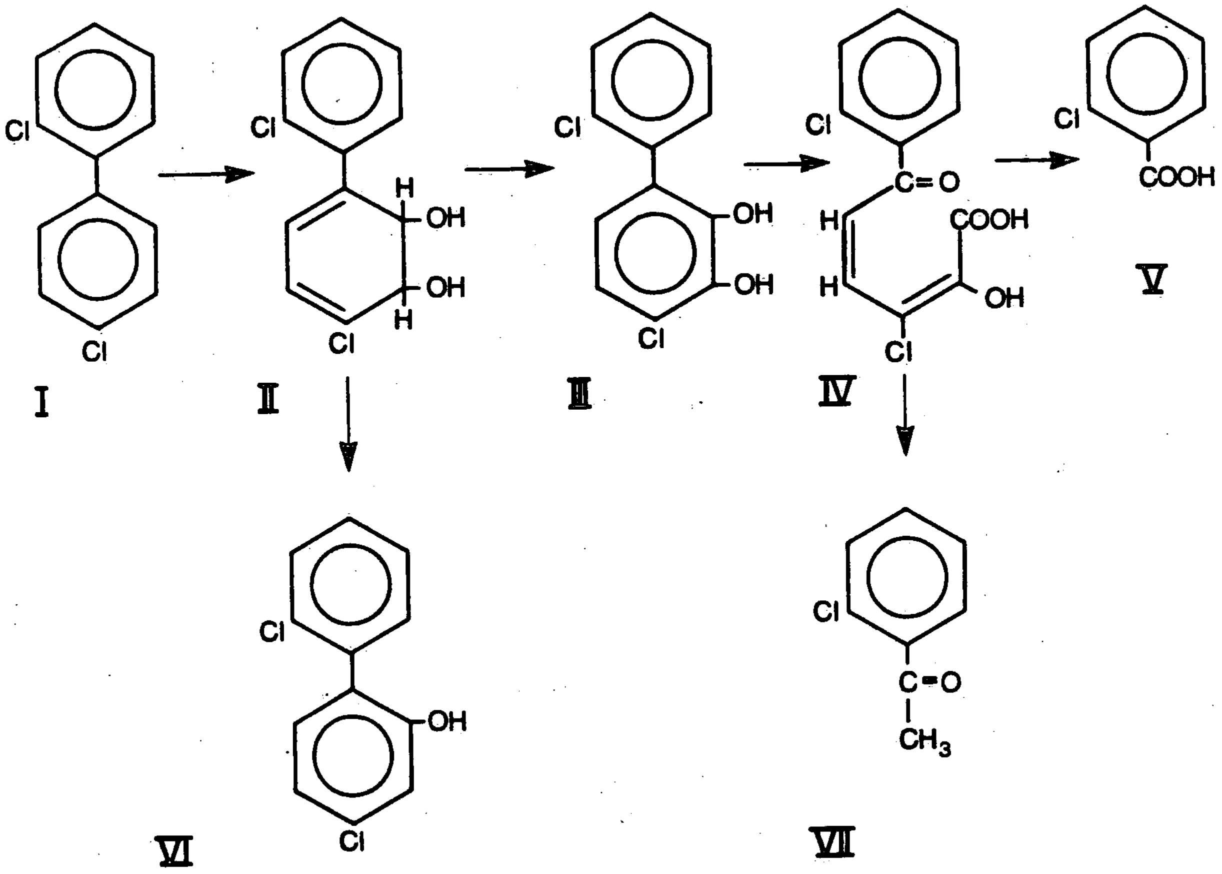
These reactions have now been investigated further. The products of metabolism and photolysis have been separated and identified by gas chromatography/mass spectroscopy.

RESEARCH RESULTS

Most experiments were performed using 2,4'-dichlorobiphenyl, which was found to give a good yield of yellow product. The principal steps in the transformation of this compound are shown in the figure.

2,4'-dichlorobiphenyl (I) is converted to a dihydrodiol (II) then to a diphenol (III) which undergoes meta-cleavage of one ring to yield a yellow product (IV). Further metabolism of this compound proceeds more slowly than its formation, so that it accumulates in the medium. It is however, slowly metabolized through unidentified intermediates to a chlorobenzoic acid (V). We also detected a monohydroxy dichlorobiphenyl (VI) but this is probably an artifact produced by the dehydration of II during the extraction procedure.

