

NWRI-UNPUBLISHED REPORTS

ENVIRONMENTAL Contaminants DIV.

Current Research 1981-1982

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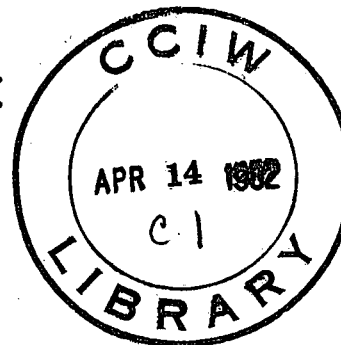


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NWRI Unpublished Manuscript

ENVIRONMENTAL CONTAMINANTS DIVISION

National Water Research Institute

CURRENT RESEARCH

1981/82

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Canada Centre for Inland Waters
867 Lakeshore Road
Burlington, Ontario L7R 4A6

March, 1982

FOREWORD

Research accomplishments of the staff of the Environmental Contaminants Division, National Water Research Institute are reported annually in this volume entitled Current Research. Each project is described in a separate report by the project leader. The reports are meant to complete the planning cycle which is initiated each year with the publication of Study Plans. The annual Study Plans say what we expect to do and why. Following this, quarterly reports are prepared internally for management control of resources. These quarterly reports are brief and deal with shifts in direction or problems encountered. Alternatively, Current Research, which is prepared in the last month of each fiscal year, describes only accomplishments. Current Research says what we have done, why and how and includes references to all reports or publications prepared under each project since the last issue.

R.J. Allan
Chief
Environmental Contaminants Division
National Water Research Institute
Inland Waters Directorate

**200: ENVIRONMENTAL CONTAMINANTS DIVISION
RESEARCH PROGRAM**

by

R.J. Allan

DIVISION OBJECTIVES

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 upon an in-depth knowledge of the pathways and thus fate of contaminants in aquatic ecosystems. The Environmental Contaminants Division conducts research to resolve these pathways. The fate of contaminants must be known to determine exposure and estimate hazard to biota, including man. Three groupings of contaminants are investigated - organics, inorganics and radionuclides. Research encompasses contaminant transformations, translocation, air-water interactions, sediment-water interactions and bioaccumulation.

The Environmental Contaminants Division consists of four sections: Organics-Properties, Organics-Pathways, Inorganics, and Radionuclides. Although the objectives of each Section are separated below, there is overlap between Sections. Information arrived at in one Section may be equally 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. The same applies to classical modelling of the future fate of contaminants in already polluted aquatic ecosystem. The former models require toxicology input. The latter models require input from biologists, aquatic ecologists and physical limnologists. Such input is obtained by cooperation with other units.

SECTION OBJECTIVES

Organics-Properties Section

The objective of this Section is to investigate the chemical and physical characteristics of organic contaminants 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 principles of properties and effects. Studies in this area can be grouped into bulk properties such as lipid-water or sediment-water partition coefficients; molecular properties such as ionization potentials; and reactions such as hydrolysis, chlorination and photodegradation. Considerable effort is devoted to the identification of contaminants and to their toxicity to bacteria and fungi. Projects also investigate the persistence and degradation of organic material in the aquatic environment with an emphasis on microbiological, photochemical, and bioaccumulation processes.

Organics-Pathways Section

The objective of this Section is to resolve the entry, fate, distribution, and transfer of organic contaminants in the aquatic ecosystems. Research is conducted at specific polluted aquatic ecosystems, in experimental ponds, and in the laboratory. Projects include studies in large and small river-lake systems. Experimental additions of organic contaminants are made to a series of artificial meso-ecosystems (ponds) located near Hamilton to examine intercompartmental transfer (water, suspended sediment, sediment, benthic fauna, and flora) and effects of organic contaminants. Atmospheric input of organic contaminants to the aquatic environment is being studied in the Great Lakes drainage basin.

Inorganics Section

The objective of this Section 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 likely polluted areas in Canada. Other research studies investigate the distribution, pathways, and bioavailability of metals in large river-lake systems. The geochemical controls of lake acidification and the response of drainage basins to airborne deposition of metals are studied in a calibrated watershed.

Radionuclides Section

The objective of this Section is to study the behaviour in aquatic ecosystems of both naturally occurring and artificial radionuclides. Studies include the determination of pathways of radionuclides discharge 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 determining the lifetimes of other contaminants in aquatic ecosystems.

COMMITTEE INVOLVEMENT

Dr. R.J. Allan and Mrs. A. Mudroch have been closely involved with the Canada-U.S. Niagara Study Committee and have made several presentations on contaminant problems in the Niagara Frontier. They are co-leaders of the National Water Research Institute's Niagara River Study Group. The early results of this research will be presented at a special symposium at the International Association of Great Lakes Research (IAGLR) meeting in May in Saulte St. Marie. 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. A comprehensive final report is nearing completion. Dr. W.M.J. Strachan continued as Chairman of the Great Lakes Water Quality Agreement, Aquatic Ecosystems Objectives Committee. An annual report was presented to the International Joint Commission. Dr. Strachan also continued to serve on the Organization for Economic Cooperation and Development Chemical Testing Program Committee on Test Guidelines. A comprehensive OECD Manual on Testing Guidelines was released this year. Dr. R.J. Maguire continued to serve on the National Research Council Environmental Secretariat Panel on Aminocarb. A Criteria publication will appear in the near future. Dr. D.S. Jeffries became Chairman of the Algoma Watershed Acid Rain Research Steering Committee. A series of special publications based on the multidisciplinary research conducted in the watershed is planned.

Major committee involvement by ECD personnel is listed in the following table.

CommitteeOfficer

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

OTHER ACTIVITIES

Special note should be made of the initiation of several field oriented studies to resolve the questions about the past, present and future contamination of Lake Ontario from sources in the Niagara River and its tributaries. Dr. D. Jeffries joined ECD to lead studies dealing with the geochemical controls of acidification of drainage basins. Dr. W.M.J. Strachan spent most the year seconded to the new Toxic Chemicals Management Centre in Ottawa. While there he contributed to developing the objectives and priorities of the Centre. On an academic level the most significant event was Dr. Y.K. Chau's gaining of the DSc degree from Liverpool University.

Dr. D.L. Liu and Dr. Y.K. Chau presented papers at three foreign conferences, the former in Scotland and the latter in Italy and the Netherlands. Twelve other conference presentations were made in Canada and the United States.

Several new staff members joined the Division while others departed. The present Divisional Staff list is presented below:

ENVIRONMENTAL CONTAMINANTS DIVISION

Chief - Dr. R.J. Allan - applied geochemistry.
Secretary - Mrs. E.M. Kerr
Administrative Officer - Mr. F. Boyd
Word Processor -

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 microorganisms.
Dr. D.L. 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.

Technologists: Mr. M.E. Comba, Mrs. K.D. Nicol,
Mr. D. Sutherland, Mrs. K. Thomson,

Organics-Pathways Section

Head - Dr. J.H. Carey - photodegradation of organic contaminants.

Researchers:

Mr. M.E. Fox - persistent organic contaminants in aquatic ecosystems.
Dr. E. Nagy - fate and effects of organic contaminants in test ecosystems.
Mrs. J. Metcalfe - biological fate of contaminants.
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,
Mr. H. Huneault

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. Semkin

- geochemical processes controlling lake acidification.

Technologists: Mr. G.A. Bengert, Mrs. T. Eguchi,
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.

Researchers:

Dr. S.R. Joshi

- aquatic pathways of radionuclides.

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

Post Doctoral Fellows

Dr. J. Cullen

- structure-activity correlations of organic contaminants.

210: METHODS FOR PREDICTING THE HAZARD OF ENVIRONMENTAL CONTAMINANTS BY STRUCTURE ACTIVITY CORRELATIONS

by

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

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) and has been identified as a Research Need by the Research Advisory Board.

The impact and pathways of organic contaminants in aquatic systems are determined by three distinct properties: toxicity, bioaccumulation potential, and persistence (1). Each of those properties is determined by its molecular characteristics and, in principle, can be predicted from the known values of those for related compounds. So far, best progress appears to have been made in correlations of bioaccumulation potentials and bioconcentration factors with the partition coefficient, P_{Oct/H_2O} (2). The lipophilicity of compounds also is strongly related to their water solubility and fugacity, hence also to toxicity (3).

RESEARCH RESULTS

Triplicate LD_{50} (lethal dose to 50% of population) values were determined for 10 para-substituted phenols and 12 chlorobenzenes, by intraperitoneal injection to small (~25 g) rainbow trout (Salmo gairdneri). Oral LD_{50} of four of the chlorobenzenes and five of the phenols were also determined as well as 96-hr lethal concentrations ($96LC_{50}$) for some phenols.

The 120-hr LD₅₀s by IPI for the chlorobenzenes ranged from 5.1 mmol/kg for 1,2,3,4-tetrachlorobenzene to 30.5 mmol/kg for 1,3,5-trichlorobenzene. The results were highly repeatable with standard deviations ranging from 2 to 9% of the means. The OI LD₅₀s for the chlorobenzenes were consistently 22 to 30% higher than the IPI LD₅₀s. There was, however, a linear correlation between the two (IPI LD₅₀ = 0.55 + 0.76 OI LD₅₀; r² = 0.99; s_b = 0.02; N = 4) that was significant at the 0.05 probability level.

The IPI LD₅₀s for phenols were lower than those for chlorobenzenes, ranging from 0.19 mmol/kg for p-cyanophenol to 4.34 mmol/kg phenol. The results were also more variable, with standard deviations ranging from 6 to 35% of means. Once again OI LD₅₀s were higher than IPI LD₅₀s, by 14 to 45% and a statistically significant correlation (P < 0.05) between the two was evident (IPI LD₅₀ = 0.044 + 0.781 OI LD₅₀; r² = 0.99; s_b = 0.04; N = 5). The LC₅₀s for the five phenols tested ranged from 0.0012 mM for p-(methylamino) phenol sulphate to 0.103 mM for phenol. A curvilinear relationship appears to exist between LC₅₀s and both OI and IPI LD₅₀s but there were insufficient data for a defined correlation.

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5. K.L.E. Kaiser and I. Valdmanis. 1982: Apparent Octanol/Water Partition Coefficients of Pentachlorophenol as Function of the pH. Can. J. Chem., submitted.

211: CHARACTERIZATION OF INDIVIDUAL TOXIC PCB COMPOUNDS
AND OTHER CHLORINATED HYDROCARBONS IN THE GREAT LAKES

by

B.G. Oliver and K.D. Bothen

INTRODUCTION

One of the Department of the Environment's mandates is to study environmental contaminants - particularly in transboundary waters. To date our study has focussed on the Niagara River and adjacent Lake Ontario and it is clear that most of the persistent organic chemicals present in this river and lake originate in the United States¹.

In addition to tracing contaminant sources a major objective of the study is to develop a better understanding of the movement and pathways of persistent organics and, if possible, to relate the ultimate fate of the chemical to its chemical and physical properties. By measuring concentrations of specific chemicals in the various aquatic compartments an estimate of human exposure via water and fish consumption can also be made.

