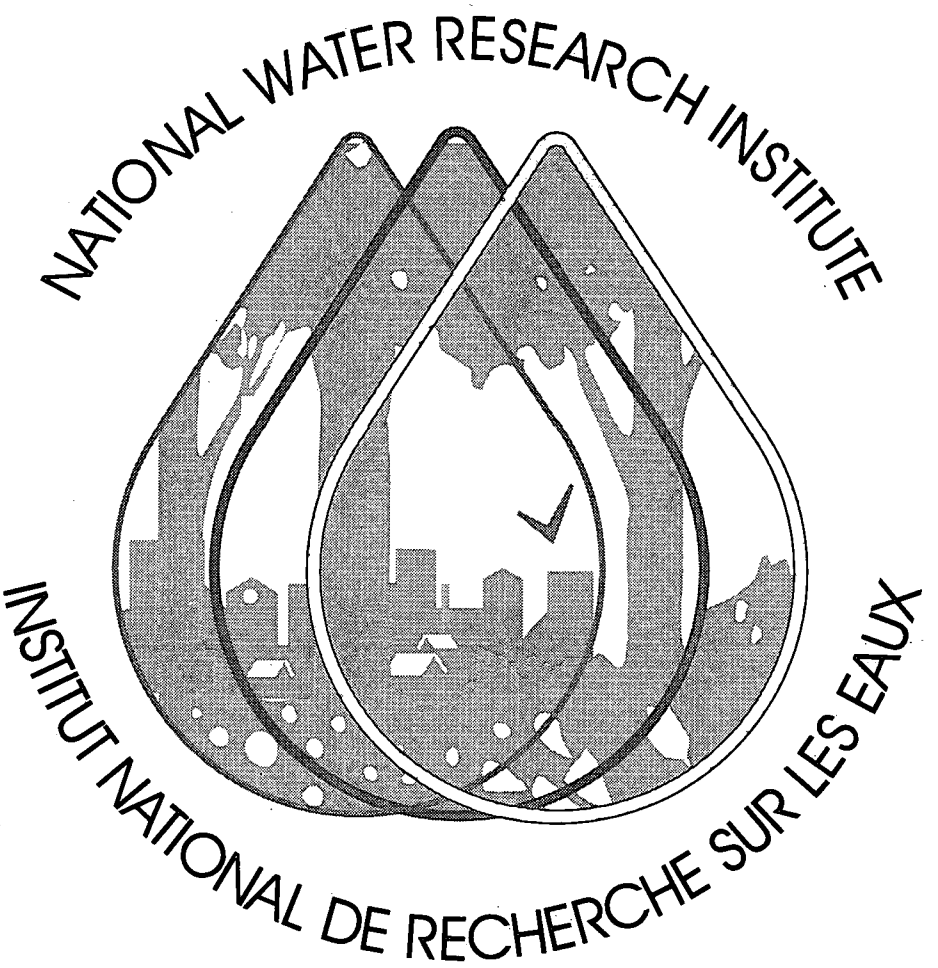


AQUATIC ECOSYSTEM PROTECTION BRANCH

RESEARCH ACTIVITIES 1995-1996

NWRI Contribution No. 96-180

AQUATIC ECOSYSTEM PROTECTION BRANCH
RESEARCH ACTIVITIES
1995-96

Aquatic Ecosystem Protection Branch
National Water Research Institute
Environment Canada
Canada Centre for Inland Waters
867 Lakeshore Road, P.O. Box 5050
Burlington, Ontario
Canada L7R 4A6

NWRI Contribution No. 96-180

MANAGEMENT PERSPECTIVE

This report presents an overview of the research carried out in 1995-96 by the Aquatic Ecosystem Protection Branch of the National Water Research Institute. You will also find some examples of collaboration and partnership, a brief description of cost recovery activities and our most recent publications. We hope that this document will provide useful information to our numerous national and international clients, visitors and collaborators.

John Lawrence
Branch Director

SOMMAIRE À L'INTENTION DE LA DIRECTION

Ce document dresse un aperçu de la recherche effectuée en 1995-96 par la Direction de la protection de l'écosystème aquatique de l'Institut national de recherche sur les eaux. Vous y trouverez aussi des exemples de partenariats et de collaboration, une brêve description des activités à recouvrement de coûts ainsi que nos plus récentes publications. Nous espérons que ce document sera utile à nos nombreux clients, visiteurs et partenaires canadiens et étrangers.

Le Directeur de la Direction
John Lawrence

NWRI Contribution No 96-180

To obtain more information, please contact the Branch:

Aquatic Ecosystem Protection Branch
National Water Research Institute
Environment Canada
Canada Centre for Inland Waters
867 Lakeshore Road, P.O. Box 5050
Burlington, Ontario L7R 4A6

Telephone: (905) 336-4928
Fax: (905) 336-4420
E-Mail: martine.allard@cciw.ca

Pour de plus amples informations, veuillez contacter la Direction à l'adresse suivante:

Direction de la protection
de l'écosystème aquatique
Institut national de recherche sur les eaux
Environnement Canada
Centre canadien des eaux intérieures
867 chemin Lakeshore, C.P. 5050
Burlington (Ontario) L7R 4A6

Téléphone: (905) 336-4928
Télécopieur: (905) 336-4420
Internet: martine.allard@cciw.ca

Aquatic Ecosystem Protection Branch - Research Activities 1995-96

CONTENTS

Aquatic Ecosystem Protection Branch - Research Activities 1995-96

The Aquatic Ecosystem Protection Branch (AEPB) was created in early 1994 as part of a major restructuring of the National Water Research Institute. AEPB focuses mainly, but not exclusively, on the development of detailed knowledge and understanding of the behaviour and impacts of priority pollutants to support informed environmental decision making and sustainable management practises.

In FY 1995-96 the Branch was composed of three projects:

- Contaminant Pathways and Controls lead by J. Marsalek
- Environmental Standards and Statistics lead by K.L.E. Kaiser
- Priority Substances lead by R.J. Maguire

Activities of the Branch include :

- identification of the patterns of behaviour of priority toxic substances in aquatic environment;
- provision of information for Priority Substances List assessment under CEPA;
- assessment of the impact of non-point source pollution on aquatic ecosystems;
- determination of the role of suspended sediment in the riverine transport of toxic substances;
- ensuring the integrity of environmental data by implementing appropriate analytical quality control and assurance; and
- enhancement of interpretive information through the use of statistics and environmetrics.

In 1995-96, the Branch's research activities directly contributed to several programs related to toxics (*e.g.,* CEPA, PCPA, PERD), to regional ecosystems initiatives (*e.g.,* Great Lakes 2000, the Northern Rivers Basin Study, The Fraser River Action Plan and international studies (*e.g.,* Boreal Ecosystem Atmosphere Study).

Research activities are described in the following sections. The various partnerships, collaborative and cost recovery activities are briefly summarized below.

Partnership, Collaboration & International Activities

The Branch's research activities are often catalyzed through sustained contacts and collaboration with other governmental agencies, or through research partnerships with Canadian universities or the international research community. The following is a sample of some of the partnerships and international involvement that took place in 1995-96.

***University Collaboration*:** AEPB staff continue to work in close collaboration with researchers at Queen's University (on stormwater management); McMaster University (urban runoff; metal speciation; marine snow and flocs characterization); and University of Waterloo (migration pathways of PAHs in urban areas); University of Guelph and McGill University (agricultural best management practices).

International Collaboration: In 1995-96, AEPB hosted visiting research scientists or graduate students from Slovakia, Germany, France, Switzerland, Austria, and China. The visitors spent periods of anywhere from a few weeks to several months, in order to do collaborative research with Branch staff.

Symposium: AEPB organized and hosted the 31st Central Canadian Symposium on Water Pollution Research on February 6 & 7, 1996, on behalf of the Canadian Association on Water Quality (CAWQ). The Symposium was a resounding success, attracting over 200 participants from across the country. The Branch also organized a special two-day session on "Stormwater Management and Control of Combined Sewer Overflows", which attracted representatives from some 20 Ontario municipalities or conservation authorities, numerous consulting firms, university researchers, federal and provincial government representatives.

Workshop: Branch staff were instrumental in the organization of a "Workshop on Organotin Compounds in the Canadian Aquatic Environment" held at the Institute of Ocean Sciences, Department of Fisheries and Oceans, Sidney, B.C. February 19-20, 1996. This workshop brought together for the first time researchers, resource managers and regulators.

Cost Recovery Activities

The Branch's expertise and facilities are also accessible, on a cost recovery basis, to clients outside of the Department. Cost-recovery activities are concentrated in the areas of quality assurance, research and engineering in the Hydraulics Laboratory, and the National Calibration Service for current meters.

Quality Assurance:

Activities supported in the area of quality assurance include the provision of audit samples, participation in interlaboratory comparison studies, assessment of laboratory performance, and the provision of reference materials (RMs) or certified reference materials (CRMs).

Efforts continued on marketing NWRI's quality assurance expertise and products. A comprehensive catalogue of quality assurance products and services was produced and distributed to several hundred research and laboratory managers within and outside Canada, particularly the NAFTA partners. NWRI's quality assurance and control products help managers across the country to select appropriate control mechanisms for research and monitoring projects to ensure data quality and compatibility.

A partnership agreement between Cambridge Isotope Laboratories, Fisheries and Oceans Canada and Environment Canada was established to evaluate the comparability of laboratories analyzing for coplanar PCBS, dioxins and furans in fish tissue and to develop three fish reference materials for coplanar PCBs.

Please note that, as of April 96, all quality assurance activities were transferred to NWRI's National Laboratory for Environmental Testing (NLET).

Hydraulics Laboratory:

The laboratory is mainly used as a research facility in support of Environment Canada's programs. Because of the unique and very specialized nature of some of its equipment, the facility is made available to both public and private organizations on a cost-recovery basis.

National Calibration Service:

The principal function of the service is to maintain, repair, calibrate and manage an inventory of current meters on behalf of the Water Survey of Canada. The tow tank used to calibrate the current meters is the only one in Canada. Because of this, the repair and calibration service is offered to other organizations on a cost-recovery basis. Our clients include hydro-electric companies, provincial and municipal agencies, universities and the private sector.

Project: **Contaminant Pathways and Controls**

Study Title: **Prevention/Remediation of Urban Nonpoint Source Pollution Impacts**

Study Leader: **J. Marsalek**

Overview

Research was completed on microbiological pollution in the Upper Great Lakes Connecting Channels Areas of Concern. Research continues on various stormwater and urban runoff management issues. Major results are summarized below.

Fecal Contamination of Urban Receiving Waters: Sources and Remediation

The closing of swimming beaches, caused by fecal bacterial contamination, is one of the most common water use impairments caused by urban pollution. Such problems have been reported in a number of Areas of Concern (AOCs) in the Great Lakes Basin and represent a major challenge in developing Remedial Action Plans leading to the delisting of the AOCs with large urban populations. The earlier initiated research of microbiological pollution in the Upper Great Lakes Connecting Channels AOCs, the St. Marys River in Sault Ste. Marie, the St. Clair River in Sarnia and the Detroit River in Windsor, has been completed by final interpretation and publication of research results.

In a comparative analysis of these three areas, the degree and extent of microbiological pollution were closely correlated with the density of sewer outfalls, discharging either combined sewer overflows (CSOs) or stormwater along the river shoreline, and dry weather sources indicating malfunctions of sewers. Thus, excellent microbiological water quality was found in the St. Marys River in Sault Ste. Marie (no CSOs, the stormwater outfall density of 1.1/km); but poor quality was found in the St. Clair River along the relatively short Sarnia waterfront (0.5 CSO outfalls/km, 1.4 stormwater outfalls/km) and along a much longer stretch of the Detroit River in Windsor (1.1 CSO outfalls/km, 1.6 stormwater outfalls/km).