Irradiation of IV lead to the loss of four carbon atoms of the aliphatic chains yielding a chloroacetophenone (VII), perhaps by a Norrish Type II mechanism.



These results are of particlar interest because they serve to illustrate that the degradation of environmental contaminants may involve a variety of processes, often, as here, acting in sequence, all of which must be considered in attempting to estimate the likely persistence of any particular substance.

TOXICITY AND BIODEGRADABILITY OF ORGANIC ENVIRONMENTAL CONTAMINANTS

by

K. Kwasniewska, K.L.E. Kaiser and D.L.S. Liu

INTRODUCTION

The study of toxicity and biodegradability is essential for the assessment of environmental impacts of existing and new chemicals to aquatic ecosystems. The bioaccumulation of toxicants in the food chain of environmental biota, including man, also depends on these parameters.

Investigations of such substances are relevant to hazard assessment, an aspect of the Environmental Contaminants Act.

Fungi, or yeast-like fungi, have almost identical geographic distributions and common habitats in aquatic ecosystems. They are known to possess several important enzymes and have a greater genetic complexity than other microoganisms. Therefore, they promise to be of great interest for the study of both toxicity and biodegradation rates of environmental contaminants.

RESEARCH RESULTS

This new project has resulted in three papers.

The biodegradation and toxicity of pentachlorophenol (PCP) have been studied using the fungi Fusarium sp. The results indicate that the fungus is more tolerant to PCP toxicity than bacteria. Apparently the rate of PCP degradation by Fusarium sp. was largely controlled by the availability of xylose and L-tyrosine in the growth medium (publication no. 1).

The interaction between eukaryotic cells and selected toxic chemicals was assessed in (2). The results indicate that the yeasts exhibited a different response to the same toxicants, probably due to different metabolic mechanisms involved.

The toxicities of chloro- and para-substituted phenols to fermentative and oxidative yeast strains were also studied (3). The results indicate that oxidative strains were more sensitive than fermentative ones and the following quantitative structure-toxicity relationship was found:

$$\log 1/C = 1.82 + 0.72 \log P + 1.48 F$$

$$(n = 8, r^2 = 0.93, s.d. = 0.30)$$

where P is the n-octanol/water partition coefficient and F is the substituent.

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BIOAVAILABILITY OF ORGANIC CONTAMINANTS IN SEDIMENTS

by

B.G. Oliver and M. Matteliano

INTRODUCTION

A large portion of the persistent contaminants discharged directly into the Great Lakes and into tributaries draining into the lakes winds up in bottom lake sediments. The sediments in Lake Ontario, in particular, are known to be contaminated with PCB's, mirex and chlorobenzenes. Analysis of macroinvertebrates shows that at least part of the sediment contaminants are available to these sediment dwelling animals. The purpose of this project is to define what portion of the organic contaminants in bottom sediments are bioavailable.

RESEARCH RESULTS

The uptake of contaminants by sediment dwelling animals can be either by direct uptake from interstitial water or by sediment ingestion. All chemicals dissolved in interstitial water are available so in the first phase of our work we designed a method to measure the concentration of chemicals in the aqueous phase of sediment/water mixtures. We are currently examining the desorption of contaminants from sediments into water as a function of temperature using this purge and trap method. In an experiment designed to study biouptake from sediment particles, oligochaete worms are being raised in laboratory aquariums on naturally contaminated sediments. Preliminary results from these experiments show that worms do take up the contaminants from the sediments and reach a steady concentration within six weeks. The bioconcentration factor (BCF), worm concentration/sediment concentration, for three samples from Lake Ontario (from the Niagara, Mississauga and Rochester Basins, respectively) are similar for specific organic contaminants such as HCB. But chemicals with different properties have very different BCF's. For example the BCF is ≈ 0.3 for HCB and ≈ 3.0 for mirex.

This project was started only five months ago, so no reports or manuscripts are available.

E. PROJECTS DEALING WITH THE MODELLING OF RATE OF ACIDIFICATION OF A RIVER BASIN AND THE GEOCHEMICAL PROCESSES CONTROLLING THIS RATE

GEOCHEMICAL CONTROLS OF AQUATIC SYSTEM RESPONSES TO DEPOSITION OF ATMOSPHERIC POLLUTANTS

by

D.S. Jeffries and R.G. Semkin

INTRODUCTION

A major departmental research objective is to "determine the ability and capacity of the ecosystem of Canada to withstand contamination due to the long-range transport of air pollutants". This objective has been initially addressed by studying a specific ecosystem, e.g., acid interaction in the calibrated Turkey Lakes Watershed (TLW) near Sault Ste. Marie, Ontario (1). The purpose is to determine the factors controlling the degree and rate of acidification of drainage basins and associated lakes by measuring the geochemical response of the TLW to the input of acids.