RESEARCH RESULTS

After development of sufficiently sensitive analytical techniques for chlorinated organics in water², and in sediments and fish³ we analyzed samples from throughout the Canadian Great Lakes. The first group of compounds for which analyses are complete are the chlorobenzenes, CB's. Our study showed that Lake Ontario water, sediments and fish contained much higher CB concentrations (10 to 20 times) than samples from Lakes Superior, Huron or Erie (see Table 1 and reference 1). A sampling cruise up the Niagara River showed that the major sources of CB's to Lake Ontario were chemical plant effluents and leachates from waste disposal sites (e.g., Love Canal) located in the United States.

Further work being carried out on CB's in the Niagara River/Lake Ontario vicinity includes: mapping of the CB distribution of Lake Ontario sediments, dating CB inputs from the Niagara River by sediment core analysis, and analyzing CB concentrations in various components of the aquatic food chain. In addition, the

concentration of specific toxic PCB isomers in these samples will be determined in the next few months.

To conclude earlier work, two studies were completed on chlorinated by-products from the reaction of chlorine with naturally occurring organic material under conditions used in drinking water treatment^{4,5}.

TABLE 1. A Comparison of Lake Ontario and Lake Erie Chlorobenzene Concentrations

| Compound* | Water Concentration (ppt) | | Sediment Concentration (ppb) | | Fish Concentration (ppb) | |
|--------------|---------------------------|--------|------------------------------|--------|--------------------------|--------|
| | L.Ontario | L.Erie | L.Ontario | L.Erie | L.Ontario | L.Erie |
| 1,4 DCB | 45 | 4 | 94 | 9 | 4 | 4 |
| 1,2,4 TCB | 0.6 | 0.2 | 94 | 3 | 5 | 0.5 |
| 1,2,3,4 TeCB | 0.1 | 0.05 | 33 | 0.7 | 12 | 0.3 |
| OCB | 0.2 | 0.04 | 32 | 1 | 16 | 0.6 |
| HCB | 0.06 | 0.04 | 97 | 3 | 127 | 8 |

* 1,4 Dichlorobenzene; 1,2,4 Trichlorobenzene; 1,2,3,4 Tetrachlorobenzene; Pentachlorobenzene; Hexachlorobenzene.

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212: IDENTIFICATION OF CONTAMINANT SOURCES IN THE GRAND, NIAGARA AND WELLAND RIVER SYSTEMS

by

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

INTRODUCTION

Many toxic and carcinogenic organics have been found in surface and municipal waters. It is important to identify such contaminants and their sources, pathways, and sinks so that corrective measures can be undertaken where necessary. The Niagara River and its tributaries have been determined to be contaminated by a large number of organic contaminants (1). This study is an integral part of several ongoing investigations on the identification of the sources, pathways and sinks of such contaminants (2).

RESEARCH RESULTS

Effluents of Cyanamid produce point source loadings of methylene chloride, carbon disulfide, dibromomethane and bromotrichloromethane to the Welland River. Such effluents also add significant levels of trichloroethylene, carbon tetrachloride, 1,1,1-trichloroethane and tap water related trihalomethanes to existing volatile levels in the river.

In 1981, Ford had an active outfall consisting mainly of tap water which also contained moderate levels of trichloroethylene, perchloroethylene, tetrachlorethane and a substantial level of dichlorodifluoromethane.

Although several of the detected compounds are known or suspected to be animal mutagens and carcinogens (NIOSH, 1976) and therefore pose health hazards also to humans, either directly through contamination of potable water or indirectly through bioaccumulation in fish, this is not likely to be of concern here because of the high dilution rates, degradation and volatilization, such that the concentrations of most of the compounds in the Chippawa power channel are near background levels. The relatively high levels of chlorodibromomethane in the water at the Adam Beck reservoir are likely to result from several discharges along the Welland River-Chippawa power channel system including those of the

Cyanamid plants. Of possible concern are the considerable discharges of carbon disulfide. Although this compound has been observed as a natural product of the sulfur cycle in marine systems (Lovelock, 1974), its concentrations there were in the order of $1 \text{ ng}\cdot\text{L}^{-1}$, approximately 1000-fold less than in Thompson Creek water. Moreover, it is unknown whether or not CS_2 is also a natural constituent of freshwater. Carbon disulfide is a well-known poison to many mammalian species with neurotoxic effects upon chronic exposure.

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213: BACTERIAL METABOLISM OF CHLORINATED BIPHENYLS

by

R.M. Baxter and D. Sutherland

INTRODUCTION

Although chlorinated biphenyls are among the most persistent of environmental contaminants, certain of them are susceptible to bacterial degradation at least to a limited degree. The literature on this subject has been reviewed (Baxter, 1981). The aim of this study has been to extend our knowledge of this topic, and to investigate possible further non-biological transformations which the products of the initial biochemical reactions may undergo.

For this purpose we have used a bacterial culture isolated by D. Liu which is capable of degrading chlorinated biphenyls. It grows rapidly in a mineral salt medium with biphenyl as its only carbon and energy source. In most experiments the organisms have been removed from the growth medium by centrifugation and suspended in phosphate buffer.

RESEARCH RESULTS

Using the Gilson apparatus, two monochlorobiphenyls and six dichlorobiphenyls were found to undergo biological oxidation as shown by oxygen uptake. One dichlorobiphenyl (the 2,6-isomer) and all more highly chlorinated biphenyls tested appeared not to be attacked.

2,4'-dichlorobiphenyl was converted to a bright yellow compound, which on the basis of the reports in the literature is probably produced by meta-cleavage of one of the two rings. A similar product is obtained from Arochlor 1016 (Monsanto), a mixture of several chlorinated biphenyls. These products are bleached in long wavelength ultraviolet light or sunlight. The nature of this reaction is being investigated.

With arochlor 1221, a mixture of less highly chlorinated biphenyls, a brownish product is formed which darkens in ultraviolet light, and more slowly on standing at room temperature, suggesting that polymerization to material resembling humic acid occurs. This reaction is also being investigated further.

These studies lead to the tentative conclusion that the products of bacterial degradation of chlorinated biphenyls undergo photochemical and spontaneous reactions leading to their further degradation and polymerization.

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215: BIODEGRADATION OF ORGANIC ENVIRONMENTAL CONTAMINANTS

by

D. Liu, K. Kaiser, W. Strachan, 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 the food-chain also depends heavily on these parameters. Such investigations are highly relevant to hazard assessment, an aspect of the Environmental Contaminants Act. Microbial degradation, in particular, provides a major route for the removal of contaminant from the environment. Chemical toxicity, on the other hand, may affect the microbial degradation process and the operation of the food-chain in aquatic ecosystems.

Because of the many variables involved, it is impractical to study a chemical's biodegradation in all natural environments. We have developed a standard laboratory fermentor system to examine a compound's degradation processes induced by microorganisms from sediment, soil and activated sludge. We have successfully determined the biodegradability of several priority chemicals listed under the Environmental Contaminants Act.

RESEARCH RESULTS

The standard laboratory procedure, capable of accurately predicting the persistence of the test chemical in various aquatic compartments, is based on the measurement of the primary degradation rates of such substance in cyclone fermentors under aerobic and anaerobic conditions, with and without cometabolites (Table 1). The biocides, fenitrothion and 2,4-D, were tested as examples in the system and results indicated that the former was less stable under anaerobic conditions and the latter was more persistent under the same environmental condition (1). In addition, several other priority chemicals including pentachlorophenol (biocide), carbaryl (insecticide) and p-nitrophenol (industrial chemical), were also tested in the system. The calculated relative persistence was compared with the published field data and good agreement was observed (2,3,4). We have also studied the

biodegradation of Aroclor 1221 type PCBs in wastewater as well as the role of fungi in the decomposition of pentachlorophenol (5,6).

TABLE 1. Effect of Environmental Factors on Fenitrothion and 2,4-D Degradation

| | Aerobic | | |
|------------------------------|-----------|-------------|---------------|
| | Control | Metabolism* | Cometabolism* |
| | | | Fenitrothion |
| 10^{-3} k, h ⁻¹ | 2.3 | 0.40 | 5.3 |
| half-life, day | 13.0 | 73.0 | 5.5 |
| r | 0.66 | 0.89 | 0.98 |
| | | | 2,4-D |
| 10^{-3} k, h ⁻¹ | 0.30 | 9.5 | 16.2** |
| half-life, day | 97.0 | 3.1 | 1.8 |
| r | 0.97 | 1.0 | 0.98 |
| | Anaerobic | | |
| | Control | Metabolism* | Cometabolism* |
| 10^{-3} k, h ⁻¹ | 1.7 | 3.9 | 38 |
| half-life, day | 17.0 | 9.8 | 1.0 |
| r | 0.77 | 0.98 | 0.86 |
| 10^{-3} k, h ⁻¹ | 0.24 | 0.21 | 0.42 |
| half-life, day | 120.0 | 135.0 | 69.0 |
| r | 0.96 | 0.70 | 0.98 |

* Calculated from percent of control at the same time and oxidation state.

** Only the last three data points were employed to account for acclimation.

Two biological tests based on the measurement of the interaction between the toxicant and the bacterial response was developed for assessment of chemical's toxicity. The tests are economical, simple, and sensitive when compared with the conventional methods. Consequently, they have the potential for use in the structure-toxicity study and for screening a large number of samples for the presence of toxic chemicals (7,8,9).

Since the chemical and biological activity in sediment may affect the fate and pathway of a contaminant in the aquatic environment, a field method based on the measurement of the reaction between resazurin and such activity was developed. This highly reproducible test offers promise of a method for ascertaining different types of activities in the sediments (10,11).

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216: CHEMISTRY OF CHLORINATED HYDROCARBONS AT THE
AIR/WATER INTERFACE

by

R.F. Platford and J.H. Carey

INTRODUCTION

This study consists of two separate investigations. The first of these is a determination of the equilibrium distribution of a few representative toxic compounds between water and the insoluble organic phase which is inevitably present in natural waters - often as a slick floating on the surface. The second is a measurement of the transport of the same compounds from one phase to another - the air being included as a phase. In other words, the transport properties refer to a system on its way to a final equilibrium state.

The quantities measured in the course of this work include vapour pressures, partitioning between the model lipid octanol and water, and hydrocarbon concentrations in the air and surface films over natural waters.