Local impacts of urban discharges on indicator bacteria levels in the receiving waters are reduced by effluent mixing and bacterial decay. In Sault Ste. Marie, except for several locally polluted shoreline sections, the microbiological water quality at the downstream end was practically the same as upstream of the city. However, in both Sarnia and Windsor, the indicator bacteria levels downstream of the study area exceeded those upstream of the city by an order of magnitude, in both wet and dry weather. The impacts of wet weather and the associated pollution discharges were observed in all the three areas and were characterized by indicator bacteria level increases ranging from 1.5 times to more than 40 times, in the immediate vicinity of sewer outfalls. After the cessation of rain, the bacteria levels returned to the dry weather levels in less than 24 hours, but extended durations of microbiological pollution indicated problems with sewer operation at some locations in Sarnia and Windsor (Marsalek et al., 1996).

For the development of remedial measures and screening of various options, a three step modelling procedure was proposed - (a) developing a source/loading model, (b) setting up a receiving water

model, and (c) modelling remedial measure effects on bacterial levels. Such a procedure was demonstrated for the St. Clair River in Sarnia, where an existing flow generation model was used in conjunction with a water quality rating curve derived from local data as a loading model (Marsalek et al., 1995), providing inputs to the receiving water (river) model, and the effects of various remedial measures were simulated by the receiving water model (Tsanis et al., 1995). Significant improvements in bacterial water quality would be possible only with extensive source controls and diversion of contaminated discharge plumes away from the river sections used for recreation.

Stormwater Pond Studies

The effectiveness of a stormwater detention pond in protecting urban ecosystems by removal of stormwater pollutants was studied at the Kingston pond. At this phase of research, the emphasis was placed on reviewing the observed removals of various pollutants by the pond and examining the means for enhancing such removals. It was noted that the wet-weather removal of suspended solids at this facility (about 40 %) could be improved by remediating unfavourable flow conditions in the pond (characterized by shortcircuiting) and reducing polluted pond water displacement by relatively clean baseflow during dry weather. Two remedial solutions were proposed - installation of internal baffles to prevent flow shortcircuiting in the pond and implementing baseflow control by bypassing clean baseflow. The first measure has been implemented and the results of the first field season are currently being analyzed. The implementation of the second measure requires further negotiations with the owner/operator of this facility (Van Buren et al., 1995).

In a somewhat related study of contaminant sources in urban runoff, the chemistry of street particulate was studied in Sault Ste. Marie (Stone and Marsalek, 1996). The street material was found to contain high levels of heavy metals, particularly of Mn (C_{mean} = 1250 ppm, exceeding the Severe Effect Level, SEL, in the Ministry of Environment and Energy sediment quality guidelines), Cr (C_{mean} = 92 ppm, approaching the SEL of 110 ppm) and Cu (C_{mean} = 87 ppm, approaching the SEL of 110 ppm). Metal speciation by sequential extraction helped to elucidate the environmental significance of the levels observed. High proportions of potentially mobile forms were observed for Cu (92 %), Zn (75 %), Pb (71 %), and Cd (66 %). The elements concentrated mostly in the residual phase and reflecting the mineral origin included Ni (the residual phase of 79 %), Fe (the residual phase of 77 %) and Cr (the residual phase of 70%). The street particulate, which could be mobilized and transported by urban runoff, was found to have a high potential of adversely impacting on the quality of receiving waters. Further research on sources, pathways and controls of heavy metals in street particulate was recommended.

Publications and Presentations in FY 1995-96

Anderson, B.C., A.A. Crowder, W.E. Watt and J. Marsalek. 1995. An integrated approach to managing urban runoff contaminants. In: Proc. Cornwall RAP Conference, Cornwall, May.

Averill, D., P. Chessie, D. Mack-Mumford, J. Marsalek and D. Weatherbe. 1996. Pilot testing of physical-chemical treatment options for CSO control. WEF Specialty Conference, Urban Wet Weather Pollution - Controlling Sewer Overflows and Stormwater Runoff, June 16-19, 1996, Quebec City.

Engel, P. and J. Marsalek. 1995. Hydraulic model study for the Keele and Nashville Trunk Relief Sewer Junction. Contract Report AEPB-TN-95-02.

Marsalek, J., B.J. Dutka, A.J. McCorquodale and I.K. Tsanis. 1995. Microbiological Pollution in the Canadian Upper Great Lakes Connecting Channels. In: Proc. 2nd IAWQ Conf. on Diffuse Pollution, Brno & Prague, Czech Republic, August 13-18, 1995, pp.156-161. (Also NWRI Contribution No. 95-55).

Marsalek, J., B.J. Dutka, A.J. McCorquodale and I.K. Tsanis. 1996. Microbiological pollution in the Canadian Upper Great Lakes Connecting Channels. *Water Science and Technology* (in press).

Marsalek, J., B.J. Dutka and I.K. Tsanis. 1995. Urban impacts on microbiological pollution of the St. Clair River in Sarnia, Ontario. *Water Science and Technology* **30**(1): 177-184.

Mayer, T., J. Marsalek and E. Delos Reyes. 1995. Nutrient and metal contaminant status of urban stormwater ponds. NWRI Contribution No 95-70.

Micin, J., P. Prax, P. Osmera and J. Marsalek. 1995. Strategy for operation of drainage systems in integrated urban areas. In: Proc. Int. on Wastewaters, Brno, Czech Republic, May 9-11, 1995, pp. 65-72.

Stone, M. and J. Marsalek. 1996. Geochemical speciation and spatial distribution of metals in urban particulate matter. *Water, Air and Soil Pollution* **87**: 149-169.

Tsanis, I.K., J. Wu and J. Marsalek. 1995. Feasibility of modelling remedial measures for microbiological pollution of the St. Clair River at Sarnia Bay. *J. Great Lakes Research* **21**(1): 138-154.

Van Buren, M., W.E. Watt and J. Marsalek. 1995. Enhancing pollutant removal by an on-stream pond. In: Proc. 2nd IAWQ Conf. on Diffuse Pollution, Brno & Prague, Czech Republic, August 13-18, 1995, pp.527-532.

Van Buren, M.A., W.E. Watt and J. Marsalek. 1996. Enhancing pollutant removal by an on-stream pond. *Water Science and Technology* (in press).

Project: **Contaminant Pathways and Controls**

Study Title: **Geochemistry of Dissolved and Sediment-Bound Organic Matter**

Study Leader: **R.A. Bourbonniere**

Overview

Research is underway on the geochemistry of naturally-occurring organic matter. One part of the research is concerned with dissolved organic matter (DOM) character, dynamics and photochemistry in the boreal forest biome. The other line of research seeks to understand natural and anthropogenic perturbations in lake basins by determining the distribution of hydrocarbon and fatty acid biogeochemical markers in dated cores of lake sediments. Major activities are summarized below.

Dissolved Organic Matter Geochemistry - Boreal Forest

The primary research effort is part of the Boreal Ecosystem-Atmosphere Study (BOREAS), which is concerned with the interactions among the terrestrial, aquatic and atmospheric components of the boreal forest and the implications of those interactions for global climate change. Most of the work was carried on at the BOREAS Northern Study Area (Thompson, Manitoba) and focused on the character and photochemistry of DOM in beaver ponds, DOM dynamics in small boreal watersheds and changes in soil organic matter and nutrients as a result of forest fire and subsequent recovery. The field work during the review period was concerned mainly with the impact of forest fire on organic matter geochemistry and trace gas fluxes from the soil. Laboratory work centred around the photochemical production of carbon monoxide (CO) and dissolved inorganic carbon (DIC) from DOM fractions isolated from a beaver pond. Activities were supported by the USEPA through a US National Research Council Senior Research Associateship, awarded for a nine month development leave in Athens, Georgia.

Major findings to date are - (a) the overall character of DOM from the BOREAS beaver pond site resembles surface and shallow groundwater sources; (b) hydrophilic fractions of DOM produce CO and DIC to a greater extent than do hydrophobic fractions when compared on an equal C basis and under laboratory photochemical exposure; and (c) labile C and N compounds can be liberated from hydrophobic fractions by photochemical processes and subsequently utilized by bacterioplankton. This work was done in collaboration with USEPA and University of Georgia colleagues from the BOREAS Science Team.

Biogeochemical Markers in Lake Sediments

This study is mainly concerned with the impacts of oil sands development upon the lower Athabasca River downstream of Ft. McMurray, Alberta, and the depositional history of organic materials, including contaminants, in northern lakes. Analyses of hydrocarbons and fatty acids from suspended sediments of the Athabasca River, the oil sands development area, and from tributaries provide "fingerprint" information for tracing sources of organics to the Athabasca. Lake sediment studies from Lake Athabasca, Great Slave Lake, Legend Lake and Weekes Lake provide the Northern River Basins Study (NRBS) with biogeochemical marker and contaminant analyses. Results on

biogeochemical marker from Great Lakes dated cores were published this year. This work was done in collaboration with colleagues from the National Hydrology Research Institute and the University of Michigan.

Biogeochemical marker results to date showed that (a) hydrocarbon and fatty acid chain length distributions can be used to track land-use changes, cultural eutrophication and petroleum pollution in sediment records from large lakes in remote or industrialized basins; and (b) natural hydrocarbon input and petroleum contamination can be determined in dated cores and can overprint modern plant hydrocarbon input to sediments.

Publications and Presentations in FY 95/96:

Bourbonniere, R.A. and P.A. Meyers. 1996. Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. *Limnology and Oceanography* 41:352-359.

Bourbonniere, R.A. and P.A. Meyers. 1996. Anthropogenic influences on hydrocarbon contents of sediments deposited in eastern Lake Ontario since 1800. *Environmental Geology* (in press).

Bourbonniere, R.A., S.L. Telford and J.B. Kemper. 1995. Depositional History of sediments in Lake Athabasca: Geochronology, bulk parameters, contaminants and biogeochemical markers. NWRI Contribution No. 95-76. (Also NRBS Series #72)

Bourbonniere, R.A., S.L. Telford and J.B. Kemper. 1995. Depositional history of sediments in Legend and Weekes Lakes: Geochronology and bulk parameters. NWRI Contribution No. 95-77. (Also NRBS Series #71)

Bourbonniere, R.A., L.A. Ziolkowski, S.L. Telford, M.A. Moran, K.L. Bushaw, W.L. Miller, M.A. Tarr and R.G. Zepp. 1995. Character and biogeochemistry of dissolved organic matter in a boreal forest beaver pond near Thompson, Manitoba, Canada. Presented at the 17th International Meeting on Organic Geochemistry Donostia-San Sebastian, Spain, September 4 - 8. *In:* Organic Geochemistry: Developments and Applications to Energy, Climate, Environment and Human History, J.O. Grimalt and C. Dorronsoro (eds.), Published by A.I.O.G.A., Donostia-San Sebastian, Spain, pp.1144-1146.

Brownlee, B.G., W.G. Booty, G.A. MacInnis, R.A. Bourbonniere and J. Lee. 1995. A two-dimensional contaminant fate and transport model for the lower Athabasca River. Presented at SETAC '95, Vancouver, BC, November 6 -10.

Bushaw, K.L., R.E. Hodson, R.A. Bourbonniere, D.A. Bronk, W.L. Miller, R. Zepp, M. Tarr, D. Schulz-Jander and M.A. Moran. 1995. The photochemical release of labile nitrogen from aquatic fulvic acids. Presented at the Humic Substances in the Environment: New Challenges and Approaches, IHSS, Atlanta, GA, August 27 - September 1.

Bushaw, K.L., M.A. Moran, R.E. Hodson, D.A. Bronk and R.A. Bourbonniere. 1995. The potential for photochemical processes to liberate labile forms of both carbon and nitrogen in humic waters. Presented at the ASLO Annual Meeting, Reno, Nevada, June.

Bushaw, K.L., R.G. Zepp, M.A. Tarr, D. Schulz-Jander, R.A. Bourbonniere, R.E. Hodson, W.L. Miller, D.A. Bronk and M.A. Moran. 1996. Photochemical release of biologically available nitrogen from dissolved organic matter. *Nature* (in press).