The study has focussed on two activities: first, assessment of the sensitivity of the TLW to acid deposition through a survey of the bedrock geochemistry, and second, determination of the importance of short-term events of acidification by intensively monitoring the major ion chemistry of lakes and streams during snowmelt.

RESEARCH RESULTS

Rock samples were collected and analyzed for major and trace elements as a means of estimating the influence of bedrock geology on the aquatic chemistry of the basin. Results for major elements are provided in Table 1. The major bedrock component of the TLW has a basaltic composition. Further evaluation of the chemistry using AFM and Jensen cation plots revealed that the basalt is tholeiitic in nature, which is common for Archean greenstone belts such as found in the study area. Elevated levels of Hg, Pb and Zn observed in the bedrock of Wishart Lake basin may be reflected in high metal concentrations in the lake sediments (2).

Table 1. **Whole Rock Chemistry (wt. %) for the Turkey Lakes Watershed**

Sample Number	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	CO_2	S	LOI
1	47.5	14.2	15.1	7.47	9.53	2.94	0.33	1.37	0.03	0.20	0.11	0.29	0.5
2	47.5	13.8	14.3	4.19	13.9	1.94	0.20	1.35	0.03	0.23	0.10	0.25	1.0
3	48.1	15.3	13.5	6.39	7.07	4.21	0.34	1.64	0.04	0.24	0.11	0.03	1.8
4	45.7	14.4	16.3	7.62	8.28	2.99	0.37	1.42	0.03	0.31	0 05	0.12	1.8
5	50.4	13.5	13 5	4 24	14 0	1 84	0.15	1.47	0.03	0.18	0.05	0.01	0.7
6	50.8	12.7	14.8	5.16	11.2	1.53	0.19	1.14	0.00	0.22	0.06	0.02	1.2
7	50.9	11.9	18.9	3.51	7.79	2.67	1.16	1.83	0.16	0.24	0.10	0.15	0.5
8	46.8	16.1	11.6	4.08	15.3	1.18	2.00	1.02	0.00	0.21	0.24	0.03	1.1
9	47.1	19.6	8.89	6.87	13.8	1.44	0.54	0.53	0.05	0.14	0.15	0.05	1.1
10	48.7	11.2	14.7	9.11	10.7	2.45	0.23	0.85	0.06	0.25	0.07	0.23	0.9
11	48.4	16.5	9.90	7.34	12.8	1.91	0.09	0.63	0.05	0.15	0.11	0.02	1.8
12	51.9	15.1	10.6	4.83	8.03	3.20	1.16	1.15	0.01	0.21	1.97	0.05	3.2
13	46.9	13.6	12.1	5.65	16.5	0.99	0.32	0.99	0.01	0.21	1.50	0.12	2.4
14	50.5	12.4	16.7	5.98	8.00	2.76	0.33	1.78	0.07	0.19	0.19	0.03	0.6
Mean	48.7	14.3	13.6	5.98	11.20	2.29	0.53	1.23	0.04	0.21	0.34	0.10	1.3
162 Samples[1]	48.9	14.5	11.2	6.27	8.74	2.51	0.45	1.06	0.07	0.21	1.93	-	-

[1] 162 samples of Archean Volcanic Rocks (Basalt) from the Superior Province of the Precambrian Shield (Goodwin, 1968).

Composite snow cores were collected in the TLW for the period 1980-1982. Analyses of the snowpack prior to any significant melt event are presented in Table 2. The pH of the snowpack over the three years averaged between 4.6 and 4.7.

Table 2. Snowpack Chemistry[1] at the Turkey Lakes 1980-1982

Parameters	March 10, 1980	February 4, 1981	January 19, 1982
Water Equivalent (mm)	210	222	216
Snow Density	0.23	0.25	0.23
pH	4.69	4.60	4.62
Ca^{2+}	0.23	0.07	0.14
Mg^{2+}	0.04	0.01	0.03
Na^{+}	0.14	0.11	0.24
K^{+}	0.15	0.04	0.05
NH_4^{+}	0.19	0.20	0.14
SO_4^{2-}	1.12	1.24	1.34
Cl^{-}	0.48	0.32	0.40
NO_3^{-}	0.34	0.33	0.82

[1] All parameters in mg/L unless otherwise stated.