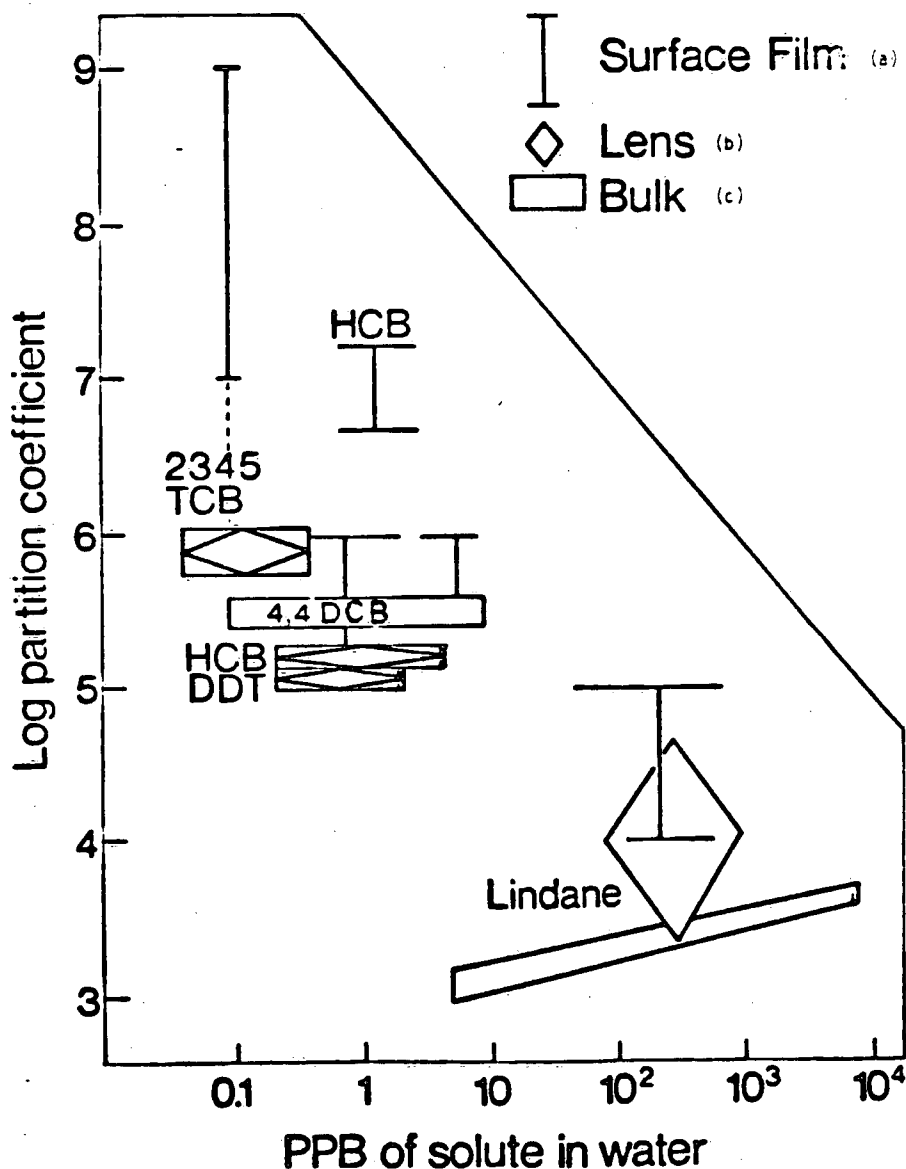
RESEARCH RESULTS

Of the five chlorinated hydrocarbons whose octanol-water partition coefficients we have measured, three have been found to be much more strongly partitioned into a thin film of octanol on the surface of water, than into bulk octanol in equilibrium with water. The results of three types of measurement are shown in the Figure:

- a) Conventionally determined partition coefficients between octanol and water.
- b) Partitioning when the octanol is in the form of a small lens floating on water, and which should give the same results as (a).
- c) Partitioning into octanol in the form of a monomolecular layer of octanol surrounding the lens in (b).

It can be seen that enhanced partitioning in surface films is observed for lindane, hexachlorobenzene and 2,3,4,5-tetrachlorobiphenyl. This surprising and important effect was not observed for these compounds in thin films of oleic acid, however, and remains to be confirmed outside this laboratory.

Future work will consist of laboratory vapour pressure measurements on chlorinated hydrocarbons, and analyses of samples taken from the Grand River and the Niagara River and from the air immediately over the surface of each river.



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Future work will consist of laboratory vapour pressure measurements on chlorinated hydrocarbons, and analyses of samples taken from the Grand River and the Niagara River and from the air immediately over the surface of each river.

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

by

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

INTRODUCTION

Studies by all levels of government in both Canada and the United States have established the Niagara River as a major contributor of toxic organic loading to Lake Ontario. This study addresses the fate of some of these substances in Lake Ontario and, in particular, to their incorporation into the aquatic food chain via benthic organisms, since this route is a suspected avenue for the contamination of commercial and sports fisheries in Lake Ontario.

The 1981 study was considered as a preliminary investigation to learn if a more in-depth study was justified. The answers to several specific questions will help to guide the direction of ongoing studies in 1982. The study focussed on three main areas:

1. Whether organic contaminants are carried into Lake Ontario primarily via suspended sediments and, if so, whether their distribution among different particle sizes and types is significant.
2. Are organic contaminants in surficial sediments of the dispersal area of the Niagara River plume bioaccumulated in benthic animals?
3. Which organic contaminants are significantly involved in the above processes?

Several other studies on different aspects of the Niagara River contamination of Lake Ontario were currently in progress at NWRI. This work was coordinated with these studies especially in the choice of sample locations in order to facilitate inter-study comparisons and conclusions.

RESEARCH RESULTS

Suspended solids were collected with a plankton net in the Niagara River near Niagara on the Lake in June, July and September, 1981. The suspended solids were divided into six fractions between 38 and 841 μm by wet sieving. High concentrations of PCB's and chlorobenzenes were observed on the suspended solids. A somewhat surprising result was the detection of significantly higher concentrations of contaminants on the larger particles, since purely physical considerations would predict the smallest particles to have the highest concentrations.

Surficial sediment, water, pore water and benthic organisms were collected from five sites in Lake Ontario near Niagara River Mouth. Fish (Lake Trout), mysids and deep water zooplankton were also obtained from one station in July. Amphipods and oligochaetes were selected as benthic organisms for analysis, based on the frequency of occurrence at all stations and differences in habitat. Although chironomids were also found at all stations their numbers were not sufficient for analysis. Concentrations of organochlorine contaminants in surficial sediments tended to fall between the values for the largest and smallest particles of Niagara River suspended sediment and exhibited a significant bioaccumulation in amphipods of the more persistent contaminants such as PCB's ($\times 35$) whereas less refractory contaminants such as hexachlorobutadiene showed no trend to bioaccumulation (Table 1). This work will be presented at the XXV Conference, International Association for Great Lakes Research in Sault Ste. Marie, May 1982.

Study plans for 1982-83 reflect indications that the bulk of the contaminant load may be associated with the dissolved phase rather than the suspended solids. Thus, to determine the fate of these substances in Lake Ontario, it is necessary to follow the Niagara plume rather than suspended solids. Intensive sampling on transects across the Niagara River plume in Lake Ontario will be carried out on several occasions. Transmissometer and EBT profiles will be obtained to define the location of the plume. A fast analysis for one or two selected organochlorine contaminants will be performed on the samples with more detailed analyses in selected samples.

TABLE 1. Concentrations of Four Organochlorine Contaminants in Niagara River Suspended Sediments and Receiving Zone Compartments in Lake Ontario Near Niagara River Mouth April-May, 1981 (ng/g dry weight basis).

| Location | Sample Compartment | Hexachloro-Butadiene | Hexachloro-Benzene | Total PCB's | Mirex |
|---------------------------|-------------------------|----------------------|--------------------|-------------|-------|
| Niagara River at N.O.T.L. | Sus. Sed. 38-74 μ m | 11 | 17 | 639 | 49 |
| Niagara River at N.O.T.L. | Sus. Sed. 7841 μ m | 710 | 92 | 5488 | 434 |
| Lake Ontario St. #207 | Surficial sediment | 31 | 260 | 680 | 3 |
| Lake Ontario St. #207 | Oligochaetes | 60 | 100 | 2200 | <10 |
| Lake Ontario St. #207 | Amphipods | 20 | 390 | 24000 | 50 |

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221: TOXIC ORGANIC SUBSTANCES IN PRECIPITATION

by

W.M.J. Strachan and H. Huneault

INTRODUCTION

Toxic organic substances, particularly the persistent organochlorine pesticides and PCBs, have been identified in wetfall in the Great Lakes area and elsewhere. Indications of deposition in this manner are such that, for PCBs, BHC and DDT, this is the major input of these materials to Lake Superior, probably the major route for Lake Huron and certainly a substantial mode for Lakes Ontario, Erie and Michigan.

A wetfall sample was designed and built under an ECCF contract and prototypes evaluated in both the field and laboratory. The purpose of this report is to summarize the results obtained and to recommend whether such samplers should be employed in the larger scale CANSOC program.

RESEARCH RESULTS

The sampler is a stainless steel funnel (0.209 m²) with an automated lid which opens when a sensor detects moisture. (A photograph is attached as Figure 1.) All sample parts in contact with the rain are heavily teflon-coated. Extraneous splashing into the funnel is prevented by covering all exposed horizontal surfaces with stainless steel mesh. A teflon column (25 cm x 2 cm i.d.) is attached to the funnel. It is partly filled with XAD resin. Resins with samples adsorbed were extruded and analyzed by IWD-WQB (Ontario Region).

The samplers and procedures were tested (triplicate) for recovery in the laboratory. Table 1 presents the recoveries for those substances tested. In addition to therecoveries, the sampler was evaluated in the field. Three samplers and a rain gauge were located at Fifty Mile Point (F samples) near Hamilton, Ontario and later at the Turkey Lake field station (T samples) near Sault Ste. Marie, Ontario. Rain volumes sampled (1.0 to 17.9 L) were determined from tipping bucket rain gauge data and the sampler area; they correspond to discrete rain events. A

number of samples were not suitable because of electrical or mechanical problems; these have been remedied. A major problem was the occasional drying-out of part of the columns during the heat of summer; solutions to this are under consideration.

TABLE 1. Recovery of Organochlorines from Sampler

| Compound | Theoretical Concentration (µg/L) | Observed Concentration (µg/L) | SD (% RSD) | Recovery (%) |
|-------------------|----------------------------------|-------------------------------|------------|--------------|
| Hexachlorobenzene | 0.123 | 0.076 | 0.007 (9) | 62 |
| Lindane | 0.254 | 0.106 | 0.007 (7) | 42 |
| Heptachlor | 0.117 | 0.029 | 0.026 (89) | 25 |
| Aldrin | 0.067 | 0.045 | 0.007 (16) | 67 |
| α-chlordane | 0.478 | 0.342 | 0.022 (6) | 72 |
| γ-chlordane | 0.713 | 0.736 | 0.035 (5) | 103 |
| Endosulfan | 0.417 | 0.340 | 0.022 (6) | 82 |
| pp'DDE | 0.542 | 0.285 | 0.025 (9) | 53 |
| pp'-DDD | 0.413 | 0.288 | 0.010 (4) | 70 |
| pp'-DDT | 0.363 | 0.206 | 0.016 (8) | 57 |
| Methoxychlor | 0.505 | 0.292 | 0.034 (12) | 58 |