Coakley, J.P., M.E. Fox, R.A. Bourbonniere and D.S. Smith. 1995. Investigation of vertical trends in coprostanol in Hamilton Harbour sediments, Lake Ontario, Canada. Presented at the 13th International Conference of the Estuarine Research Federation, Corpus Christie, TX, November 12 - 16.

Dutka, B.J., R. Bourbonniere, R. McInnis, K.K. Kwan and A. Jurkovic. 1995. Bioassay assessment of impacts of tar sands extraction operations. *Environmental Toxicology and Water Quality* **10**:107-117.

Miller, W.L., R.A. Bourbonniere and R.G. Zepp. 1996. Photochemical CO production in a boreal beaver pond. Presented at the AGU/ASLO Ocean Sciences Meeting, San Diego, CA, February 12 - 16.

Silliman, J.E., P.A. Meyers, A.J. Tomasek, S.M. Havach, J.M. Stewart and R.A. Bourbonniere. 1995. Record of postglacial organic matter delivery and burial in sediments of Lake Ontario. Presented at the 17th International Meeting on Organic Geochemistry Donostia-San Sebastian, Spain, September 4 - 8. *In:* Organic Geochemistry: Developments and Applications to Energy, Climate, Environment and Human History, J.O. Grimalt and C. Dorronsoro (eds.), Published by A.I.O.G.A., Donostia-San Sebastian, Spain, pp. 857-859.

Tarr, M.A., D. Schulz-Jander, R.A. Bourbonniere, W.L. Miller, R.G. Zepp, K.L. Bushaw, D.A. Bronk, R.E. Hodson and M.A. Moran. 1995. Photo-ammonification: Effects of solar ultraviolet radiation on the release of ammonium from aquatic humic substances. Presented at the Humic Substances in the Environment: New Challenges and Approaches, IHSS, Atlanta, GA, August 27 - September 1.

Zepp, R.G., W.L. Miller, R.A. Bourbonniere and M.A. Tarr. 1995. Interactions of changing solar ultraviolet radiation and organic matter photo oxidations in northern peatlands. *In*: Preprints of papers presented at the 210th ACS National Meeting, Chicago, IL, 35(2):394-397.

Project: **Contaminant Pathways and Controls**

Study Title: **Oil Sands Research**

Study Leader: **B. Brownlee**

Overview

A two-dimensional contaminant fate and transport model was calibrated for the lower Athabasca River downstream of Fort McMurray, Alberta. Further ecotoxicological studies were carried out on sediments from the Athabasca River. A new study was initiated on base/neutral compounds from oil sands fine tailings. Both of these studies are funded under the Program for Energy Research and Development (PERD). Scientific leadership was provided for Northern River Basins Study (NRBS) projects on contaminant fate and food chain modelling for the Athabasca River. Key findings and activities are summarized below.

Contaminant Transport in Rivers

The purpose of our research is to provide supporting information for the assessment of licence applications for water releases to the Athabasca River from new oil sands operations or process changes to existing ones.

One of the oil sands plants (Suncor Inc.) near Fort McMurray has a licensed discharge which contains low (μg/L) concentrations of two- and three-ring aromatic compounds suitable for calibration of a contaminant fate and transport model for the Athabasca River. We have developed a two-dimensional model to account for the mixing and persistence of several of these compounds. Preliminary estimates for the half-life of one of them (2,4-dimethylbenzothiophene) are 12-24 hours. Mixing properties of the Athabasca River were calculated using elevated sodium and chloride concentrations from a major tributary, the Clearwater River, as a tracer.

In earlier work on the ecotoxicology of suspended and bottom sediments from the lower Athabasca River we had obtained a strong response for organic solvent (dichloromethane) extracts of sediments using the acute Microtox™ test. Using Toxicity Identification Evaluation (TIE) experiments, we have found that most of the toxic response can be accounted for by elemental sulfur extracted from the sediments by the organic solvent. Elemental sulfur is a common co-extractive in organic analyses of sediments and it's EC_{50} is about 30 μg/L, considerably lower than many organic compounds.

Environmental Dynamics of Base/Neutral Compounds from Oil Sands Fine Tailings

The oil sands companies have in storage several hundred million cubic metres of fine tailings which result from the hot water extraction of bitumen from oil sands. The tailings are presently stored above ground in large tailings ponds. Another management option would consist in their transfer in water-capped lakes. The purpose of our newly initiated study is to provide knowledge on the behavior of base/neutral compounds released from these fine tailings in support of risk assessment.

We have begun work in three areas: (1) characterization of the base/neutral maltene fraction extracted from fine tailings by dichloromethane, (2) a bench scale system to simulate porewater release from consolidating fine tailings, and (3) relative rates of biodegradation of model compounds using a bacterial culture which actively degrades polycyclic aromatic compounds. The biodegradation studies are being carried out in collaboration with the University of Alberta.

Northern River Basins Study - Contaminant Modelling

A project team of federal, provincial and industry scientists was established to oversee the modelling work which was carried out by private sector consultants under contract to the Northern River Basins Study (NRBS).

The contaminant fate model, WASP4, was calibrated initially for the Athabasca River from Hinton, Alberta, to the Athabasca Delta using existing sediment transport routines which did not allow for sediment resuspension. In collaboration with B.G. Krishnappan, NWRI, the consultants wrote a new sediment transport routine for WASP4 which incorporates sediment settling and resuspension and predicts a seasonally dynamic pattern for organic carbon and contaminant concentrations in the Athabasca River bed sediments. These concentrations are predicted to increase during the ice-covered, low flow winter months and then to rapidly decline when flows increase in the spring and bed sediments are resuspended and transported downstream.

The initial food chain model provided for NRBS was a steady state version of the Thomann-Connolly bioenergetic model. This has subsequently been refined and a stochastic, time variable food chain model is now available for the upper Athabasca River.

Publications and Presentations in FY 1995/96

Brownlee, B.G., S.L. Kenefick, G.A. MacInnis and S.E. Hrudey. 1995. Characterization of odorous compounds from bleached kraft pulp mill effluent. *Water Science and Technology* 31:35-40.

Brownlee, B.G., W.G. Booty, G.A. MacInnis, R. Bourbonniere and J. Lee. 1995. A two-dimensional contaminant fate and transport model for the lower Athabasca River. Presented at the Second SETAC World Congress, Vancouver, BC, November 5-9, 1995.

Brownlee, B.G., G.A. MacInnis and R. Marr. 1995. An experimental protocol for measurement of properties used in modelling the aquatic fate of organic compounds. Presented at the 78th Canadian Society for Chemistry Conference, Guelph, Ontario, May 28-June 1, 1995.

Kenefick, S.L., B.G. Brownlee, T.R. Perley and S.E. Hrudey. 1995. A chemical and sensory study of odour compounds in the Athabasca River, Alberta, Canada. *Water Science and Technology* 31:15-21.

Kenefick, S.L., N.J. Low, S.E. Hrudey and B.G. Brownlee. 1995. A review of off-flavour tainting of water and fish by pulp mill effluents. *Water Science and Technology* 31:55-61.

Kenefick, S.L., B.G. Brownlee, G.A. MacInnis and S.E. Hrudey. 1995. A chemical and sensory study of pulp mill related odour compounds in the Athabasca River. Presented at the 78th Canadian Society for Chemistry Conference, Guelph, Ontario, May 28-June 1, 1995.

MacInnis, G.A, B.G. Brownlee and J.W. Penders. 1995. Toxicity Identification Evaluation of suspended sediments from the Athabasca River. Presented at the 22nd Annual Aquatic Toxicity Workshop, St. Andrews, NB, October 1-5, 1995.

Marsalek, J., B. Brownlee, T. Mayer S. Lawal and G. Frazer. 1996. Heavy metals and PAHs in highway bridge runoff. Presented at the 31st Central Canadian Symposium on Water Pollution Research, Burlington, Feb. 6-7, 1996.

Muir, D.C.G., G.M. Pastershank, R. Crosley, L. Noton, S. Ramamoorthy and B. Brownlee. 1995. Pathways of accumulation and temporal trends of PCDD/Fs from a bleached kraft pulp mill on the Athabasca River (Alberta). Presented at DIOXIN '95, Edmonton, Alberta, August 21-25, 1995.

Project: **Contaminant Pathways and Control**

Study Title: **Sustainable River Development**

Study Leader: **P. Engel**

Overview

Our work is directed at research and applications of fluid mechanics, sediment transport in rivers, development of techniques for monitoring river processes and flow-structure interaction. Emphasis is placed on providing information for operational branches in Environment Canada, in particular the Water Survey of Canada. However, our results are also useful to other departments and water resources managers. Research was initiated on turbulent channel flow over porous beds and in vegetated channels. Work continued on the determination of hydraulic resistance of alluvial streams and evaluation of the performance characteristics of current meters and sediment samplers used by Environment Canada. Key activities are summarized below.

Flows Over Permeable Boundaries

Natural streams have beds formed of permeable materials. While there is much information on turbulent flow over impervious, smooth and rough boundaries, very little is known about the interaction between pervious bed and turbulent flow. Usually, the pervious bed is considered to be equivalent to an impervious boundary of the same texture, clearly ignoring the effects of the permeability on the flow. It is now clear that the coupling of the main flow and the porous bed is significant. Important consequences must be recognized for the transport of solute over and through the bed, for flow resistance, for groundwater recharge and for stream ecology. The flow zone adjacent to the riverbed is affected by the boundary, and characterized by strong gradients of physical, chemical and biological variables. A literature review is underway to determine present knowledge on these processes.

Flows in Vegetated Waterways

The current promotion of natural development of wetlands and other environmental restoration projects often favour the growth of reeds and other aquatic vegetation. Such vegetation influences the resistance of the water course and consequently the flow velocities and depths. Vegetation may protect both the streambed and the banks from being eroded by reducing the average velocity of the flow and shear stress at the soil surface below that required to cause erosion. Vegetation also induces deposition of sediments thereby contributing to bed and bank stability and detention of contaminants. Turbulent flow in a vegetated channel is essentially a movable boundary problem and has many similarities to sediment transport phenomena. The essential similarity is that the boundary or roughness elements of the channel are deformed by the flow within the channel. Consequently, any practical solution for the resistance and sediment retention of such vegetated waterways must be expressed in terms of flow conditions and physical properties of the sediment and vegetation. A literature review is underway to determine present knowledge on these processes.

Hydraulic Model Study of Multiple Sewer Junction

The Delcan Corporation, an engineering consulting firm, is in the process of designing the Nashville Trunk Relief Sewer, which is part of the Keele Trunk Relief Sewer, for the Municipality of Metro Toronto. Because of the hydraulic complexity of the proposed structures, hydraulic modelling, using Froudian similitude at a scale ratio of 1:10, was used to assist in the design process. Important information on flow capacity, flow conditions, energy dissipation and dry weather flow (DWF) benching was provided.

Publications and Presentations in FY 95-96

Engel, P. 1995. Bed-Load Sampling in Sand Bed Rivers. Discussion. *J. Hydraul. Eng.*, ASCE (in press).

Engel, P. and Y.L. Lau. 1995. Estimation of Mean Velocity in Ice Covered Channels. Discussion. *J. Hydraul. Eng.* ASCE (in press).

Engel, P. and Y.L. Lau. 1996. Methods for Measuring Discharge under Ice Cover. Discussion *J. Hydraul. Eng.* ASCE 121(2): 52-54.

Engel, P. and J. Marsalek. 1995. Hydraulic Model Study for the Keele and Nashville Trunk Relief Sewer Junction. Contract Report No. AEPB-TN-95-02, National Water Research Institute, Burlington, Ontario.

Project: **Contaminants Pathways and Controls**

Study Title: **Transport Characteristics of Fine Sediments in Rivers**

Study Leader: **B. G. Krishnappan**

Overview

Fine sediments in rivers are known to adsorb and transport many toxic contaminants and hence play an important role in determining the health of river ecosystem. The transport characteristics of the fine sediment, therefore, become essential parameters for modelling the transport, fate and bioaccumulation of contaminants in river system. Research on transport characteristics of fine sediment continued in support of the Fraser River Action Plan (FRAP). A summary of key elements of the research is given below.