A comparison of water equivalent in cumulative bulk precipitation and in the snowpack at the APN station revealed that evaporation from the snow cover was minimal over the winter of 1982. An evaluation of the chemistry of bulk precipitation and of the snow packed showed that:

(1) The total cation content of bulk precipitation and of the snowpack were comparable prior to any significant snowmelt.

(2) The volume-weighted pH of the bulk precipitation for the period November 21, 1981 to March 3, 1982 (i.e., when the snow cover was accumulating) was 4.39 with hydrogen accounting for 50 to 60% of the total cation content.

(3) Three samples of snowpack collected at the APN station over the same time period produced pH values ranging from 4.59 to 4.76 with hydrogen averaging 32% of the cation concentration.

(4) A comparison of the cation composition of cumulative bulk precipitation and the snow pack (Figure 1) indicated that the hydrogen ion concentration in the melted snow samples was lower while the sodium and calcium content was higher relative to that found in bulk precipitation.

(5) The ionic strength of the snow cover in the watershed decreased through the melt periods in 1981 and 1982. Chemical constituents were leached from the snow pack in both years, concurrent with increasing spring temperatures. Values of specific conductance decreased from about 15 to 6 µmho/cm during the melt; pH values increased from 4.57 to 5.42 (January to April, 1981) and from 4.62 to 5.31 (January to April, 1982).

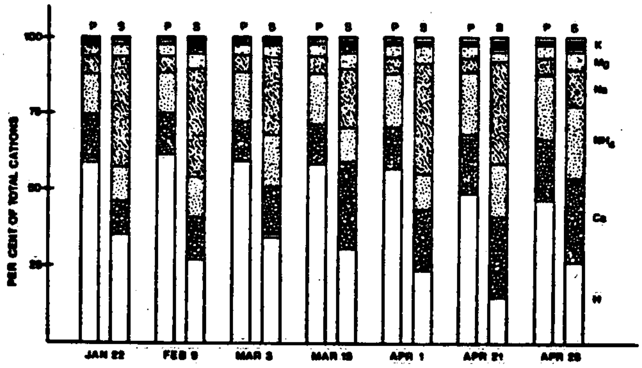

Figure 1 **Relative Cation Composition of Cumulative Bulk Precipitation (P) and Snow Pack (S) at SN 10**

PUBLICATIONS

1. Jeffries D.S. and Semkin, R.G. 1982. Basin description and information pertinent to mass balance studies of the Turkey Lakes Watershed. Turkey Lakes Watershed Unpublished Report No. TLW-82-01, 34 pp.

2. Semkin, R.G. and Jeffries, D.S. 1983. Rock chemistry in the Turkey Lakes Watershed. Turkey Lakes Watershed Unpublished Report No. TLW-83-03, 9 pp.

HYDROGEOCHEMICAL RESPONSES OF THE TURKEY LAKES WATERSHED TO ACID PRECIPITATION

by

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INTRODUCTION

The Turkey Lakes Watershed (TLW) has been established as one of five calibrated watersheds in eastern Canada with the purpose of determining the effects of acidic deposition on sensitive terrain. Specifically, information from this study will be used to quantify pollutant pathways and to define cause-effect relationships from which predictive models of ecosystems effect can be developed and verified. The physical characteristics of the TLW have been previously described (1). The hydrogeochemical response of the watershed to acid inputs is being evaluated using a mass balance in an effort to determine the geochemical mechanisms and/or factors controlling the relationship. The use of calibrated watersheds has been shown to be a productive approach in this type of investigation (2).

RESEARCH RESULTS

Acquisition and manipulation of the data required for calculation of mass balances for the lakes has continued. Daily flow data for the lake outlet streams for 1980 and 1981 have been obtained. Only stream station S4 (Turkey Lake Outlet) has an unbroken record at this time (Figure 1); however, since strong statistical relationships exist among the flows at the different outlet stations, missing discharge values will be estimated by simple linear regression.