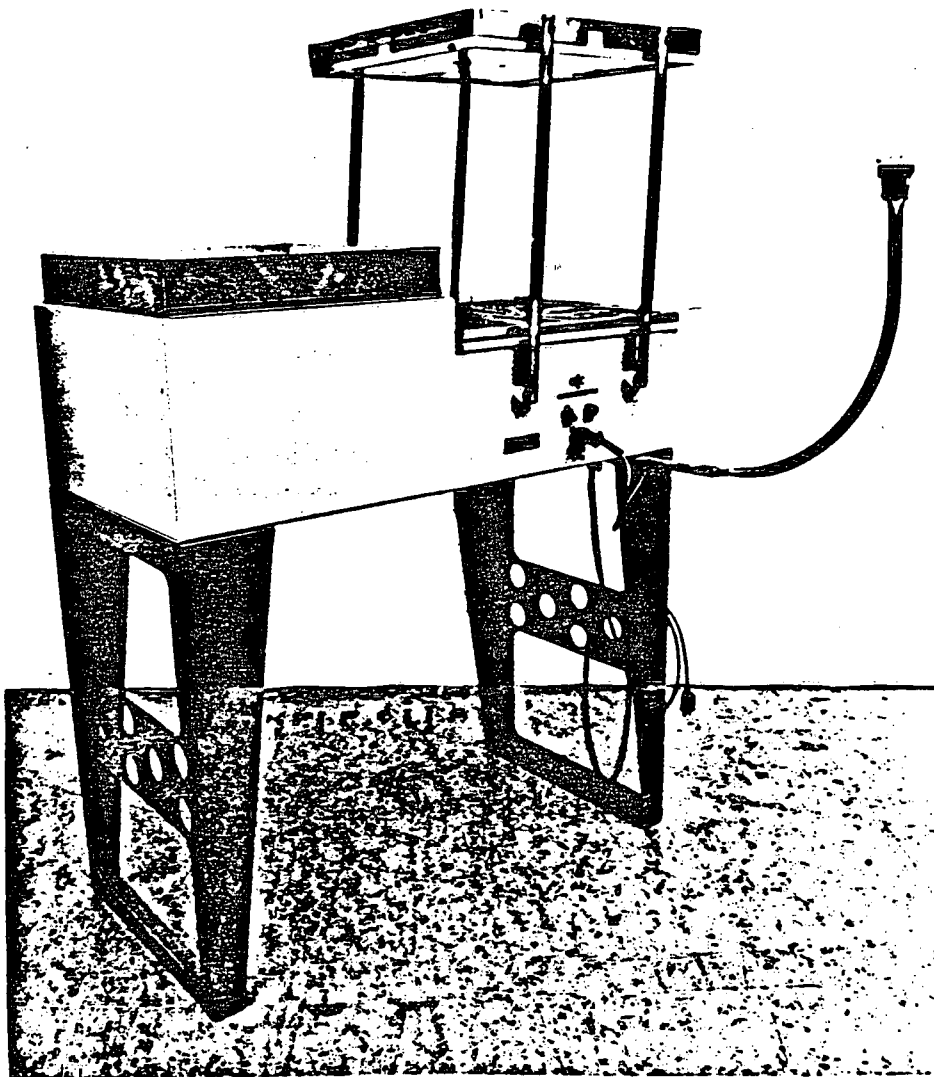
Mean values for field samples are presented in Table 2 for those substances which consistently gave values statistically different from zero. Other sample sets have been collected and will be added to the table as they become available.

TABLE 2. Significant Precipitation Results

| Sample | Concentrations in µg/L (%RSD) | | |
|--------|-------------------------------|------------|-------------|
| | α-BHC | γ-BHC | PCB |
| F1404 | 0.034 (49) | 0.007 (21) | - |
| F2404 | 0.038 (15) | 0.011 (15) | 0.011 (8) |
| F0505 | 0.010 (31) | 0.005 (35) | 0.041 (10)* |
| T0206 | 0.005 (2)* | 0.001 (4)* | 0.001 (36) |
| T0406 | 0.025 (2)* | 0.006 (3)* | 0.008 (28) |

* Average and % RSD for duplicates; third value differed grossly from others.

No discernable pattern is apparent for precision for the above. For the three substances noted, therefore, a mean percent relative standard deviation of 20, 16 and 21% is reported for oc-BHC γ -BHC and PCB, respectively. The number of sample sets is small and final evaluation of the errors associated with the sampler will await further sets currently collected and undergoing analysis. A repeat is also being undertaken for the recovery tests. In the meantime, however, the apparatus and precipitation would seem to be an improvement over the much smaller collection sampler (0.06 m²) and resultant volumes and frequencies of the CANSOC samples.



222: SEDIMENT-WATER PARTITIONING OF TOXIC ORGANIC SUBSTANCES

by

W.M.J. Strachan and H. Huneault

INTRODUCTION

Knowledge of the distribution of chemicals in the environment is a prerequisite to the evaluation of the hazard they represent and partitioning, transformation and transfer constants are among the primary factors which govern such distribution. Central to most descriptions of chemical behaviour is the aquatic segment of the ecosystem and within that compartment, partitioning between the dissolved and adsorbed phases will be a major influence on the fate and behaviour of persistent, hydrophobic contaminants.

A number of empirical methods exist to estimate the sediment (or soil) - water partition constant, all of which assume that only the incorporated organic matter determines this constant. It has also been reported that such adsorption is a two process mechanism; further, it is difficult to use these methods to predict results obtained in different studies employing different sediments or soils. The purpose of this study is to investigate the suitability of these predictive approaches particularly as they apply to the several size fractions of natural sediments.

RESEARCH RESULTS

Study progress was somewhat hindered by the secondment of one of the study team. Preliminary tests, however, were undertaken to evaluate procedures. The 2,4,6,2',4',6'-hexachlorobiphenyl isomer (HCBP) was partitioned between whole sediment and either distilled water or 0.01 N NaCl. Two sediment samples were employed - one "high" in organic content (2.44% P.O.C.) and one "low" (0.84% P.O.C.). In addition, a more soluble organic substance, hexachlorobenzene (HCB), was examined using a different "high" organic sediment. Recovery of both organics from distilled water was: HCBP, 76% (range 69-82, n=4) and HCB, 76%, while from the total system it averaged 45% for HCBP and 71% for HCB.

TABLE: Sediment Sorption of 2,4,6,2',4',6'-Hexachlorobiphenyl and Hexachlorobenzene

| Sediment Type* | mg/L or mg/kg | | | Sorption | | |
|-----------------------------------|---------------|--------------|--------------|------------------|--------------------------------|---|
| | Susp. Conc'n | Solid Conc'n | Water Conc'n | Sediment Conc'n | $10^{-3} K_d$ (\pm %RSD) | $10^{-6} K_{oc}$ ($K_d \times 100 / \%oc$) |
| 2,4,6,2',4',6'-Hexachlorobiphenyl | | | | | | |
| LO | 20,25 | 0.008,7 | 420,720 | 77(\pm 44) | 9.2 | |
| LO (saline) | 18,41 | 0.006,5 | 480,270 | 69(\pm 38) | 8.2 | |
| HO-1 | 19-28 | 0.005-10 | 490-810 | 96(\pm 29) | 3.9 | |
| HO-1 (fines) | 22-34 | 0.006-8 | 170-230 | 30(\pm 22) | 1.2 | |
| HO-1 (saline) | 18,21 | 0.007,8 | 930-440 | 95(\pm 64) | 3.9 | |
| Hexachlorobenzene** | | | | | | |
| HO-2 | 22,29 | 0.092,69 | -, - | [8.4(\pm 42)] | *** | |
| | 15-28 | 0.058-104 | 268-679 | 5.1(\pm 24) | *** | |

* LO - low organic sediment HO-1 - high organic sediment
Sample 1, HO-2 wet sediment Sample 2 (76.1% water) used, fines were sieved as 45 μ m.

** Water and sediment concentrations are presented as $10^3 \times$ observed.

*** Organic content not determined

Indications from the above are that considerable variability exists for results obtained under apparently similar conditions. Salinity does not appear to be a factor but the sediment size fraction does appear to be significant. Further investigation will include factors such as sorption on filters, homogeneity and preparation of sediment substrate, recovery of substance particularly from the sediment, possible volatilization of substance during removal of solvents.

224: CONTAMINANT STUDIES IN MESO-ECOSYSTEMS

by

B.F. Scott, E. Nagy, J. Hart, S. Painter, J. Wood, J. Sherry,
B. Dutka, A. Kwan, W. Taylor, A. Nimii, A. El-Shaarawi,
M. Charlton, J. Mackie, M. Dickman and J. Metcalfe

INTRODUCTION

The pathways, fate and impact of contaminants are high priority issues concerning the Department and the Service. To address this concern, we have developed meso-ecosystems, namely, lined ponds. They allow us to examine the chemical and follow biological changes in the system induced by the contaminant, without the removal of the chemical and elements of the biota from the experiment systems by currents and diffusion processes. In addition, the system have low environmental risk as the sediment and pond liners prevent contamination of adjacent soil and groundwater by the chemical under study. We have satisfactorily concluded a study on oil and dispersant mixtures using meso-ecosystems (1,2) and have initiated another study in 1980. The latter involved the fate and effect of 2,4-D when applied to control aquatic weeds. The control of macrophytes was a Departmental priority at the time of the study's inception and retains that designation. NRC has recommended that research related to environmental assessment for this and similar chemicals be carried out (3). The herbicide, 2,4-D, extensively used in Canada for crop control and in water, to control weeds, is a toxicant as is its first breakdown product, 2,4-dichlorophenol (DCP).

We have used a holistic approach to the study of the fate and impact of the chemical involving the expertise of professionals from many of the aquatic life sciences. Samples have been collected and analyzed for 2,4-D and DCP in water, sediment, particulate material and selected biota. Compounds of the biota monitored throughout the study period included protozooplankton, mezozooplankton, micro- and macrozoobenthos, phytoplankton, periphyton, fish, and macrophytes. In addition, water samples were analyzed for DO, nutrients, pH and major ions.

RESEARCH RESULTS

In July of 1981, the two control ponds of the 1980 series of tests were treated with the same formulation of 2,4-D to determine the degree of replication of the previous year's results (4,5). Concentrations of 2,4-D in the water column after the 1981 treatment followed the same trends as the 1980 values (Fig. 1). In the ester-treated ponds for both years, one half of the maximum concentrations were reached 55 days after treatment. This is the same time required by the amine-treated pond in 1981 to reach half of its maximum concentration. During the 1980 studies, 2,4-DCP persisted in the sediment and water column. In the 1981 studies, very little 2,4-DCP was detected. This difference was undoubtedly caused by the higher pH's in the ponds in 1981, which favour formation of the ionic form of the phenol. The ion will react faster photochemically than the undissociated parent phenol. For both years, 2,4-D concentrations in the sediment were higher in the ester-treated ponds relative to the amine-treated ponds. (The ester treatment used a pelletized formulation.) Also, there was uneven distribution of the 2,4-D on the sediment of all ponds.