Transport Characteristics of Fraser River Sediments

The transport characteristics of the Fraser River sediments were studied both in the laboratory and in the field during the FY 95-96. In the laboratory investigation, the sediment and water sample collected from the Fraser River at Quesnel were tested in the rotating flume. The objective of the testing was to determine the transport functions for deposition and erosion of the sediment as a function of bed shear stress. The experiment involved placing of the sediment water mixture of the Fraser River in the flume and running the flume at different speed combinations to produce different shear stress conditions. Results from the tests were used to formulate a new sediment transport algorithm for the Fraser River sediments. The new algorithm accounts for the differences in the critical conditions for erosion and deposition of the fine sediment and therefore reflects the true behaviour of cohesive sediment.

The field study was carried out in the Thompson River system near Kamloops, B.C. Both the North and the South Thompson rivers were sampled along with the reach below the confluence. The reach below the confluence received effluents from the Weyerhaeuser Pulp Mill and the Kamloops City Sewage Treatment Facility. The objective of the field survey was to determine the extent of flocculation of the suspended sediment in the river system and to quantify the impact of the outfalls on the transport characteristics of the suspended sediment.

A summary of the progress made so far on our sediment work was presented at a FRAP Progress Review Workshop in Vancouver, February 20-22, 1996. The work carried out so far has shed some new light on the transport characteristics of the fine sediment and the associated contaminants in the Fraser and Thompson river systems. The new sediment transport algorithm developed from our laboratory investigation will improve our ability to make realistic predictions of sediment and contaminant transport in these river systems. The new algorithm is being implemented in the Simon Fraser University Model in collaboration with Prof. F. Gobas.

The new sediment transport algorithm was also extended to the Athabasca River based on our work carried out for the Northern River Basins Study (NRBS) last year. The algorithm is being implemented in the WASP model in collaboration with Golder Associates, Calgary, for NRBS.

Role of Fine Sediment in the Accumulation of Pulp Mill Chemicals by Fish

Experiments to study the effect of pulp mill effluent and particulate matter on mixed function oxygenase (MFO) induction activity in fish continued in the rotating flume. This study was carried out jointly with P. Hodson and J. Parrot, AECB-NWRI for the Fraser River Action Plan. In these experiments, small rainbow trouts were placed in the rotating flume for four days for each test. At the end of the test period, the fish were taken out and their MFO induction activities measured. The results showed that the flow velocity and the temperature played a significant role in the fish response, and therefore needed to be controlled and/or monitored. A preliminary report was prepared for FRAP and an extended study plan was developed. FRAP approved the study plan and provided additional funds to build six linear flumes which will be used to study the effect of swimming effort on MFO induction. The experiments in the rotating flume will resume once the effect of exercise is quantified.

PAH Adsorption onto Fine Sediment

To exploit the fluorescence quenching technique for studying the adsorption of PAH's onto the flocculating sediment in the rotating flume, a particle separation system is needed. A cascade filtration system was tried but was found unsatisfactory for continuous operation because of filter clogging and build up of excessive pressure in the line. Alternate particle separation systems were explored during the current review period. The water elutriation system that we used for separating suspended sediment in different size classes was selected as a possible device that could overcome the filter clogging problem. The feasibility of using this device for PAH adsorption study is being explored.

Publications and Presentations in FY 1995-96

Hodson, P.V. and B.G. Krishnappan. 1995. Role of particles in the accumulation by fish of chemicals from the pulp mill effluents. Report submitted to the Fraser River Action Plan.

Krishnappan, B.G. 1995. Effect of pulp mill effluent on the transport characteristics of suspended sediment in the Athabasca River in Canada. In: Proc. 6th International Symposium on River Sedimentation, New Delhi, India.

Krishnappan, B.G. and Members of CSCE Task Committee on River models. 1995. Evaluation of one dimensional river models - A Canadian Experience. Proc. US-Taiwan Bilateral workshop on understanding sedimentation processes and model evaluation, San Francisco.

Krishnappan, B.G. 1996. Transport characteristics of fine suspended sediments in the Athabasca River in the vicinity of the pulp mill at Hinton, Alberta, Canada. Proc. International Conference on Sustainable Forestry Partnership: Forging a network of excellence, Edmonton, Alberta.

Krishnappan, B.G. 1996. Sediment Transport. In: Issues and Directions in Hydraulics-Proceedings of the Iowa Hydraulics Colloquium held in Honour of J. F. Kennedy- published as a book by Balkema.

Krishnappan, B.G. 1996. A new algorithm for fine sediment transport. NWRI Contribution No. 96-160.

Krishnappan, B.G. 1996. In-River flocculation processes and the transport of suspended sediments in the Fraser and Thompson river systems. Presented at FRAP Research Program Workshop, Vancouver, February 20, 1996.

Krishnappan, B.G. and R. Stephens. 1996. Critical shear stresses for erosion and deposition of fine suspended sediment from the Athabasca River. Final Report submitted to the Northern River Basins Study.

Skafel, M.G. and B.G. Krishnappan. 1995. Deposition of fine grained sediment under wave action. Proc. Canadian Coastal Conference 1995, Dartmouth, Nova Scotia.

Project: **Contaminant Pathways and Controls**

Study Title: **Sediment/Contaminant Transport in Rivers**

Study Leader: **Y.L. Lau**

Overview

Research was conducted on the persistence of cyanazine in the aquatic environment and on the formation of frazil and anchor ice in rivers. Work continued on the relationships between biofilm formation and the characteristics of open-channel flows. Major activities are summarized below.

Persistence of Cyanazine in the Aquatic Environment

The herbicide cyanazine is a selective triazine herbicide used for annual broadleaf and grass weed control in corn, sorghum, potatoes, soybeans and triazine-resistant canola. It is one of the most heavily used agricultural pesticides in Ontario and yet there is virtually no information on its aquatic fate. Both the U.S. Environmental Protection Agency and the Evaluation and Interpretation Branch, Environment Canada, have noted that more information is required on the occurrence, persistence, fate and toxicity of cyanazine.

Some preliminary experiments were carried out to investigate the volatility of cyanazine from the aqueous phase and its adsorption by bottom-attached biofilms. The experiments were conducted in beaker tests and in a channel flow, at temperatures up to 35°C. It was found that cyanazine was essentially nonvolatile. Some evidence of uptake by biofilms was found but further confirmation is required. The results of this work will be useful for determining the hazards posed by cyanazine to the aquatic environment.

Frazil and Anchor Ice Formation in Rivers

Frazil and anchor ice can greatly affect the hydraulics of river flows and yet there is still very little understanding of their formation and growth. Knowledge of these processes can help the effective use of water resources, efficient power production as well as protection of shorelines.

A study, funded by several hydropower companies, has been conducted in cooperation with the National Hydrology Research Institute. A circular flume, in which the bed and the walls rotate separately, was designed and built in the cold room. Experiments were conducted and the results provided the first successful measurements of velocity distribution in frazil-laden flows and demonstrated that frazil formation can have pronounced effects in reducing the discharge in a river.

Growth of Biofilm in Open Channel Flows

In many shallow streams, the uptake of contaminants by biofilms on the riverbed is the principal reason for the disappearance of contaminants from the water column. It is therefore important to investigate the various factors controlling biofilm growth in order to achieve a good understanding of the pathway of contaminants in the aquatic ecosystem.

Experiments on biofilm growth were carried out in two identical channels located side by side. Because each pair of flows was subject to the same weather conditions and had the same water supply, any difference in the rate of biofilm accumulation could be ascribed to the difference in hydraulic conditions. It was found that the biofilm accumulation rate was well correlated with the mean flow velocity but not correlated with the bed shear stress. Although the reason for this is not completely clear, it indicates that the flow velocity rather than the shear stress should be used as the variable for studying the effect of hydrodynamics on bottom-attached biofilms.

Effect of Biofilm on Critical Shear Stress for Sediment Transport

It has been suggested that biofilms can increase the shear stress required for the initiation of sediment motion because of the polysaccharides which are present. However, this effect has never been quantitatively demonstrated. An experiment has been designed to measure the critical shear stress with and without biofilm formation. An apparatus to measure the bed shear stress in-situ has been designed and constructed and is undergoing modifications. Experiments will proceed in 1996.

Publications and Presentations in FY 95-96

Lau Y.L. 1995. Relative importance of mean velocity and bed shear on biofilm accumulation in open-channel flows. Presented at the International IAWQ Conference Workshop on Biofilm Structures, Growth and Dynamics, Noordwijkerhout, the Netherlands, August, 1995. and *Water Science and Technology* 32 (8):193-198.

Lau, Y.,L., D.L.S. Liu and G.J. Pacepavicius. 1996. A Preliminary Study of the Persistence of Cyanazine in the Aquatic Environment. NWRI Contribution No. 96-155.

Pacepavicius, G., Y.L. Lau, D. Liu, H. Okamura and I. Aoyama. 1996. A rapid biochemical method for estimating biofilm mass. NWRI Contribution No. 96-154.

Tsang, G., Y.L. Lau and R. Yan. 1995. Laboratory Investigation of Frazil Evolution, Flocculation and the Formation of Anchor Ice. NHRI Contribution .

Tsang, G. and Y.L. Lau. 1995. Frazil and Anchor Ice Laboratory Investigation - Phase 2. Presented at the 8th workshop on the Hydraulics of Ice-Covered Rivers, Kamloops, B.C., Aug 16-18.

Project: **Contaminant Pathways and Controls**

Study Title: **Characterization of Physically-Unstable Aquatic Colloids Relevant to Flocculation**

Study Leader: **G. G. Leppard**

Overview

Research was completed on the fundamental aspects of the molecular architecture of a variety of aquatic flocs, all of which can be analyzed as colloid systems by minimal perturbation techniques. The principal conclusion was that almost all natural and industrial flocs have basic similarities in molecular architecture; thus they are not the unanalyzable "black box" of the past. With our new information and novel technology, we are pursuing the hypothesis that details of floc structure, especially colloidal structure not previously amenable to analysis, provide insight into activity which will lead to better management practices. Recent progress is summarized below.

Contaminant Transport

In a pilot study on Hamilton Harbour, we demonstrated that one type of particle accounted for most of the binding and particulate transport of PAHs. Using electron-optical technique, the particle type, a mixed organo-mineral floc, was found be an aggregate of several colloid types (including submicron-sized microbes) which were cross-linked by organic fibrils of 0.005 μm diameter. The particles were of a broad size range from 20 μm up to many times that diameter. They accounted for 75% of the total PAHs measured in the water column. They were highly selective for phenanthrene, accounting for 97% of the particulate phenanthrene, and almost as selective for fluoranthene and pyrene. A smaller version of this floc "species" (10-20 μm diameter range) was selective for the genotoxic benzo[a]pyrene, a priority pollutant. Electron-optical analyses (0.001 μm resolution) of the molecular architecture of the matrix of the carrier floc revealed that it was constructed like a porous sponge with an exceptional surface-to-volume ratio which we are attempting to quantify with regard to the total surface available for binding in the water column.

Sedimentation / Resuspension Processes

Electron-optical analyses of many floc types, which were selected for their slow sedimentation / rapid resuspension characteristics, revealed a common morphological feature. All types had an exceptionally high porosity (despite a sometimes solid appearance by optical microscopy), with over 99% water content and with a colloidal substructure resembling that of a dilute gel. This architectural feature could be demonstrated, despite the physical instability of these flocs, through the use of minimal perturbation technology in conjunction with a novel multi-method preparatory approach, both developed within NWRI. Because our work is done at much finer resolution, we can see pore systems within the pores as defined by the engineers. It is anticipated that the standard concept of "pore water" will have to be redefined for practical use by engineers.