Lake evaporation has been estimated for 1980 and 1981 using an energy balance technique (3). Evaporation ranged from 415 mm yr^{-1} (Little Turkey Lake, 1980) to 521 mm yr^{-1} (Batchawana Lake North, 1980) which is slightly below that suggested by the Hydrological Atlas of Canada.

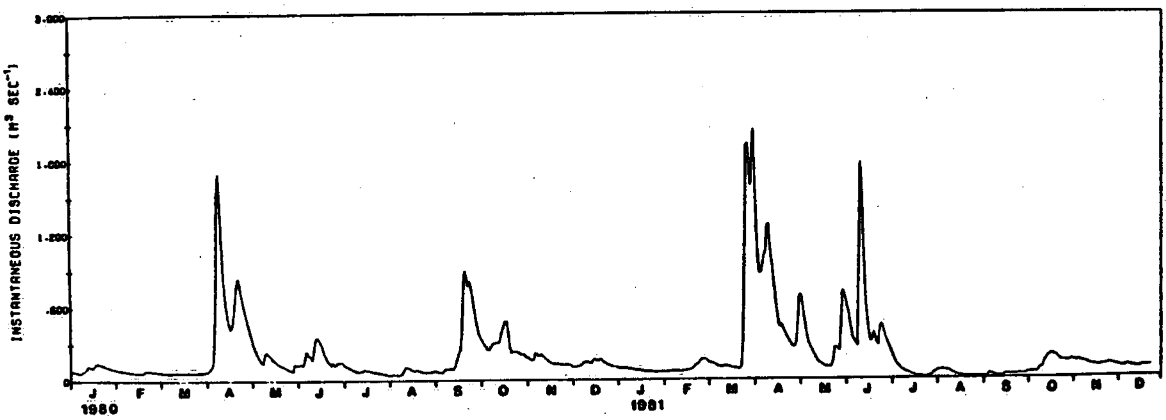

Figure 1. Turkey Lake outflow-hydrograph for 1980-81

Data for the major ion composition of streamwaters collected at the six NWRI sampling stations in the TLW from January 1980 to May 1982 have been stored in the computerized data base, NAQUADAT, assessed for accuracy, and presented in a data report (4). A gradient in composition is evident from the least buffered at the top of the watershed (mean alkalinity = 2.65 mg L^{-1} $CaCO_3$) to the most buffered at the bottom (mean alkalinity = 9.20 mg L^{-1}).

Many parameters exhibit seasonal variation in concentrations. For example, Figure 2 shows the variations observed in alkalinity at the Little Turkey Lake outflow (station S3). The major reductions in alkalinity leaving the lake in the spring are related to dilution and acidification of the surface waters during snowmelt.

Data for the major ion composition of the six lakes for January 1980 to May 1982 has been stored in NAQUADAT and is presently being assessed for accuracy. Temperature isopleth diagrams have been prepred for all lakes for 1980 and 1981. Figure 3 gives an example for Batchawana Lake South in 1981.