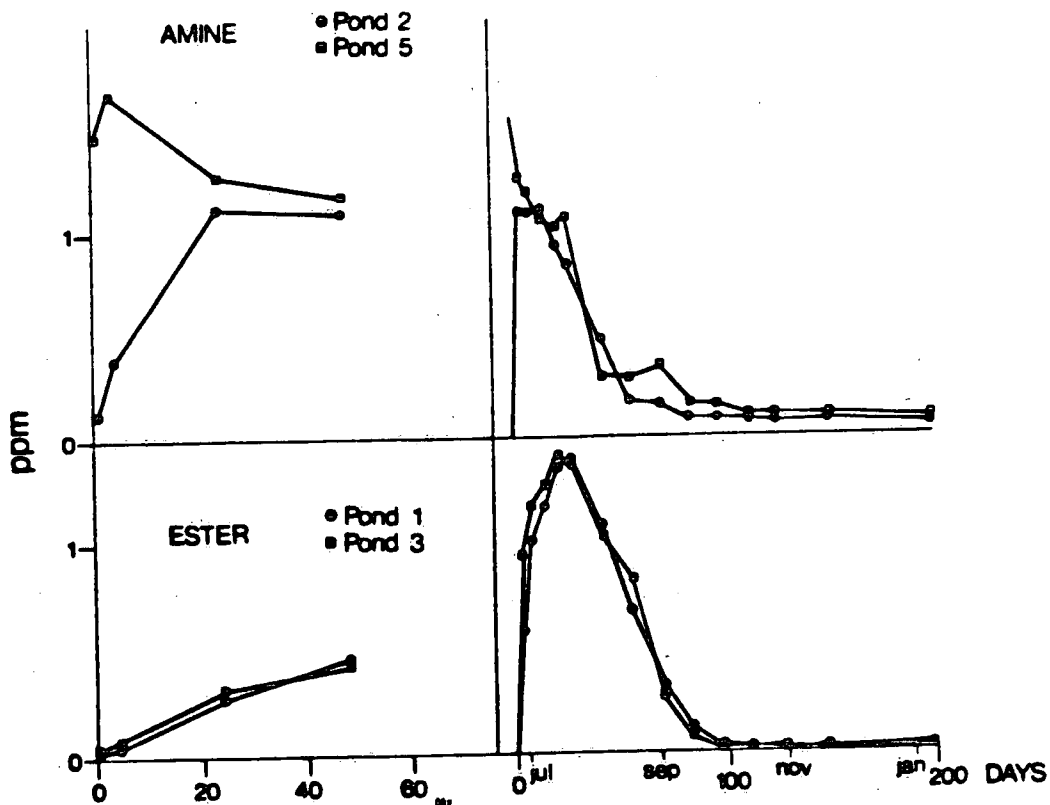


FIG. 1. 2,4-D Concentration

All target plants, Myriophyllum spicatum, had succumbed within 14 days of treatment in both years. There was no gross depletion of oxygen except within 6 cm of the bottom once the plants had collapsed. This is contrary to some predictions made from laboratory studies and subsequent modeling. Also, there was no sudden release of nutrients from the decaying plants which resulted in algal blooms.

All water quality parameters (nutrients, etc.) experienced similar fluctuations throughout the course of the experiment, with the exception of alkalinity. This parameter increased in the two treated ponds of 1981 after the plants had fallen to the bottom of the ponds. We believe this increase resulted from the decaying plants releasing CaCO they had encrusted on their leaves back into the system. This was partially confirmed by simultaneous increases in the Ca ion content of the water.

Fish toxicity of fingerlings over the first week after treatment was moderate (20%) in 1980 and was very low in 1981. This difference resulted from there being less phenol present and most of that which was in the water column being in the ionic form which is less toxic than the parent phenol.

Analytical methods have been modified and tested for the simultaneous extraction and analysis of 2,4-D and 2,4-DCP from clams, milfoil and fish.

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225: ACCUMULATION AND DEGRADATION OF ORGANIC CONTAMINANTS
IN FLUVIAL SYSTEMS

by

J.H. Carey, M. Fox, J. Metcalfe, L. Coletta and R. Tkacz

INTRODUCTION

Research into the transport and degradation of contaminants is needed in order to adequately assess risks from environmental pollution and is a high priority for both the Department and Service. In conjunction with laboratory studies, there is a need for field studies of the behaviour of contaminants under actual environmental conditions. As a step in meeting this need, the Canagagigue Creek Project was begun in 1979. The project has adopted the ecosystem approach and is attempting to determine the factors affecting the accumulation and disappearance of synthetic organic compounds introduced to the stream at the town of Elmira. Results for the first year's study indicated that chlorophenols were the most prominent contaminant at most times of the year. These substances appear in the stream as a result of leaching activity in the area of a disused chemical waste dump. In addition, other synthetic organic compounds such as methyl thiobenzothiazole, MMBT, were observed in the discharge of a sewage treatment plant receiving industrial wastes. Also in the effluent of the sewage treatment plant we observed unidentified acidic compounds at concentrations higher than the fatty acids. These compounds appeared to be the result of degradation of unidentified precursors in the STP.

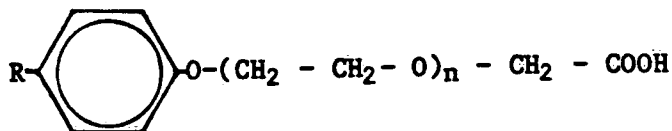
Research for FY 81-82 was planned to examine the above areas in greater detail. Specifically, the factors affecting the distribution and fate of MMBT and chlorophenols in the stream and biota were to be addressed and the identity and origin of the acidic compounds examined. In a related part of the study, the importance of photolysis in degrading TFM was to be assessed in Oakville Creek.

RESEARCH RESULTS

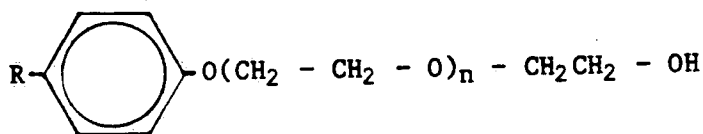
Several factors complicated our work this past fiscal year. The first of these was the near total absence of MMBT from Canagagigue Creek. It appears that the chemical plant which is the source of this compound switched production to other products. A determined effort to find another water soluble electron capture detector active compound in the stream at levels high enough to study volatilization failed. In any case, laboratory studies revealed that its vapour presence is lower than anticipated and volatilization is probably not the major environmental route of disappearance for this compound. In cooperation with Dr. D.L. Liu, a study of the effect of humic compounds on the biodegradation of MMBT has revealed that fulvic acid enhances this degradation route. A publication is being prepared from these results.

A more serious problem involved the accidental release of large (>1000 gal) quantities of nonyl phenol into Canagagigue Creek on several occasions during the field season. This material, which now appears to have entered the stream from the chemical plant, was present at concentrations well above the LD₅₀ for all aquatic organisms that have been tested. The result has been a severe disruption in the Canagagigue benthic community downstream of Elmira. A report on these incidents has been prepared at the request of OME who are evaluating what action is now to be taken. Our studies of uptake of chlorophenols by benthic biota were severely affected. Nevertheless, several aspects of these studies have proceeded. We have succeeded in analyzing six leech species for chlorophenols and find significant differences in the levels of these contaminants accumulated by each species. A publication on this subject will be prepared in the coming year. In addition, several fish species were obtained from Canagagigue downstream of Elmira and these were dissected into individual organs and analyzed. The results reveal that chlorophenols accumulate in different fish organs than neutral organochlorines such as lindane. A paper on these results will also be prepared when all analysis are complete.

With regard to the identity of the acidic series of products found in Canagagigue in 1980, they have now been identified and their routes of formation elucidated. These products have the general structure:



where R is an octyl or nonyl group and n 1-3. They arise from degradation of the appropriate alkyl phenol polyethoxylate surfactant



where n = 8-30.

These substances are widely used as industrial detergents and as surfactants in the chemical industry. The route of formation of these compounds has been confirmed in some preliminary experiments in collaboration with Dr. D.L. Liu. After further confirmation and synthesis of these compounds in the coming year, a paper will be prepared from these results.

Finally, with regard to the photolysis of TFM in Oakville Creek, this study was not carried out totally as planned due to the last minute cancellation of the Oakville Creek treatment by the Sea Lamprey Control Centre. We were able to switch part of the study to Lynde Creek and to observe that our predicted photoproducts were in fact found under field conditions. There is not enough data for a publication at this point but it is planned to pursue this subject in the coming FY.

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230: TRACE METAL BIOAVAILABILITY

by

K.R. Lum

INTRODUCTION

Current models/conceptions of the roles of trace metals in vivo indicate that both 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.

This study, in part, addresses the problem of the disposal of dredged spoil and other contaminated solid wastes, e.g., mine tailings, sludges. For Canadian ports, it was estimated in 1980 that $2 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ of sediments were dredged with attendant multi-million dollar disposal costs. The approach to predicting possible scenarios for the metals contained in such materials involves the use of a sequential chemical extraction procedure which has been applied to a wide range of environmental sample types (Tables 2 to 4).

Synergistic and antagonistic interactions exert an important influence on the toxicological effects at sub-lethal concentrations of the mixtures of metals present in the environment. Hence, this study has not emphasized the behaviour and transformations of any one element. Thus, the suite of metals investigated so far include Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn and the non-metal, P. This range is being extended to the determination of Ag, As, Be, Hg, Mo, Se and V.

Because colloidal metal forms may comprise the major fraction of what is conventionally regarded as dissolved metal ions, we have also studied the particulate phases and their particle size associations. Although there is considerable interest here and elsewhere in chemical speciation, little emphasis has been given to determinations of the molecular nature of metal

complexes in solution. Such work, though important to furthering our understanding of trace metal pathways, may produce confusion at a higher level as it were, because of the very low levels of dissolved metals present in natural waters and the difficulty of obtaining precise and accurate concentration data. In addressing this problem, work is being done using electrothermal atomization atomic absorption spectrometry for ultra-trace analyses and to delineate the sources of interferences which are commonly encountered with this technique.

Another aspect of the study has been the development of a chemical procedure which may be used to model the availability of dissolved metal forms to phytoplankton. We have evaluated differential pulse polarography as a means of distinguishing and quantitating labile and inert metal forms. This work is intended to further our understanding of the ameliorating effects of dissolved organic matter and colloidal material on metal ion toxicity.

RESEARCH RESULTS

In a study of the partitioning of trace metals in Lake Erie, we found that the average amounts of Al, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in dissolved forms were 6, 79, 93, 71, 4, 43, 89, 68 and 81% of the respective total metal concentrations. The analysis of particulate metals from the Lake showed that Cd, Co, Cu, Pb and Zn are generally associated with particles smaller than 8 μm , whereas Fe and to a lesser extent Al and Mn, occur appreciably with particles larger than 8 μm .

Meltwater and sediment from the Rhône Glacier were similarly studied. Greater than 80% of the total Cd, Cu, Mn, Ni and Zn were found to be in operationally defined (0.4 μm) dissolved forms. Fe and Al in the meltwater are primarily associated with particles in the size range 0.4 to 8 μm , while Cd, Cu, Mn, Ni and Zn occur with particles smaller than 0.1 μm . For the sediment, Cu, Ni and Pb were significantly (14, 38 and 52%) present as readily exchangeable forms.

The sequential chemical extraction procedure adopted for this study has been shown to yield valuable information on the availability of trace metals (see Tables 2 and 3) in environmental samples. The readily exchangeable metal forms distinguished by this procedure can be considered to arise from inputs of salt-laden water during the spring run-off period as a consequence of road-salting during winter. The metal ions in this fraction are then available to the biotic community at a very sensitive stage in the life cycle of many organisms.

The carbonate and surface-oxide bound forms can be regarded as arising from inadvertent inputs of acidic effluent in areas adjacent to industries or from the melting of acid-laden snow and acid precipitation. In Tables 2 and 3, the percent available column reflects the sum of these two fractions which are operationally defined by the extraction procedure.