Engineered Decontamination of Water

Multi-method analyses were used to compare populations of normal and dysfunctional biological flocs from diverse water treatment systems. The immediate goal was to develop new technology to ascertain morphological correlates of floc function/dysfunction in decontamination tanks. The long-term goal is to help water treatment professionals to detect problems at the earliest possible stage, and to provide insight into the most effective ways to address the problems. A novel battery of correlative microscopic techniques was devised under a joint NSERC Strategic Grant. Molecular markers were developed for several of the quantitatively important colloids within the flocs. We are now mapping the details of flocs in order to find correlates of specific dysfunctions; this work is done through a very successful co-operation with the industrial, municipal and university sectors. After the first-year of this 3-year project, classical barriers precluding success with correlative microscopy have been overcome and it was possible to quantify some of the morphological analyses.

Biogeochemical Processes on a Planetary Scale

Biological flocs in the ocean can buffer the planet against high atmospheric carbon dioxide levels, and thus modulate global warming. These algae-rich flocs accomplish this by transporting photosynthetically-fixed carbon dioxide into the ocean interior at a faster rate than normal when atmospheric carbon dioxide levels are high. In response to requests and funding from international agencies, we undertook the characterization of a population of marine transporter flocs selected for us, with the goal of ascertaining the colloidal substructure of the flocs. The colloidal aspects of these flocs were deemed to hold the key to understanding floc behaviour in relation to transport functions on a planetary level. As a result of the minimal perturbation technology developed within NWRI, in conjunction with valued European and McMaster University collaborations, we succeeded. The physical instability of the colloidal substructure of the flocs (dehydration-provoked shrinkage and collapse plus extraction artifact), which frustrated earlier attempts at characterization, was the result of dynamic fibril associations within the marine flocs. We were able to stabilize these associations prior to the characterization analyses.

Publications and Presentations in FY 95-96

Droppo, I.G., D.T. Flannigan, G.G. Leppard and S.N. Liss. 1996. Microbial floc stabilization and preparation for structural analysis by correlative microscopy. *Water Sci. Technol.* (in press).

Droppo, I.G., S.N. Liss, G.G. Leppard, C. Jaskot and D.T. Flannigan. 1995. Activated sludge and BVF floc characteristics for Cavendish Farms food processing plant, Charlottetown, P.E.I., Canada. NWRI Contribution No. 95-152.

He, Q.H., G.G. Leppard, C.R. Paige and W.J. Snodgrass. 1996. Transmission electron microscopy of a phosphate effect on the colloid structure of iron hydroxide. *Water Res.* 30:

Heissenberger, A., G.G. Leppard and G.J. Herndl. 1996. Ultrastructure of marine snow: II. Microbiological considerations. *Mar. Ecol. Prog. Ser.* (in press).

Leppard, G.G., 1996. Colloidal organic fibrils of acid polysaccharides in surface waters: Electron-optical characteristics, activities and chemical estimates of abundance. *Colloids & Surfaces - A. Physicochemical & Engineering Aspects* (in press).

Leppard, G.G., A. Heissenberger and G.J. Herndl. 1996. Ultrastructure of marine snow: I. Transmission electron microscopy methodology. *Mar. Ecol. Prog. Ser.* (in press).

Liss, S.N., I.G. Droppo, D.T. Flannigan and G.G. Leppard. 1996. Floc architecture in wastewater and natural riverine systems. *Environ. Sci. Technol.* **30**: 680-686.

Munawar, M., I.F. Munawar, T. Weisse, G.G. Leppard and M. Legner. 1995. The significance and future potential of using microbes for assessing ecosystem health: the Great Lakes example. *J. Aquatic Ecosystem Health* **3**: 295-310.

Tessier, A., D. Fortin, N. Belzile, R.R. De Vitre and G.G. Leppard. 1996. Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: Narrowing the gap between field and laboratory measurements. *Geochim. Cosmochim. Acta* **60**: 387-404.

Project: **Contaminant Pathways and Controls**

Study Title: **Fate and Transport of Inorganic and Organic Contaminants in Aquatic Systems**

Study Leader: **T. Mayer**

Overview

Research was conducted on the fate and transport of nutrients and other contaminants in a variety of aquatic ecosystems. The study focussed on the development of criteria for identification of sediment sources in agricultural watershed, and on the investigation of the fate and transport of heavy metals and nutrients in urban and agricultural runoff. Research on the nutrients sources verification in freshwater wetlands continued. Major activities are summarized below.

Fate and Transport of Nutrients and Heavy Metals in Agricultural and Urban Runoff

Urban stormwater runoff represents a major pathway of contaminants such as heavy metals and nutrients to receiving waters. The study of the fate and transport of nutrients and heavy metals in urban stormwater detention ponds was completed. The results showed the highest heavy metals concentrations in suspended and bottom sediments from ponds receiving runoff from primarily industrial and commercial catchments, followed by ponds receiving runoff from residential catchment. The concentrations of Cu, Pb, Zn in suspended sediments of the detention pond from industrial/commercial area exceeded even the concentrations of severe effect levels of the Ministry of Environment and Energy (MOEE) Guidelines (110, 250, and 820 μg/g, respectively). The residential ponds exhibited highly eutrophic conditions in the summer with chlorophyll *a* concentrations of 30 μg/L.

A study investigating the sources of sediments and sediment associated nutrients (phosphorus) in the agricultural watershed of South Tobacco Creek was completed. South Tobacco Creek is one of the first order streams of Red River, Manitoba. The Red River is a major tributary of Lake Winnipeg and one of the major non-point source contributor of sediment and nutrient loads to the lake. Concern over the eutrophication of the South Basin of Lake Winnipeg has risen in recent years. The purpose of the study was to develop criteria that could be used to determine sediment sources in the watershed. This led to determination of the geochemical characteristics of the source material (surficial soils and bank material) which then, can be related to the geochemical characteristics of the fluvial sediments. The comparison of geochemical properties can then be used for identification of the sediment sources. A simple mixing model can be employed to assess the relative contributions of sources to the tributary sediment loads. The statistical analysis showed that geochemical properties such as Fe, Al, forms of P and carbon can be used to fingerprint sources of sediments.

Verification of Nutrients Sources in Freshwater Wetlands

Study continued on the identification of nutrients sources at Point Pelee National Park. Anthropogenic input, possibly from the park septic system, may contribute to nutrients loads in the marsh, thus profoundly impacting water quality. Preliminary results showed elevated phosphorus (P) concentrations in wetland sediments adjacent to the shore, located in the proximity of the Blue Heron

picnic area, equipped with public washrooms. To ascertain that observed spatial differences in P concentrations were not just of natural origin, coprostanol, a sewage-specific indicator, was used to differentiate between natural and anthropogenic P inputs. The results show that the surficial nearshore sediments contained higher concentrations (~10 μg/g) of coprostanol than the offshore sediments. The concentrations decreased to background levels (0.5 μg/g) with sediment depth.

Publications and Presentations in FY 95-96

Marsalek, J., B. Brownlee, T. Mayer and G. Frazer. 1996. Heavy metals and PAHs in highway runoff. Presented at the 31st Central Canadian Symposium on Water Pollution Research, Burlington, Ontario, 6 & 7 February 1996.

Mayer, T. 1996. Geochemical Characteristics of Potential Source Material Contributing to Particulate Phosphorus Loads in South Tobacco Creek. NWRI Contribution No. 96-156.

Mayer, T. and E. Delos Reyes. 1996. Phosphorus and metal contaminants transport in two southern Ontario Rivers: the Grand River and its tributary, the Nith River. *Water Qual. Res. J. Canada* 31: 119-151.

Mayer, T., J. Marsalek and E. Delos Reyes. 1995. Nutrients and metal contaminant status of urban stormwater detention ponds. Presented at NALMS 15th International Symposium, Toronto, Canada, November 6-11, 1995.

Mayer, T. and S. Telford. 1995. The role of sediments in nutrient dynamics of Point Pelee Marsh. Presented at the 38th IAGLR Conference, East Lansing, MI, May 28 - June 1, 1995.

Project: **Contaminant Pathways and Controls**

Study Title: **Agricultural Non-point Sources of Pollution and Sustainable Agriculture**

Study Leader: **H.Y.F. Ng**

Overview

Five research studies were completed on agricultural non-point sources of pollution. Work continues on the farm-scale demonstration study of controlled drainage/subirrigation systems to determine their economic benefit to the producer. Key findings on the completed studies are summarized below.

Comparative Study of Metolachlor Analysis - An Interlaboratory Collaborative Study

Monitoring for metolachlor in Canadian waters requires specialized instrumentation such as gas chromatograph, specific detectors and highly trained personnel. Several new technologies have been developed for detection of metolachlor in water and other substrates. An enzyme linked, immunosorbent assay and solid phase microextraction are two such analytical technologies for metolachlor and other pesticides in water. Testing of metolachlor treated water has increased dramatically over the past few years. Current testing techniques are time-consuming, expensive and require specialized instrumentation. Determination of residues of metolachlor from treated agricultural runoff water is required to enable environmental management practices at low cost. For this reason, a study was initiated to compare three different methods for determination of metolachlor residues, i.e., solid-phase microextraction (SPME) followed by GC-EC solvent extraction followed by GC-MSD, and immunoassay. Field runoff samples were split and analyzed by collaborators at University of Manitoba, Agriculture and Agri-Food Canada's Research Station, Harrow, and NWRI's National Laboratory for Environmental Testing. Our results showed that metolachlor concentration in water samples were highly correlated among the techniques with coefficients ranging between 0.89 to 0.98.

Assessment of Cyanazine Persistence in Water

Cyanazine is an important selective herbicide used for the control of several annual grassy weeds in fields of corn, soybeans, and triazine-resistant canola. Cyanazine ranked in fourth of the five largest quantities of herbicides used in Ontario field crops. An assessment of the persistence was conducted with native soil microorganisms. A mixed cocktail of soil leachates and cyanazine treated runoff collected from Woodslee Experimental Plots, was used in the laboratory experiment without any addition of nutrient or inoculum. The resistance of cyanazine to microbial degradation was further evaluated with the white rot fungus *Phanerochaete chrysosporium* (ATCC20696). Our laboratory results shown that cyanazine is a very stable compound in water. No apparent biodegradation or biotransformation of cyanazine was observed in a mixed cocktail of the cyanazine treated agricultural runoff and soil leachate. Our results imply that extensive use of cyanazine as a herbicide may have a long-lasting impact on the Canadian aquatic ecosystem. Since cyanazine has a strong tendency to complex with soils, its ultimate fate in the aquatic sediment transport warrants further exploration.

Combined Crop/Tillage/Water Management Practices Associated with Herbicide Treatment

The combined effects of crop, tillage, water management practices associated with banded and entire area herbicide treatments were studied in 16 field plots for losses of metolachlor in surface runoff and in tile drainage.

The crop/tillage treatments were the conventional tillage using a moldboard (MB) plowed and the conservation tillage using soil savers (SS). The plot with MB plowed was tilled to a maximum depth of 25 cm in the fall, with or without ryegrass intercropped (IC). The plot with conservation tillage using a modified seven shanks chisel was tilled to a maximum depth of 10 cm in the spring, with or without ryegrass intercropped. Water table management treatments were controlled drainage/subirrigation and free drainage. Herbicide treatment was banded at 38 cm over the seed row in plots intercropped with ryegrass and an entire area application to a monocropped plot, after planting. Thus, the area of monocropped treatments received twice the amount of herbicide compared to the intercropped treatments although the rate of application was the same.

In this study we took advantage of the metolachlor data that were generated from the methodological comparison study. Our results showed that the moldboard tillage with water table control associated with entire area herbicide treatment had the largest loss (53.72 mg/ha) of metolachlor in the surface runoff where the combination of conservation tillage, free drainage associated with entire area herbicide treatment showed that the largest loss of metolachlor in the tile drainage was 3.19 mg/ha (17 times less than the surface runoff). Our finding of this study implies that water table control is a viable technology to reduce contaminated water moving to the deeper soil zones, because the groundwater, once contaminated in the deep soil zone is far more difficult than surface water to clean up.