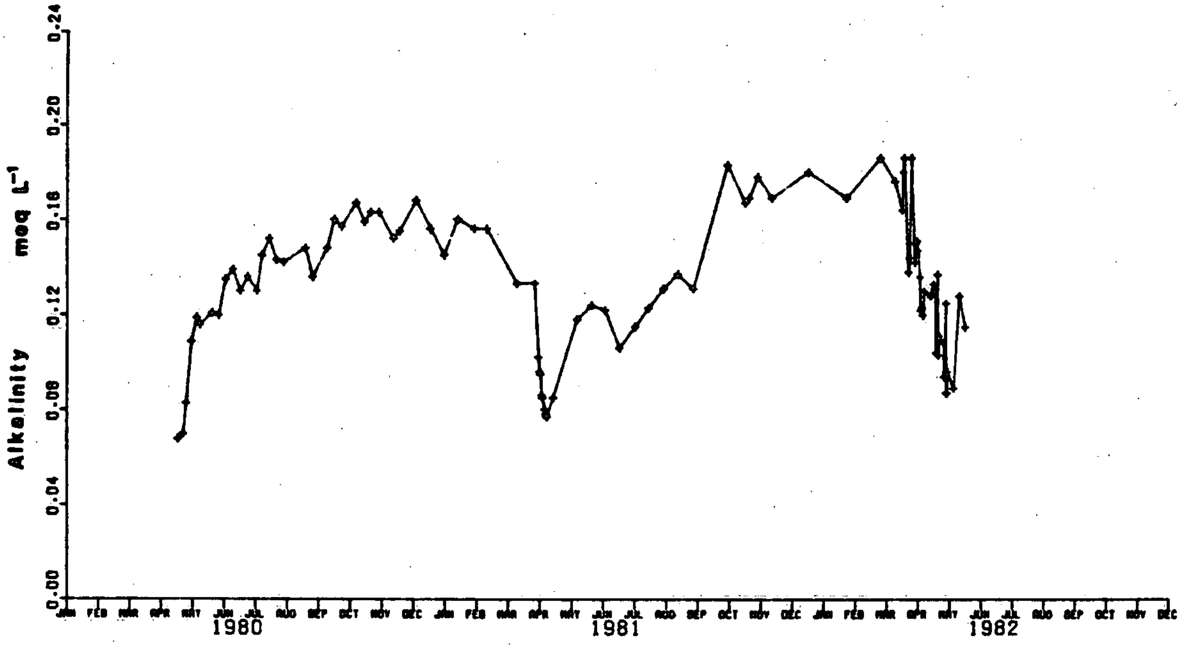

Figure 2. Variation in alkalinity (meq L^{-1}) at stream station S3 for 1980-82

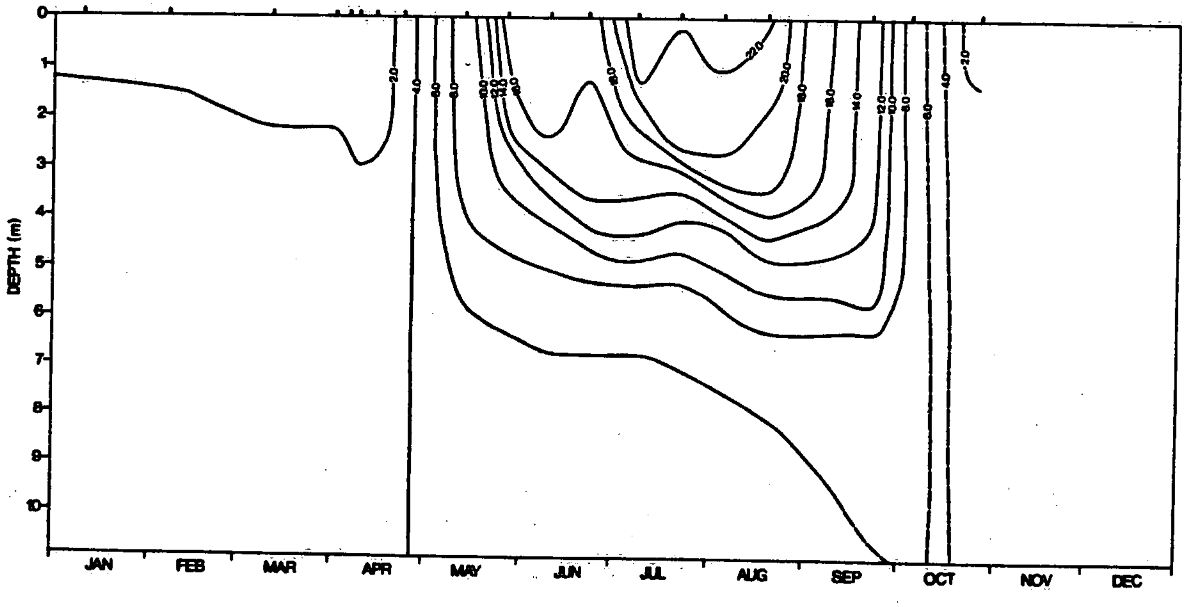

Figure 3. Temperature isopleths for Batchawana Lake (South Basin) for 1981

PUBLICATIONS

1. Jeffries, D.S. and Semkin, R.G. 1982. Basin description and information pertinent to mass balance studies of the Turkey Lakes Watershed. Turkey Lakes Watershed Unpublished Report No. TLW-82-01, 34 pp.

2. Dillon, P.J., Jeffries, D.S. and Scheider, W.A. 1982. The use of calibrated lakes and watersheds for estimating atmospheric deposition near a large point source. Wat. Air. Soil Pollut., 18: pp. 241-258.

3. Jeffries, D.S. 1983. Lake evaporation and energy budgets in the Turkey Lakes Watershed (1980-81). Turkey Lakes Watershed Unpublished Report No. TLW-83-04, 57 pp.

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