The procedure also distinguishes elemental forms associated with Fe and Mn-oxides and bound to organic matter and sulphides. The latter forms may become available as a result of microbial decomposition of organic matter or as a result of the oxidation of sulfidic sediments dredged and dumped in an oxic environment thus leading to the production of acid seepage. In the case of elemental forms bound to Fe and Mn oxides, they may become potentially available under anoxic conditions. Such conditions are in most cases temporary and hence re-sorption of released elements may be expected once mixing with oxygenated water occurs.

As a result of the growing awareness that the common use of slowly responding analog recorders can lead to serious errors in data interpretation, a microcomputer has been interfaced to a Zeeman Effect Atomic Absorption Spectrometer. We have been able to develop a data acquisition system which has an effective response time of better than 20 ms which offers the following features: 1) the use of electrodeless discharge lamps, 2) simultaneous temperature and absorption recording, and 3) hard copy using an X-Y recorder and calculation of integrated absorption and background only absorption. We are presently using the system to resolve the transient signals (which may be as short as 0.05 s) produced in the graphite furnace in order to understand atomization processes and aid in the selection of optimum experimental conditions and the detection and removal of matrix interferences.

In Table 4 is summarized the results on the determination of labile and inert complex forms of Pb, Cd and Zn in the carbonate/surface-oxide bound forms for some selected samples.

TABLE 1. Dissolved Metals in Nearshore Areas of the Great Lakes.
Units in $\mu\text{g l}^{-1}$

| | Cd | Cr | Cu | Pb |
|------------------------------|------|------|------|------|
| Lake Ontario | 0.04 | 0.40 | 1.1 | 0.14 |
| Hamilton Harbour | 0.14 | 0.66 | 1.9 | 3.0 |
| Collingwood Harbour | 0.11 | 0.22 | 0.65 | 1.0 |
| Oshawa Second Marsh | 0.35 | 0.60 | 2.5 | 1.0 |
| Leslie St. Spit/Aquatic Park | 0.18 | 0.40 | 4.8 | 1.3 |

TABLE 2. Potential Availability of Metals in Suspended and Bottom Sediments. Units in $\mu\text{g g}^{-1}$. nd = none detected.

| | Cd | Co | Cr | Cu | Ni | Pb | Zn |
|----------------------------------|-----|-----|-----|-----|-----|-----|------|
| Average Background | 0.4 | 11 | 25 | 9 | 15 | 10 | 44 |
| Lake Ontario | 2.5 | 22 | 155 | 66 | 79 | 190 | 290 |
| % Available | nd | nd | nd | 6 | 15 | 10 | 10 |
| Hamilton Harbour | 16 | 18 | 265 | 140 | 110 | 365 | 1970 |
| % Available | 37 | 26 | 2 | 19 | 28 | 11 | 19 |
| Oshawa Second Marsh | 2.4 | 19 | 120 | 45 | 108 | 89 | 143 |
| % Available | nd | nd | nd | 2 | 3 | 2 | 1 |
| Niagara River | 3.9 | 22 | 113 | 38 | 48 | 82 | 260 |
| % Available | 26 | 1.6 | 0.2 | 6 | 11 | 20 | 7 |
| Collingwood Harbour | 1.4 | 17 | 93 | 100 | 89 | 170 | 170 |
| % Available | nd | 10 | 4 | 3 | 4 | 4 | 8 |
| Leslie St. Spit/ Aquatic Park | 2.7 | 30 | 104 | 100 | 73 | 480 | 455 |
| % Available | nd | nd | 1 | 1 | 4 | nd | nd |

TABLE 3. Potential Availability of Metals in Environmental Samples. Units in $\mu\text{g g}^{-1}$. nd = none detected.

| | Cd | Co | Cr | Cu | Ni | Pb | Zn |
|--------------------------|-----|------|------|------|-----|------|-------|
| Urban Particulate Matter | 75 | 17.6 | 403 | 609 | 82 | 6550 | 4760 |
| % Water Soluble | 10 | nd | 0.7 | 16 | 22 | 0.7 | 37 |
| % Readily Available | 73 | 20 | 1.3 | 30 | 36 | 46 | 67 |
| Incinerated Sludge Ash | 9 | 100 | 5200 | 2500 | 640 | 1640 | 14000 |
| % Available | nd | nd | 0.05 | nd | 0.1 | 0.1 | 0.1 |
| Podzolic Soil (B) | 0.2 | 13 | 16 | 7 | 12 | 21 | 124 |
| % Available | nd | nd | nd | 15 | 18 | 2 | nd |
| Chernozemic Soil (A) | 0.4 | 15 | 61 | 22 | 26 | 16 | 94 |
| % Available | nd | nd | nd | 7 | 3 | 6 | nd |

TABLE 4. Determination of Labile and Inert Complex Forms of Cd, Pb and Zn Extracted from Suspended and Bottom Sediments. Units in $\mu\text{g l}^{-1}$

| Sample | Cd | | Pb | | Zn | |
|-------------------------------|--------|-------|--------|-------|--------|-------|
| | Labile | Inert | Labile | Inert | Labile | Inert |
| Stn 2:2 m Hamilton Harbour | nd | 0.090 | 0.060 | 0.056 | 1.00 | 1.33 |
| Stn 4:2 m Hamilton Harbour | nd | 0.007 | 0.118 | 0.054 | 1.03 | 0.03 |
| Niagara River | nd | nd | nd | nd | 0.16 | nd |
| Collingwood Harbour | nd | nd | nd | nd | 0.09 | 2.0 |
| Leslie St. Spit | 0.03 | nd | nd | 0.05 | 0.13 | 0.19 |

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231: HYDROGEOCHEMICAL RESPONSES OF THE TURKEY LAKES
WATERSHED TO ACIDIC PRECIPITATION

by

D.S. Jeffries, R. Semkin, R. Neureuther and N. Seymour

INTRODUCTION

Within the general interdepartmental objective to "develop a clear understanding of the occurrences and effects of long-range transport of air pollutants (LRTAP) within Canada", ECS has established a goal of studying "selected ecosystems to quantify pathways and to define cause-effect relationships from which predictive models of ecosystem effect can be developed and verified" (1). The Turkey Lakes Watershed (TLW), Algoma, Ontario, is one of the "selected ecosystems". The 1050 ha watershed is located in acid sensitive shield terrain, is composed of a staircase of five lake basins, and experiences moderate acid deposition (precipitation pH =4.5). The hydrogeochemical response of the watershed to this acid input is being evaluated using a mass balance approach (2) in an effort to determine the geochemical mechanisms and/or interactions controlling the relationship. The TLW is one of five calibrated basins under study by various federal and provincial organizations in eastern Canada. Information from all of these basin studies will be required to completely address the above objectives.

RESEARCH RESULTS

Hydrological and chemical monitoring of the inputs and outputs of the five component lake basins within the TLW was performed throughout the year. This involved continuous measurement of precipitation quantity and stream flow (five stations), daily monitoring of atmospheric deposition, and weekly to bi-weekly chemical sampling of stream, lake, and groundwaters. During periods of high flow such as spring melt, sampling frequency was increased to allow better resolution in the data.

The data generated within this study are being stored in the computerized NAQUADAT data bank. Mean major ion concentrations at the five major stream gauging stations are given in Table 1. Stream station S1 is located just below the headwater

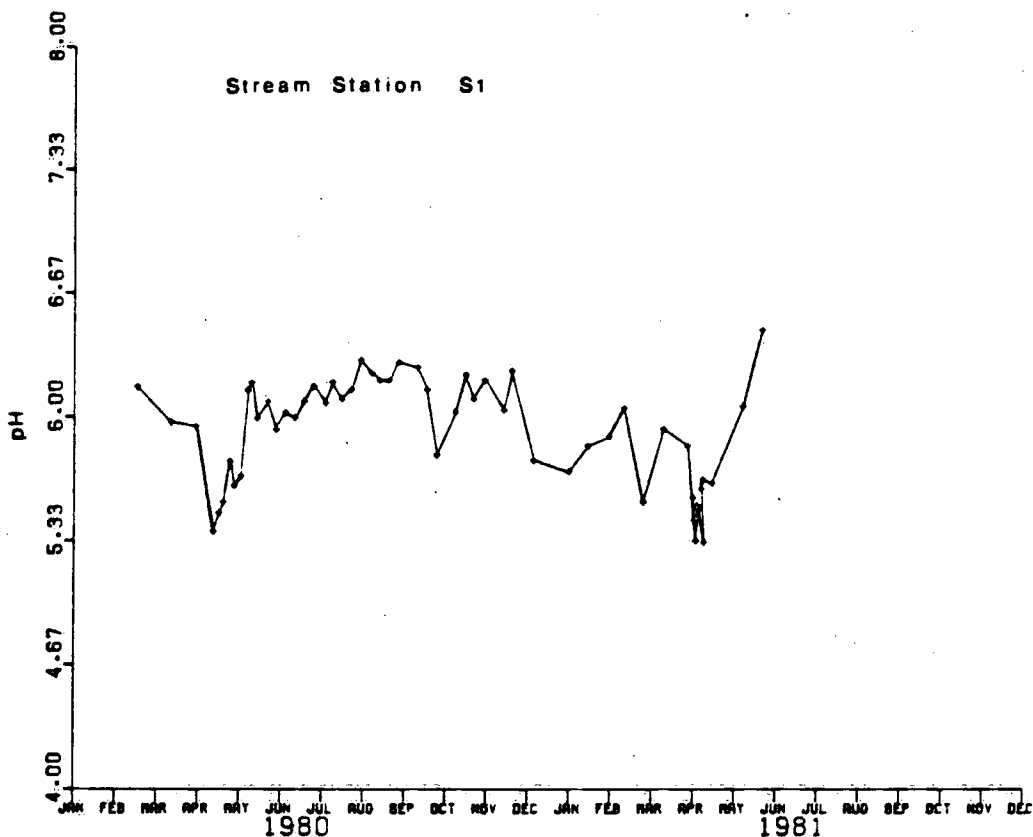
lake and each subsequent station is correspondingly lower until S5, which is at the exit of the overall basin.

TABLE 1. Mean pH and Major Ion Concentrations (meq L⁻¹) at Stream Stations in the Turkey Lake Watershed (January 1980 to May 1981)

| Station | pH | Ca ²⁺ | Mg ²⁺ | Na ⁺ | K ⁺ | SO ₄ ²⁻ | HCO ₃ ⁻ | Cl ⁻ | NO ₃ ⁻ |
|---------|-----|------------------|------------------|-----------------|----------------|-------------------------------|-------------------------------|-----------------|------------------------------|
| S1 | 5.9 | 0.15 | 0.04 | 0.02 | 0.01 | 0.13 | 0.04 | 0.01 | 0.04 |
| S2 | 6.3 | 0.19 | 0.04 | 0.02 | 0.01 | 0.13 | 0.08 | 0.01 | 0.03 |
| S3 | 6.4 | 0.22 | 0.04 | 0.02 | 0.01 | 0.13 | 0.14 | 0.01 | 0.03 |
| S4 | 6.6 | 0.26 | 0.04 | 0.02 | 0.01 | 0.13 | 0.19 | 0.01 | 0.03 |
| S5 | 6.6 | 0.27 | 0.04 | 0.03 | 0.01 | 0.14 | 0.19 | 0.01 | 0.03 |

The data show that there is an increase in pH, Ca²⁺ and HCO₃⁻ from the headwaters to the exit of the watershed. The headwaters are of the Ca²⁺-SO₄²⁻ type while the waters further down are of the more "normal" Ca²⁺-HCO₃⁻ type suggesting that sulphuric acid is the more important weathering agent (compared to H₂CO₃) in the upper reaches to the TLW where soil-precipitation interactions are minimized. Monitoring activities will continue throughout the next year.