Herbicide Transport and Loss in Transient Runoff from an Agricultural Watershed

Agricultural activities and chemical used in crop productions are important sources of contaminants affecting the water quality of the Great Lakes. Watershed monitoring has been useful in identifying the magnitude and trend of contaminant loadings from agricultural practices. In this study we assessed the amount of losses of two herbicides and magnitude of transport, during runoff episodes after herbicide application. Runoff data from 1990 and 1991 in the Nissouri Creek agricultural watershed were studied for losses of atrazine and metolachlor. Our results indicated that majority of losses of the applied herbicides occurred in surface runoff and interflow. The combined losses in surface runoff and interflow accounted to about 75% and 65% of the total loss of atrazine and metolachlor respectively. The loss occurred within 70 days of application and during a large storm event, shortly after a herbicide application. Herbicide concentrations showed a steady disappearance with pseudo first-order half-lives of 54 days for atrazine and 50 days for metolachlor. The key point of obtaining half-lives is to estimate the time required for a herbicide to potentially reach the aquatic system after its application to the agricultural area.

Modelling and Testing of Nitrate Leaching and Phosphorus Transport in Clay Soil

In this work, we used both monitoring and modelling approaches for the evaluating the effects of a combination of water management, tillage and cropping practices on the reduction of nitrate and phosphorus pollution to surface and subsurface water sources. Measured data, the LEACHM model and a statistical additive model were used. The nitrate data (1992-1994) and phosphorus (1993-1994) data were monitored from Woodslee Experimental Farm. The nitrate data for 1992 were used to calibrate the LEACHM model. Simulations were performed for the 1993-1994 period using the calibrated parameters. The results showed that free drainage management systems would result in

high nitrate leaching. Water table control/subirrigation decreases nitrate leaching, under soil-saver tillage with intercropped practices.

The measured nitrate and phosphorus data were also utilized to test the significance of the combined management practices (tillage/crop/water) for nitrate leaching and phosphorus transport using a statistical additive model. Our results showed that water table control was significantly reducing nitrate leaching, but phosphorus losses in surface and tile drainage were not significantly influenced by the combined management practices. More than 70% of the phosphorus was transported in surface runoff in particulate form throughout the year. The greater P losses in particulate form reflect the affinity of P to clay soil.

Publications and Presentations in FY 95-96

Graham, K.N., L.P. Sarna, G.R.B. Webster, J.D. Gaynor and H.Y.F. Ng. 1995. Solid-phase microextraction of herbicide metolachlor in runoff and tile drainage water samples. *Journal of Chromatography A* 725: 129-136.

Ng, H.Y.F. 1995. The losses and transport of atrazine and metolachlor in runoff events from an agricultural watershed. Presented at Watershed Management Symposium, Burlington, Ontario, December 6-8.

Ng, H.Y.F. and S.B. Clegg. 1995. Atrazine and metolachlor losses in runoff events from an agricultural watershed: the importance of runoff components. NWRI Contribution No. 95-68.

Ng, H.Y.F. and S.B. Clegg. 1995. Atrazine and metolachlor losses in transient runoff events from an agricultural watershed. Invited paper presented at the IAWQ Symposium on Uncertainty, Risk and Transient Pollution Events, Exeter University, Exeter, UK, 26-28 July 1995.

Ng, H.Y.F., J.D. Gaynor, C.S. Tan and C.F. Drury. 1995. Dissipation and loss of atrazine and metolachlor in surface and subsurface drain water: a case study. *Water Research* 29(10): 2309-2317.

Ng, H.Y.F., J.D. Gaynor, G.R.B. Webster, D.A. Cancilla, C.S. Tan, C.F. Drury and J.R. Maguire. 1996. Metolachlor transport in surface runoff and in tile drainage during a large storm event from field plots. Presented at the 31st Central Canadian Symposium on Water Pollution Research, Burlington , Ontario, February 6-7.

Pacepavicius, G.J., D. Liu, R.J. Maguire and H. Ng. 1996. Assessment of Cyanazine Persistence in Water. *Environmental Toxicology and Water Quality: An International Journal* 11: 27-36.

Webster, G.R.B., K.N. Graham, L.P. Sarna, H.Y.F. Ng and J.D.Gaynor. 1995. SPME-GC-Ec compared with more conventional methods for metolachlor residues in agricultural runoff and tile drainage water. Presented at the XXVII Eastern Canada Pesticides Residue & Environmental Contaminants Workshop & Symposium on Environmental Behaviour of Pesticides, Sault Ste. Marie, May 25-27.

Project: **Environmental Standards and Statistics**

Study Title: **Toxicity - Organic Contaminants**

Study Leader: **K.L.E. Kaiser**

Overview

Research was completed on a survey of organic contaminants in zebra mussels (*Dreissena polymorpha*) in the lower Great Lakes and upper St. Lawrence River, and on a comparison of the different methods used to normalize contaminant residues in these organisms. Research was also completed on a survey of PCB contamination in the Cornwall/Massena area of the St. Lawrence River. Research continued on CEPA-related or other priority chemicals: Further investigations were carried on the relationships between acute toxic effects of chemicals and their structural and physico-chemical properties; and on the 'internal consistency' of environmental data published in the scientific literature. Major activities are summarized below.

A Survey of Organic Contaminants in the Lower Great Lakes - Upper St.Lawrence River

Zebra mussels (*Dreissena polymorpha*) have invaded the lower Great Lakes and St. Lawrence River system in the last several years. Their presence in water intake systems, on ship hulls and other fixed strata in the upper water column has led to severe economic repercussions as well as to changes in the food web structure. Zebra mussels are filter feeders. They accumulate contaminants from suspended particulates, primarily algae, in the water and, therefore, may be useful biomonitors. Our results show that mussels from most sites contained measurable quantities of most of the analytes. Mean concentrations were (in ng/g, whole mussel dry weight basis): 154 ΣPCB, 8.4 ΣDDT, 3.5 Σchlordane, 3.4 Σaldrin, 1.4 ΣBHC, 1.0 Σendosulfan, 0.80 mirex and 0.40 Σchlorobenzene. Concentrations varied greatly between sites, i.e., from 22 to 497 ng/g for ΣPCB and from 0.08 to 11.6 ng/g for ΣBHC, an indication that mussels are sensitive to different levels of contamination. Levels of ΣPCB and Σendosulfan were highest in mussels from the St. Lawrence River, whereas mirex was highest in those from Lake Ontario. Overall, mussels from Lake Erie were the least contaminated. These observations agree well with the spatial contaminant trends shown by other biomonitoring programs. PCB congener class profiles in zebra mussels are also typical for nearby industrial sources, e.g., mussels below an aluminum casting plant contained 55% di-, tri- and tetrachlorobiphenyls vs. 31% in those upstream.

Five different methods for expressing contaminant concentrations were investigated, i.e., wet and dry whole mussel weights, wet and dry soft tissue weights, and lipid normalized bases. The method used for normalizing the contaminant residues influenced the rankings or spatial trends. Site ranks based on residues normalized to lipid content were poorly correlated (using Kendall's *tau-b*) with ranks based on residues normalized to wet or dry whole mussel or soft tissue weights. Normalizing to soft tissue dry weight was considered to be the most reliable method. We are proposing the use of zebra mussels as biomonitors of organic contamination in the Great Lakes and recommending the use of soft tissue dry weight as basis for expressing contaminant concentrations.

Structure-Activity Relationships of Contaminants and Data Quality

In order to develop useful structure-activity relationships of chemicals (i.e., correlations between the structure and physico-chemical properties, such as partition coefficients, and their environmental fates and effects) data have to be normalized to common units of measurement. This includes both the transformation of toxicity and solubility data commonly expressed in weight per volume units to molarity-based units and, because of the large ranges of effects observed (in many cases approximately ten orders of magnitude) to a logarithmic scale. For this purpose, several years ago, a novel, computerized spreadsheet type database was developed under the trademark COMPUTOX. Using this database, we detected a variety of data inconsistencies of both recent and historical origins. These include, for example, toxicity values which exceed the solubilities of the chemicals (sometimes by as much as one thousand times) and recent data which show nineteen orders of magnitude difference between the most and least sensitive aquatic species for a certain chemical. Our research has elucidated a number of problems, including major transcription errors in some widely used databases.

Using the Microtox test system, we have also measured the acute toxicity of a large number of chemicals for which no or little other data is available. As our research indicates, there are highly significant correlations between this test and a number of other acute aquatic toxicity bioassays, such as the 96-hr fathead minnow test. The much faster and less costly Microtox test allows the estimation of novel chemicals' toxicities for those other species. Other results of this work indicate the potential usefulness of statistical methods, such as neural networks, to the analysis of structure-activity and inter-species correlations.

Publications and Presentations in FY 95-96

Comba, M.E., S. Backus, V.S. Palabrica, D. Boyter and K.L.E. Kaiser. 1995. Occurrence, Characterization and Distribution of PCB in the Cornwall/Massena Reach of the St. Lawrence River. NWRI Contribution.

Kaiser, K.L.E. 1995. Quality Assurance, Products and Services, 1995/96 Catalogue, National Water Research Institute, 48 pp.

Kaiser, K.L.E. 1995. Letter to the Editor on SAR and QSAR. *Environ. Sci.* 3:151-159.

Kaiser, K.L.E. 1995. Erroneous Data: Avenues for Detection and Prevention. *Quintessence* 1(4): 13-16.

Kaiser, K.L.E. 1996. Inter-species toxicity correlations between Microtox (*Photobacterium phosphoreum*) and several fish and other aquatic species, using the COMPUTOX database. Presented at USEPA / AAFC Environmental Fate and Effects Test Methods Workshop, Washington, DC., March 25-26.

Kaiser, K.L.E. and M.B. McKinnon. 1995. COMPUTOX Toxicity Database, version 5.0, on CD-ROM.

Kaiser, K.L.E., S.P. Niculescu and M.B. McKinnon. 1995. A qualitative approach for predicting the Microtox (*Photobacterium phosphoreum*) toxicity of nitriles and nitro compounds using neural networks. Poster presented at 2nd SETAC World Congress, Vancouver, BC, November.

Project: **Environmental Standards and Statistics**

Study Title: **External Quality Assurance and Quality Management**

Study Leader: **K. I. Aspila**

Overview

Direct and indirect support in the form of external quality assurance (QA) studies was provided to several agencies. A study was initiated to overview the delivery of quality assurance studies and the production of certified reference materials, with the objective of defining and developing the quality system and associated manuals for registration under the International Standards Organization (ISO).

Long Range Transport of Atmospheric Pollutants (LRTAP)

Two interlaboratory performance evaluation studies were conducted on softwater and rainfall. The studies were distributed to approximately 55 different laboratories in Canada and the United States. Each participant was requested to analyze up to twenty five different inorganic constituents. The results were evaluated for systematic error (laboratory bias) and all individual results that deviated significantly from target values were assigned flags. Performance of an individual laboratory was considered poor if the frequency of flagged data and frequency of biased measurements was high. Excellent performance occurred in those laboratories that had few flags and few biased measurements. Each laboratory was provided with specific performance report after completion of each study.

Canadian Association for Environmental Analytical Laboratories

Aqueous reference materials were produced and delivered to the Canadian Association for Environmental Analytical Laboratories (CAEAL). CAEAL, a not-for-profit organization, has, through the Standards Council of Canada, the authority to audit and assess the performance of Canadian laboratories and to provide accreditation and certification. In this fiscal year, samples for two large audit studies were distributed in October 1995 and in March 1996. Test materials consisted of water samples for major ions, total phosphorus, trace metals, total kjeldhal and pH for approximately 160 laboratories. The other part of the audit schedule involved 20 bioassay laboratories. These laboratories were provided toxicant solutions (1000 to 6000 ppm phenol) for their bioassay assessments for microtox, rainbow trout and *Daphnia*. In total, approximately 3700 individual test samples were prepared and delivered to the laboratories during the fiscal year.