In addition to the gradients in "average" composition found in the TLW, considerable temporal variation in stream composition have also been observed. Figure 1 illustrates the degree of variability observed for pH at S1. Note the distinct pH depressions occurring during spring melt (3). Similar pH depression have been observed (4,5) elsewhere in Ontario. Further quantification of the magnitude and extent of this short term acidification are being addressed by intensive snowpack, stream and lake sampling programs throughout late winter and spring of 1982.



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by

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

INTRODUCTION

Metals in the aquatic environment are subject to biotic and abiotic reactions resulting in the formation of organometals and organometalloids with different toxicological behaviours and bioaccumulation characteristics (1). Such transformation also has environmental consequences in mobilization of the element from sediment, and transmethylation of other elements. Identification of the chemical forms of an element is of prime importance and will be of significance to the program under the Great Lakes Water Quality Agreements, annexes 7, 11 and 12. Organotin and organolead compounds are of high priority under the Environmental Contaminants Act priority list. The observations of alkyllead and alkyltin compounds in environmental samples (2) indicate a great need to investigate the transformation mechanisms of these elements and also the forms of lead and tin in the environment.

An important area of environmental studies is the development of analytical techniques for chemical speciation. The combination of chromatography and an element-specific detection will provide a powerful system for the identification and analysis of both volatile and non-volatile organometals in the sample (3).

RESEARCH RESULTS

Laboratory experimentation established the fact that tetraalkyllead compounds can be accumulated by fish with the highest concentration in the lipid tissue (4). We then carried out a survey of the occurrence of alkyllead compounds in fish, sediment, aquatic plants and water in high lead areas. Only fish was found to contain tetraalkyllead (5).

Environmental survey of the occurrence of trialkyllead species (Me_3Pb^+ , Et_3Pb^+) has confirmed that Et_3Pb^+ can be formed in fish containing Et_4Pb . This finding would have significant bearing in the toxic effects of tetraalkyllead on fish because the Et_3Pb^+ species has been known to be responsible for Et_4Pb toxicity

in mammals. More data will be collected before we publish the results.

The role of metals in catalyzing the formation of Me Pb in the Pb(II) + MeI system was studied after our finding that Pb(II) could be methylated by MeI (6). It was found that electro-positive metals (Al, Mg, Zn) reduced Pb(II) species to Pb metal available for reaction with MeI to form Me Pb.

The study of the effect of pH on the methylation of Pb, Hg, As and Se showed that pH affected the methylation of different elements in lake sediments. The formation of tetramethyllead from trimethyllead acetate increased with increasing pH and proceeded through both biological and chemical mechanisms. Methylmercury was formed from inorganic mercuric chloride only in the pH range 5.5 to 6.5. Dimethylmercury was not detected. Arsenic methylation was enhanced below pH 5.5, but occurred over the pH range of 3.5 to 7.5. The levels of methylated Se compounds were low at pH 3.5, and generally, increasing pH favoured the methylation of Se (7).

Both Sn(II) and Sn(IV) salts can be methylated to MeSn^+ , Me Sn^+ , Me Sn^+ compounds in lake sediment (8). A comparative toxicity study with various organotin compounds on freshwater algal showed that toxicity is related to length of the carbon chain, degree of alkyl substitution and also to the oxidation number of tin, with the trialkyltin being the most toxic form.

The results of two field trips to various lakes, rivers, harbours and marinas in Ontario to survey the environmental occurrence of methyltin compounds showed that there were significant amounts of methyltins in water. Whether these are the results of degradation of other organotins or methylation products of inorganic tin remains to be investigated. These findings are, however, significant. This is the first report on the occurrence of methyltin species in Canadian waters (Table 1).

A Contract study "Effects of acid water on leaching of metals from domestic water supplies" was completed by Barringer Co., The Contract involved a laboratory study of the effect of pH, temperature, and hardness on the leaching of metals from three types of domestic plumbing materials, namely, lead, copper, galvanized pipes under static and dynamic conditions. Major findings are: decreasing pH increased the rates of leaching of Pb, Cu and Zn. A decrease of pH from 8 to 6 resulted in substantial increase of leaching of Pb and Cu from the most widely used copper pipes; dramatic effects of metal leaching from all types of pipes were

Table I Concentrations ($\mu\text{g/L}$) of Methyltin Species in Unfiltered Subsurface Water^a

| Location | Me_3Sn^+ | $\text{Me}_2\text{Sn}^{2+}$ | MeSn^{3+} |
|--|--------------------------|-----------------------------|--------------------|
| Lake Superior (Thunder Bay) | - | 0.03 | 0.15 |
| Lake Superior (Red Rock) | 0.05 | 0.03 | 0.23 |
| Lake Superior (Marathon) | - | 0.03 | 0.21 |
| Turkey Lake 1 | - | 0.05 | 0.24 |
| Turkey Lake 2 | - | 0.02 | 0.11 |
| Turkey Lake 3 | - | 0.05 | 0.18 |
| Turkey Lake 4 | - | 0.04 | 0.20 |
| Turkey Lake 5 | - | 0.05 | 0.25 |
| Sault Ste. Marie Harbor | - | 0.04 | 0.25 |
| Ramsey Lake (Sudbury) | - | 0.04 | 0.22 |
| Nepewassi Lake (Sudbury) | - | 0.03 | 0.20 |
| Lake Nipissing (North Bay) | - | 0.09 | 0.23 |
| Plastic Lake | - | 0.04 | 0.17 |
| Collingwood Harbor | - | 0.05 | 0.20 |
| Owen Sound Harbor | - | 0.04 | 0.17 |
| St. Clair River 1 | - | 0.18 | 0.64 |
| St. Clair River 2 | - | 0.21 | 0.68 |
| Lake St. Clair (Mitchell Bay) | - | 0.10 | 0.35 |
| Lake St. Clair (marina) | - | 0.22 | 0.53 |
| Thames River (400 m upstream from mouth) | - | 0.21 | 0.67 |
| Port Dover Harbor | - | 0.16 | 0.61 |
| Grand River (mouth) | - | 0.14 | 0.37 |
| Hamilton Harbor | - | - | 0.06 |
| Toronto Harbor | - | 0.29 | 0.96 |
| Whitby Harbor | - | 0.28 | 1.20 |
| Belleville Harbor | - | 0.24 | 0.92 |
| Kingston Harbor | - | 0.40 | 1.22 |
| St. Lawrence River 1 | - | 0.03 | 0.28 |

^a minimum detectable concentration of each species approx. 0.04 $\mu\text{g/L}$;
for concentrations of Sn(IV) species, see Table I; precise sampling
locations available upon request.

observed in static tests where the waters of various pH, hardness were kept in piping for 2-hr, 12-hr, 10-d periods over that of dynamic tests; survey of 105 homes and apartments in Toronto areas substantiated much of the findings of the laboratory studies. The first-drawn water always contained more metals than that after 5 min running. Only Pb was found at concentrations higher than the recommended level (50 ppb) at some sites in the static samples.

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233: 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 biocides. 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 - ref. 1).

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 approach is to combine field observations with results from the laboratory on well-defined transformation pathways. Accordingly, this study will cover, under laboratory studies, (1) hydrolysis, (2) photolysis, (3) volatilization, (4) adsorption to sediments and suspended solids, (5) microbial transformation, and (6) accumulation in algae and fish, and, under field studies, (7) preliminary sampling of likely polluted sites to determine the presence of a particular pollutant in such "compartments" as water, sediment, algae and fish, and (8) based on (7), selection of a specific site at which to conduct a detailed investigation of the persistence and fate of butyltins.

RESEARCH RESULTS

TBTO does not hydrolyze over a period of two months at 25°C and at pH 3, 7 and 11. An experiment on the volatilization of TBTO from distilled water at room temperature showed that no

Ref. 1 - Canada Department of the Environment and Department of National Health and Welfare, Environmental Contaminants Act: Priority Chemicals - 1979, in The Canada Gazette, Part 1, Ottawa, Dec. 1, 1979, p. 7365.

volatilization occurred over a 62-day period at 22°C. Although there was a possibility of adsorption of TBTO to glass, it is likely that in natural water bodies adsorption to organic matter would be even more pronounced, and that volatilization would not be a significant pathway of environmental distribution. Preliminary experiments on the sunlight photolysis of TBTO indicate little photolytic conversion over a period of 83 days. Laboratory experiments are under way with more intense light sources so that a definite conclusion may be made on whether TBTO photolyzes (i) directly, or (ii) as a result of photosensitization by naturally-occurring humic material.

A survey was made of butyltins in water at 30 locations in Ontario. Butyltin contamination is widespread; the table below shows the most significant results.

TABLE. Butyltins in Unfiltered Subsurface Water, $\mu\text{g L}^{-1}$

| Location | [Bu_3Sn^+] | [$\text{Bu}_2\text{Sn}^{2+}$] | [BuSn^{3+}] | [Sn^{4+}] |
|-------------------------|------------------------------|---------------------------------|------------------------|----------------------|
| Collingwood Harbour | 1.0 | - | - | 50.1 |
| Lake St. Clair (Marina) | 2.9 | 7.3 | 8.5 | 6.0 |
| Toronto Harbour | 0.8 | 0.3 | - | 1.0 |
| Ramsey Lake (Sudbury) | 0.7 | 0.02 | - | 48.7 |

This is the first report of butyltins in Canadian waters. The concentrations of tri-n-butyltin in the locations above are 15 to 60% of the LC_{100} 12-d value for a sensitive aquatic species, rainbow trout yolk sac fry.

The surface microlayer (approximately 60 μm thick as sampled with a glass plate) was also sampled at the same 30 locations. The most notable results were (i) for Nepewassi Lake (Sudbury) and Lake Nipissing (North Bay), in which the amounts of Sn^{4+} in the surface microlayer were 38% and 18%, respectively, of the amounts in the whole depth of subsurface water, and (ii) for Whitby and Belleville Harbours, in which the amounts of dibutyltin in the surface microlayer were 30% and 23%, respectively, of the amounts in the whole depth of subsurface water.

In FY 82/83, research will focus on areas 4, 5, 6, and 8 above.