Quality Management

Work was initiated on the development of a documented quality system for the production of our reference materials in order to comply with the ISO Guide 34 on Quality System Requirements for the Production of Reference Materials. All relevant ISO documents were acquired and valuable experience was gained by participating as a laboratory assessor reviewing quality systems in four different laboratories for the Canadian Association of Environmental Analytical Laboratories (CAEAL). We are anticipating to finalize the appropriate documentation in the next fiscal year.

Publications and Presentations in FY 1995-96

Aspila, K.I. and N. Arafat. 1995. LRTAP Interlaboroatory Study L-38 for Major Ions and Nutrients. National Water Research Institute AEPB-TN-95-01.

Aspila, K.I., K Jankovich and E. Kokotich. 1996. LRTAP Interlaboratory Study L-39 for Major Ions and Nutrients. National Water Research Institute AEPB-TN-96-01.

Project: **Environmental Standards and Statistics**

Study Title: **Trends in Central Lake Erie**

Study Leader: **H.F.H. Dobson**

Overview

Work continued on the development of a water quality atlas for Lake Erie. Long-term monitoring of nutrients and plankton in the Great Lakes is necessary for the wise management of their water quality. The Canadian government has been monitoring water quality in the Great Lakes since 1966. In order to display the information accumulated over the years and to assess long term trends and changes related to eutrophication, our atlas will report information on bathymetry and morphometry, temperature, transparency, chlorophyll *a*, dissolved oxygen, nutrients.

Publications and Presentations in FY 95-96

Dobson, H.F.H. 1995. Lakes Ontario and Erie in the 1970's and 80's - Looking at water quality data to find out the response to reduced external loading of phosphorus. Presented at the Meeting of the North American Lake Management Society (NALMS), Toronto, November 9.

Project: **Environmental Standards and Statistics**

Study Title: **Statistics Modelling of Water Quality Changes**

Study Leader: **A.H. El-Shaarawi**

Overview

Activities were focused on developing cutting edge research in environmental statistics and furthering its applications in support of Canada's water quality assessments efforts. Our research effort is concentrated on (1) modeling trends in water quality of rivers, and (2) the development of techniques for data quality assessment, both with appropriate transfer of technology within and outside Canada. A report was completed on the changes over time in the concentrations and the loads of 20 chemicals of concern in the Niagara River at the upstream station (Fort Erie) and downstream station (Niagara-on-the-Lake). The findings will be used by the Canadian and US representatives to assess the progress made towards achieving the 50% contaminant load reductions by 1997 as required under the Canada Ontario Agreement. Methodologies were developed for assessing the quality of field and analytical data sets and for merging data sets generated by several agencies.

Publications and Presentations in FY 1995-96

Arnbjerg-Nielsen, K., A.H. El-Shaarawi, H. Spliid and P. Harremoes. 1995. Modeling of Tipping Bucket Rain Gauges: Single Rain Events, Rain Series and Geographical Variation. Presented at the 6th International Conference on Environmetrics, Malaysia, December 6-9.

Elliot, J.R. and A.H. El-Shaarawi. 1995. Sediment Lead Loads in the Niagara River, 1986-1992. *J. Great Lakes Res.* 21(3): 324-332.

El-Shaarawi, A.H. 1995. Trend Detection and Estimation with Environmental Applications. *Mathematics and Computers in Simulation* 39: 441-447.

El-Shaarawi, A.H. 1995. Trends Assessment in Water Quality in the Fraser River Basin. NWRI Contribution No. 95-64.

El-Shaarawi, A.H. 1995. Handling Censored Data in Environmental Studies. Presented at the Conference on Statistics in Environmental Applications, American Statistical Association, University of Delaware, April 27-29.

El-Shaarawi, A. H. 1995. Principle Components Analysis in the Presence of Missing Data. Presented at the 4th Scandinavian Symposium on Chemometrics, Lund, Sweden, June 12-16.

El-Shaarawi, A. H. 1995. Environmental Impact Assessment. Presented at the Statistical Society of Canada Meeting, Montreal, July 12.

El-Shaarawi, A. H. 1995. Combining Environmental Information. Presented at NIWA, Hamilton, New Zeland, November 16.

El-Shaarawi, A.H. 1995. Trend Analysis. Presented at the International Congress on Modelling and Simulation, University of Newcastle, Australia, November 27-30.

El-Shaarawi, A.H. 1995. Principal Component Analysis in the Presence of Missing Data with Water Quality Applications. Presented at the 6th International Conference on Environmetrics, Maylasia, December 6-9.

El-Shaarawi, A.H. 1996. Developing a Data Quality Control System: Detecting, Locating and Identifying Causes of Variability. Presented at EMAN, Halifax, January 17-20.

Jakeman, A.J, A.H. El-Shaarawi and M. McAleer (Eds). 1995. Environmental Modelling Techniques and Applications. *Environmetrics* 6: 429-458.

Shaw, D.P. and A.H. El-Shaarawi. 1995. Patterns in Water Quality at Selected Stations in the Fraser River Basin (1985-1991). DOE FRAP 1995-20.

Project: **Environmental Standards and Statistics**

Study Title: **Organic Quality Assurance for Regional Ecosystems**

Study Leader: **Y.D. Stokker**

Overview

Five organic interlaboratory quality assurance studies were completed and a sixth is nearing completion. Research efforts continued on the monitoring and certification of the sediment reference materials for PAHs, PCBs, chlorobenzenes, trace metals, dioxins and furans. The development of new sediment reference materials certified for PCB congeners was initiated. Work also continued on the promotion of the quality assurance products and expertise. Major activities are summarized below.

Quality Assurance Studies

The provision of interlaboratory quality assurance studies for various organic parameters is a valuable and very necessary service for any laboratory involved in environmental management, monitoring and surveillance, or research. Under this study, efforts are focussed on conducting interlaboratory QA studies to ensure organic analytical data in programs such as the GLAP, FRAP and the National Dioxin QA Program, are generally reliable and of good and comparable quality. Each participating laboratory receives a summary of all interlaboratory data from which peer appraisals have been made. Precision and accuracy data are determined for each laboratory when blind duplicates and reference materials are included among the samples distributed. Thus, by providing vital information on laboratory performance, each manager has the opportunity to take corrective action to improve their laboratory measurement process. In the case of the interlaboratory studies conducted by the Canadian Environmental Association for Environmental Analytical Laboratories (CAEAL), the participants who perform well also receive a certification recognized by the Canadian environmental industry acknowledging their proficiency in the analysis of selected parameters. More importantly, assurance of data quality enables the department to provide authoritative and credible scientific advice on control and remediation strategies derived from the interpretation of scientific data.

Four interlaboratory studies were prepared in support of the CAEAL certification program for organic analyses: two studies for OCs and PCBs in water and two studies for PAHs in water.

A national dioxin interlaboratory QA study on the analysis of coplanar PCBs, dioxins and furans in fish tissue was completed. In addition to supporting a partnership agreement with Cambridge Isotope Laboratories (CIL) and Fisheries and Oceans Canada on the development of three fish reference materials, this work fulfills research needs identified by Environment Canada on the development of reference materials for toxic organics. The availability of a reference material for coplanar PCBs, the most toxic of the PCB congeners, will help ensure the reliability of data generated in this field of environmental analysis. Furthermore, the results of the interlaboratory study will enable the department to evaluate the capabilities of Canadian and American laboratories to analyze for these parameters and to assess the comparability of the data currently being generated for these compounds in support of the various research programs under Great Lakes 2000 and the Fraser River Action Plan.

An organic interlaboratory QA study on the analysis of congener PCBs in sediments was initiated. Preliminary results show that while a few laboratories have the capability for accurate and precise PCB analysis, the majority of participants demonstrated poor comparability with their peers. Possible reasons could be the wide variety of extraction methods that were employed by the participants, and the even wider range of analytical techniques that were used to quantitate the PCB congeners. The results of the study also illustrated the need for PCB congener certified reference materials (CRMs) and for establishing the comparability of calibration standards.

Reference Materials

The effectiveness of interlaboratory QA programs, intralaboratory quality control and analytical methods research is strongly dependent on the availability and use of reference materials (RMs) and certified reference materials (CRMs). Currently, there are relatively few RMs commercially available for Canadian laboratories for the in-house quality control of their environmental monitoring and assessment activities. To meet this need, research is conducted on the preparation, development and characterization of reference materials in the form of sample extracts and natural substrates such as water, sediment and fish tissue. First, homogeneity is evaluated with respect to the parameters of interest. The target value for each parameter is then established by numerous in-house analyses and is supported by the project's external round-robin studies. Lastly, each RM and CRM is periodically monitored to ensure the stability of all parameters over time. Under this study, efforts are also devoted to the development and maintenance of stocks of organic analytical reference standards, both as single component solutions and as blended mixtures. Periodic monitoring of these solutions ensures that their integrity is preserved under the conditions of their storage.

Five of the organic reference sediments were analyzed this year to verify the stability of their PAH, PCB and chlorobenzene content. To date, there have been no signs of any losses or degradation of the natural levels of these contaminants in these reference materials during storage times of up to fifteen years. Replicate analyses were also conducted on one of the inorganic reference sediments to confirm stability as well as to verify homogeneity with respect to the fourteen trace metals of interest.

Certified reference values for the 2,3,7,8-substituted chlorinated dibenzo-p-dioxins and dibenzofurans in DX-1 and DX-2 were finalized using only high resolution GC/MS congener data. This was achieved in a unique and extremely cost-effective scientific exchange of goods for services, whereby the expensive HRMS dioxin analyses of these two sediments were conducted by the client laboratories at no charge to the department, in exchange for a small quantity of the materials for their own in-house quality control.

Publications and Presentations in FY 95-96

Stokker, Y.D. and E. Kaminski. 1995. Development of the First Great Lakes Sediment Reference Materials for Chlorinated Dioxins and Furans. NWRI Contribution No. 95-60. Also presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August.

Tashiro, C., D.W. Potter, B. Sharratt, B. Yeo, B.G. Chittim and Y. Stokker. 1995. HRGC/HRMS Analysis of PCB Congeners: Method Development and Analysis of Reference Materials. Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August.

The Preparation and Validation of Check Samples for CAEAL Organic Studies C6 and C7 (Round VII: OCs, PCBs and PAHs). July 1995.

National Dioxin Interlaboratory QA Study No.6 on the Analysis of CoPlanar PCBs, Dioxins and Furans in Fish Tissue. Data Summary and Report. December 1995.

The Preparation and Validation of Check Samples for CAEAL Organic Studies C6 and C7 (Round VIII: OCs, PCBs and PAHs). February 1996.

Organic Ecosystem Interlaboratory QA Study No.7 on the Analysis of Congener PCBs in Sediments. Data Summary Report. March 1996.

Project: **Priority Substances**

Study Title: **Fate of Pesticides and Industrial Chemicals in Water**

Study Leader: **R.J. Maguire**

Overview

Research was completed on the toxicity of sediment-bound tributyltin to aquatic organisms, and on the national survey of water and sediment for organotins. The results of both studies are presently being written up. Research continues on the persistence of tributyltin in sediment cores, on the toxicity of sulfonylurea herbicides to aquatic plants, and on the occurrence of certain priority chemicals in industrialized areas (nonylphenol and ethoxylates, chlorinated paraffins, trialkyl/aryl phosphates) in collaboration with other study leaders. Major activities are summarized in other study leaders' contributions.

Publications and Presentations in FY 95-96

Chau, Y.K., R.J. Maguire, M. Brown, F. Yang and S.P. Batchelor. 1996. Butyltin compounds in the Canadian environment - a review of their occurrence since regulation of the antifouling uses of tributyltin in 1989. Presented at the Tributyltin Workshop, Sidney, B.C., Feb. 19-2

Liu, D., R.J. Maguire, G. Pacepavicius and I. Aoyama. 1995. Microbial biotransformation of metolachlor. Presented at the 7th International Symposium on Toxicity Assessment, Santiago, Chile, May 7-12.

Maguire, R.J. 1995. Distribution, transformation, fate and effects of toxic chemicals in aquatic ecosystems. Presented at the International Workshop on Aquatic Toxicology, Universiti Pertanian Malaysia, Serdang, Selangor, Malaysia, April 16-25.