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234: HEAVY METAL CHEMODYNAMICS AND POTENTIAL AVAILABILITY TO
PHYTOPLANKTON IN THE NIAGARA RIVER AND PLUME

by

A. Mudroch

INTRODUCTION

The nearshore zone of the Niagara River mouth has been designated by the GLWQB in the past as a problem area. A number of industrial discharges to the Buffalo River and to the Upper and Lower Niagara River contribute to the pollution of water and suspended loads of Niagara River (Lakes Erie-Ontario Advisory Board, 1971). The 5500 m³/sec discharge of Niagara River carrying annually 4.8 million tons of fine-grained sediment into Lake Ontario (i.e., about 52% of total input to the Lake; Kemp and Harper, 1976) has a significant effect on the water and sediment quality of the Western Basin of Lake Ontario, and most likely affects the whole lake. The mercury and PCB distribution in Lake Ontario sediments pinpoint the Niagara River as the major source of input. Suspended sediment is primarily of concern because of its capability to bind contaminants.

RESEARCH RESULTS

Concentration of profiles of heavy metals in sediment at the Niagara River mouth showed a small decrease of Cr, Zn, Cu, Ni and Pb, and a significant decrease in Hg inputs to Lake Ontario by the River. However, Hg concentrations in the surficial sediment in the vicinity of the River mouth remain high, up to 7 µg g⁻¹ dry weight (Mudroch, 1982). The scanning for organic pollutants in the sediment showed about 45 various compounds present in the neutral fraction of the extracts in concentrations many times higher than in the Niagara River water. These were identified as polycyclic aromatic hydrocarbons (PAH's), chlorinated aliphatic and aromatic hydrocarbons, and nitrogen and sulfur containing hydrocarbons (Onuska, Mudroch and Terry, 1982). Occurrence and composition of the nepheloid layer in the Western Basin of Lake Ontario was studied to investigate the possible transport of contaminants by this layer over the entire Lake Ontario (Sandilands and Mudroch, 1982). Next fiscal year the study will continue, including investigation of occurrence and nature of organic pollutants

and metals in suspended and bottom sediment in the Eastern Basin of Lake Erie and their possible transport via Niagara River. Concentration of organic pollutants and metals in the nepheloid layer in Lake Ontario will be determined. Investigation will be carried out on effects of sediment-associated pollutants on phytoplankton and zooplankton by using natural plankton population and contaminated sediment from the Niagara River ecosystem. The methods developed in 1981/82 (Mudroch and Munawar, 1982a, 1982b, 1982c; Munawar and Mudroch, 1982; Munawar, Mudroch and Thomas, 1982) will be applied to these studies.

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235: GEOCHEMICAL CONTROLS OF AQUATIC SYSTEM RESPONSES TO
DEPOSITION OF ATMOSPHERIC POLLUTANTS

by

D.S. Jeffries, B.G. Oliver, R. Semkin and G. Slawych

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 (LRTAP)" (1). Recognizing the overall complexity of such an endeavour, we have initially addressed this objective by studying specific ecosystem - acid interactions in calibrated watersheds in Nova Scotia and Ontario. The purpose is to determine the factors controlling the degree and rate of acidification of these drainage basins and associated lakes by measuring the geochemical response of the watersheds to the input of acids. Both watersheds are located in areas considered to be sensitive to excessive atmospheric loading of acid and are part of a network of calibrated systems in Canada and the U.S.A. which are under study to define the effects of LRTAP (2).

Questions related to the source of acid present in acidifying systems were addressed through measurement of the organic acid contribution to the total acidity of lakes and rivers in Nova Scotia, while the importance of short term acidification was studied by intensively monitoring the major ion chemistry of the lakes and streams of the Turkey Lakes Watershed (Algoma, Ontario) throughout the spring melt of 1981.

RESEARCH RESULTS

We have been successful in developing methods to measure the contribution to acidity contribution of organic acids for natural water susceptible to acid precipitation. The organic acids from two natural waters were isolated and studied in detail to quantitate their dissociation behaviour and carboxylic acid content. A simpler fluorescence quenching technique was developed so the organic acids content of samples could be determined directly and the H^+ supplied by dissociation, easily estimated (3).

The free H^+ concentration, total H^+ supplied by the dissociation of organic acids, and the total organic carboxylic acid content of several lakes and rivers in Nova Scotia are shown in Table 1.

TABLE 1. Acids in Nova Scotian Surface Waters ($\mu M L^{-1}$)

| Sample | Free H^+ | Total H^+ from Organic Acids | Total Organic Acids |
|---------------------|------------|--------------------------------|---------------------|
| West River | 50 | 73 | 120 |
| Medway River | 16 | 87 | 120 |
| Mersey River | 32 | 34 | 52 |
| Beaverskin Lake | 4 | 21 | 25 |
| Pebbleloggitch Lake | 25 | 110 | 160 |
| Kejimkujik Lake | 5 | 22 | 27 |

Clearly, organic acids are an important source of H^+ for these Nova Scotian waters. Some of the H^+ from organic acids must have been neutralized by reaction with basic species since the free H^+ is generally lower in concentration.

Data collected during spring runoff in the Turkey Lakes Watershed (4) showed that short term acidification "events" did occur in 1981.

Maximum variation in H^+ concentration was observed at the stream station below the headwater lake where H^+ increased $-3\times$ during a minor melt in late February and $-5\times$ during the major melt in early April, e.g., pH from 6.0 to 5.3. Variation in SO_4^{2-} and NO_3^- concentrations were also observed. The near surface waters of the lakes also experienced pH depressions although these were of a lesser magnitude (5).

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240 : TRENDS IN RADIOACTIVE CONTAMINANTS
OF THE GREAT LAKES

by

R.W. Durham, G.H. Jamro, S. Livermore and E. Kokotich

INTRODUCTION

Concern over the potential buildup of radionuclides in the Great Lakes, due to the developing nuclear power program along the shoreline, was expressed in the Canada/U.S.A. Water Quality Agreement of 1982. Development of a radiological water quality objective began at that time and was included in its final form in the 1978 Agreement. Our annual measurements of radionuclide concentrations in open waters of the Great Lakes which started in 1972 helped in the development of the objective which is that no individual drinking water from the Great Lakes system should receive in a year a dose of more than one millirem.

Annual samples from near the surface and the bottom at each major basin of all lakes have been collected with the cooperation of U.S. EPA, GLBL and Technical Operations Division of NWRI. Analysis of these samples as well as sediment and fish, for specific radionuclides have enabled radiological dose calculations to be made and determine relative importance of different sources and the resultant pathways of radionuclides to overall trends of radioactivity in the Great Lakes.

RESEARCH RESULTS

Open water samples from all the Great Lakes and fish samples from all but Lake Michigan were obtained in the summer of 1980 and analyses for the radionuclides ^{90}Sr , ^{137}Co and ^{125}Sb were completed by the summer of 1981. The results of these analyses and their interpretations were given in an NWRI report and included in the IJC Water Quality Board Annual Report for 1981. The radionuclides measured were apparently all introduced by fallout from nuclear weapons testing since no evidence was found of radionuclides specifically related to nuclear industry. The radiological doses to individuals drinking water from each lake were calculated to be; Lake Superior, 0.05 mrem; Lake Michigan, 0.10 mrem; Lake

Huron, 0.11 mrem; Lake Erie, 0.06 mrem; Lake Ontario 0.13 mrem. All lakes gave similar results as the previous year with the exception of Erie which was 50% lower. Bioaccumulation of ^{137}Cs in fish showed large differences between species with rainbow trout at 2600 being much lower than pickerel at 22,200.

Earlier work on a new approach to determine the very low levels of radionuclides in the Great Lakes was published during 1981.

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**241: RADIUM PATHWAYS FROM PORT GRANBY
WASTE MANAGEMENT SITE TO LAKE ONTARIO**

by

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

INTRODUCTION

An earlier study of the ^{226}Ra , As and NO_3^- levels in Lake Ontario off the Port Granby waste management site of Eldorado Nuclear Ltd. showed that these contaminants were leaving the site although the two creeks, which historically drained the site, had been dammed. The Atomic Energy Control Board which licenses the site and Eldorado Nuclear Ltd., which owns it, both have need of scientific information on pathways and rates of transfer of radioactive and other contaminants to Lake Ontario.

A study of the groundwater leaching of ^{226}Ra from the site was undertaken to calibrate the hydrogeologic parameters used in the NWRI two-dimensional contaminant transport model in order to predict future leaching from the site.

RESEARCH RESULTS

The wastes are buried in sandy soil at the top of the bluffs rising about 30 metres from the narrow beach. A till layer of clay, cobbles and boulders underlies the waste and causes seepage of leachate at the face of the bluffs. The major groundwater flow is through a lower sandy layer to the lake, the water table being about 50 cm below the beach surface at the front of the bluffs. A series of 12 piezometers were jetted into the beach to a depth of two metres between the eastern and western boundaries of the site. Samples of groundwater were taken periodically from the piezometers and the seepage sites and analyzed for ^{226}Ra . The level of the water table in each piezometer was monitored also during the field season. Analytical results show that the main contamination of the groundwater is occurring at the centre of the site where the seepage is taking place. The seepage ^{226}Ra concentration was fairly steady during the period, averaging about 13 pCi/L but the nearest piezometer showed a decline from 50 pCi/L to about 10 pCi/L.

A contractor was brought in at the end of the field season to drill two deep holes to bedrock and install piezometers, sealed with bentonite, at three depths. Hydraulic characteristics and ^{226}Ra levels will be determined at these depths when the beach is free of ice.

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242: AQUATIC PATHWAYS OF RADIONUCLIDES

by

R.W. Durham, S.R. Joshi, J. FitzGerald and S. Livermore

INTRODUCTION

In assessing environmental impact of nuclear power development it is necessary to understand the behaviour of radionuclides released to the environment. Pathways of naturally occurring radionuclides such as ^{210}Pb and other decay products of uranium and thorium and fallout radionuclides such as ^{137}Cs can be studied in the natural environment and related to the behaviour of radionuclides discharged during operation of the nuclear fuel cycle. We have studied the transfer of ^{210}Pb and ^{137}Cs from the atmosphere through the water column and sediments of Lake Huron and developed a technique for measuring sedimentation rates and age profiles of sediments. These age profiles can be used, along with other contaminant analyses of the sediments, to determine the time that these contaminants were first introduced into the aquatic ecosystem.

RESEARCH RESULTS

Age profiles of sediment cores from 12 lakes in northern and eastern Ontario were determined in a cooperative study with Fisheries and Oceans Canada to determine historical inputs of heavy metals to these lakes. Similarly, ^{210}Pb and ^{137}Cs profiles of cores from Oshawa Second Marsh were measured to determine sediment accumulation rates and predict future water levels in the marsh. A reassessment of ^{210}Pb and ^{137}Cs data from three cores from Nipisson Bay, Lake Superior showed that toxic dehydroabietic acid discharged from a nearby pulp mill degraded very slowly in the sediments compared with the water column.

Sediment accumulation rates are currently being measured in cores taken in Lake Ontario about 1 km off the mouth of the Niagara River in order to determine the history of several contaminants known to be present in the river. Three cores taken from supposedly similar locations have given sedimentation rates of 1.3, 0.8 and 0.6 cm per year. Since the rates appear to change

rapidly over short distances it is important that the other contaminants studied are analyzed in the same core used for age profiling. The possible introduction of transuranium elements into the Niagara River from a shut-down fuel reprocessing plant at West Valley, New York, via Cattaraugus Creek and Lake Erie, is being studied. A separation technique for Pu, Am, U and Th using isotopic tracers is being developed.

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