Maguire, R.J. 1995. Adsorption and volatilization pathways of organic chemicals in aquatic ecosystems. Presented at the International Workshop on Aquatic Toxicology, Universiti Pertanian Malaysia, Serdang, Selangor, Malaysia, April 16-26.

Maguire, R.J. 1996. Canadian Environmental Protection Act assessment of non-pesticidal organotin compounds. Presented at the Tributyltin Workshop, Sidney, B.C., Feb. 19-20.

Maguire, R.J., J. Kochany, S.P. Batchelor and C.A. Sullivan. 1995. Sunlight photodegradation of metolachlor in water. Presented at the International Workshop on Aquatic Toxicology, Universiti Pertanian Malaysia, Serdang, Selangor, Malaysia, April 16-26.

Maguire, R.J., S.P. Batchelor and C.A. Sullivan. 1995. Reduction of the efficiency of extraction of lipophilic chemicals from fresh water by dissolved organic matter. Presented at the International Workshop on Aquatic Toxicology, Universiti Pertanian Malaysia, Serdang, Selangor, Malaysia, April 16-26.

Maguire, R.J., Y.K. Chau, M. Brown, F. Yang and S.P. Batchelor. 1995. Hazard assessment for organotin compounds in the Canadian environment. Presented at the 78th Canadian Society for Chemistry

Conference and Exhibition, Guelph, Ontario, May 28 - June 1.

Ng, H.Y.F., J.D. Gaynor, G.R.B. Webster, D.A. Cancilla, C.S. Tan and R.J. Maguire. 1996. Metolachlor transport in surface runoff and tile drainage during a large storm event from field plots. Presented at the 31st Central Canadian Symposium on Water Pollution Research, Burlington, Ontario.

Pacepavicius, G.J., D. Liu, R.J. Maguire, H. Ng, J.D. Gaynor, H. Okamura and I. Aoyama. 1996. Assessment of cyanazine persistence in water. *Environmental Toxicology and Water Quality: An International Journal* 11: 27-36.

Ridal, J., M.E. Fox, D. St. Arnaud, A. Mazumder, D. Lean and R.J. Maguire. 1995. Assessment of new solid phase extraction technologies for the analysis of organic contaminants in lake water: the influence of dissolved organic carbon on analyte recovery. Presented at the 27th Eastern Canada Pesticide Residue and Environmental Contaminants Workshop, and Symposium on Environmental Behaviour of Pesticides, Sault Ste. Marie, Ont., May 25-27.

Scott, B.F., E. Sverko and R.J. Maguire. Determination of benzothiazole and trialkylphosphates in water samples from the Great Lakes basin by gas chromatography - atomic emission spectrometry. *Water Quality Research Journal of Canada* (in press).

Sullivan, C.A., M.E. Fox and R.J. Maguire. Evaluation of the Zymark Autotrace (disk version) solid phase extraction system. Presented at the 27th Eastern Canada Pesticide Residue and Environmental Contaminants Workshop, Sault Ste. Marie, Ont., May 25-27.

Project: **Priority Substances**

Study Title: **LC-GC-MS Identification of Toxic Substances**

Study Leader: **D.T. Bennie**

Overview

Research continues in the following areas: the occurrence of nonylphenol and nonylphenol polyethoxylates in natural waters, textile mill effluent, pulp mill effluent and municipal sewage treatment plant effluent; the occurrence of trialkyl/triaryl phosphates in natural waters, textile mill effluents and municipal sewage treatment plant effluents; and the occurrence of chlorinated paraffins in natural waters in the vicinity of major cities in the Great Lakes basin and on the St. Lawrence River. Major activities are summarized below.

Occurrence of Nonylphenol and Nonylphenol Polyethoxylates in Canadian Aquatic Environment

Nonylphenol polyethoxylates (NPE_n) are nonylphenol-derived surfactants that have a myriad of industrial applications in coal processing, in latex paint formulations, as emulsifiers for greases and lubricating oils, in hospital cleaning agents and as pesticide diluents. They are not used in household consumer products in North America because of low biodegradability. The primary Canadian users of NPE_n are the textile and pulp and paper industries. Total domestic demand, in 1990, was 4.4 kt while total domestic production was 3.9 kt. Very little information exists on the concentrations of NPE_n and their more toxic degradation product, nonylphenol (NP), in the Canadian environment. NPE_n and NP are PSL2 chemicals. This study was undertaken to provide, initially, information on occurrence for the PSL2 assessment.

During 1995, samples were collected from municipal sewage treatment facilities in Southern Ontario, from streams, rivers and harbours in the Great Lakes basin and on the St. Lawrence River, and from the Yamaska River region, Quebec. Samples of primary influent, final effluent and digested sludge (if produced) were collected from plants in Hamilton, Burlington, Galt, Waterloo, Elmira, Toronto, Guelph, Niagara Falls and St. Catharines in Ontario, and from plants in Granby and Cowansville, Quebec. Effluent and digested sludge samples from major cities across Canada were also extracted and analyzed for NP/OP (OP = octylphenol) and NPE. The following tables summarize the results obtained to March 1996.

Table 1

	NP (µg/L)	OP (µg/L)	NPE 1 (µg/L)	NPE 2 (µg/L)	NPE 3 (µg/L)
Natural Waters	N.D. - 4.25	N.D. - 0.61	N.D. - 10.29	N.D. - 10.43	N.D. - 0.07
Pulp Mill Effluent	N.D. - 26.2	N.D.	N.D. - 3780	N.D. - 67.8	N.D. - 10.9
Primary Sewage Effluent	0.82 - 375	0.06 - 20.8	0.47 - 10.4	0.030 - 1.34	N.D. - 34.1
Final Sewage Effluent	N.D. - 13.2	N.D. - 0.54	0.019 - 43.4	N.D. - 32.6	N.D. - 12.3

Table 2

	NP (µg/L)	OP (µg/L)	NPE 1 (µg/L)	NPE 2 (µg/L)	NPE 3 (µg/L)
Bottom Sediment	0.17 - 72.2	0.01 - 1.78	N.D. - 38.1	N.D. - 6.02	N.D. - 25.7
Sewage Sludge	8.40 - 850	N.D. - 20.0	3.92 - 437	20.3 - 297	N.D. - 362

In natural waters, the levels of the various compounds are not very high and do not appear to be toxicologically important. The pulp mill effluent levels were mill-dependent. It should be noted that effluents from the 4 thermomechanical process mills did not have any detectable levels of nonylphenol, and the highest levels were in bleached kraft mill effluents. Thirteen mills were sampled. The sewage effluent results indicate that the highest levels of contaminants are found in primary influent samples, and in the final effluents from plants that treat textile mill discharges.

Municipal wastewater treatment plants that digest sludge by anaerobic means yielded consistently higher levels of the NP/OP/NPEs than did aerobic-digestion plants. Samples of bottom sediments from sites close to wastewater treatment plant discharges were also found to have higher NP/OP/NPE levels than other bottom sediments from rivers, creeks and harbours. The consequences of these high levels are still not yet clear, but the high level of contaminants in sewage treatment plant-generated sludge does require some research to investigate the possible effects of NP/OP/NPE when the digested sludge is sold and used as agricultural fertilizer.

Occurrence of Trialkyl/triaryl Phosphates in Aquatic Environments across Canada

Trialkyl and triaryl phosphates (TAAPs) are used extensively in industry as flame retardant plasticizers, fire retardant hydraulic fluids, lubricants, adhesives and coatings. In hydraulic fluids, they are used as replacements for polychlorinated biphenyls (PCBs). Annual global production is estimated to be approximately 77×10^6 kg. Significant quantities are released into the environment inadvertently. These chemicals have been found in surface waters, ground water and drinking water in Canada, U.S.A., Japan and Germany. As a result of their low water solubility, high lipophilicity and high adsorption to particulate matter, they have also been found in sediments and fish. TAAPs have been found to bioaccumulate in fish to levels 1000 times greater than concentrations to which they had been exposed. Delayed neurotoxic effects in cattle and chickens and some mutagenic effects have been attributed to some of these substances. Growth reduction, enlarged livers, eye disorders and spinal abnormalities in fish are also associated with low-ppb levels of TAAPs. Due to concerns about these substances, especially regarding human toxicology and economically important species (fish

and cattle), there is a need for studies on their environmental occurrence, fate and persistence.

This study is attempting to fill the need for knowledge of the environmental occurrence of these compounds. Samples of water, sediment, sewage treatment plant effluent and digested sludge were collected from various sites in Ontario and Quebec. Among these sites are rivers, creeks, harbours, lakes and municipal wastewater treatment plants. Analytical results, however, will not be available until later in the 1996/97 fiscal year.

Occurrence of Chlorinated Paraffins in Major Cities in the Great Lakes Basin and on the St. Lawrence River

Chlorinated paraffins were on the first Priority Substances List and the resulting assessment concluded that short chain chlorinated paraffins (C_{10}-C_{13}) are toxic. These substances are used as additives for flame retardants, plastics, lubricants, metal working fluids, paints, adhesives and sealers. In some applications, they are being used as substitutes for polychlorinated biphenyls (PCBs) because of their physical and chemical properties. There is very little data on environmental levels in Canada.

In 1994-95, an NWRI report (NWRI Contribution No. 95-62) was issued on the occurrence of chlorinated paraffins in the St. Lawrence River near Cornwall and this study was extended in 1995-96 to include waterways in the vicinity of Montreal, Toronto and Hamilton. Samples were collected and extracted but have not been analyzed yet. Analytical results for these samples will not be available until the 1996-97 year. It is also hoped to expand this study to include research into the levels of short chain chlorinated paraffins in Great Lakes fish.

Publications and Presentations in FY 95-96

Bennie, D.T., H.-B. Lee, C. Sullivan and T.E. Peart. 1995. Nonylphenol in Canadian aquatic environments. Presented at the 27th Eastern Canada Pesticide Residue and Environmental Contaminants Workshop, Sault Ste. Marie, Ont., May 25-27.

Parrot, J.L., P.V. Hodson, D.E. Tillitt, D.T. Bennie and M.E. Comba. 1995. SPMDs accumulate fish MFO inducers from pulp mills and oil refineries. Poster presented at the 2nd World Congress (16th Annual Meeting), Society for Environmental Toxicology and Chemistry Meeting, Vancouver, British Columbia, November 5-9.

Parrot, J.L., P.V. Hodson, D.E. Tillitt, D.T. Bennie and M.E. Comba. 1996. Accumulation of fish mixed function oxygenase (MFO) inducers by semipermeable membrane devices (SPMDs) in river water and effluents, Athabasca River, August and September 1994. Northern River Basins Study Project Report No. 83. Edmonton, Alberta.

Parrot, J.L., P.V. Hodson, D.E. Tillitt, D.T. Bennie and M.E. Comba. 1996. Semipermeable membrane devices (SPMDs) accumulate inducers of fish MFO from pulp mill and oil refinery effluents. In: Proceedings of the 22nd Annual Aquatic Toxicity Workshop: October 2-4, 1995, St. Andrews, New Brunswick, K. Haya and A.J. Niimi (eds.), *Can. Tech. Rep. Fish. Aquat. Sci.* **2093.**

Project: **Priority Substances**

Study Title: **Environmental Effects of Metals and Organometals**

Study Leader: **Y.K. Chau**

Overview

Research was completed on the national survey for organotin compounds in water and sediment, the relationship between tributyltin levels in an invertebrate and its toxicity, and the development of an analytical technique for the gasoline additive MMT (methylcyclopentadienylmanganese tricarbonyl). Major activities are summarized below.

National Survey on the Occurrence of Organotin Compounds in the Canadian Environment

The results of the 1993 and 1994 national surveys for organotin compounds in harbours, rivers and sewage treatment plants have been compiled and analyzed. The highest concentrations of tributyltin (TBT) in sediment were found in harbours, *e.g.*, Halifax (1909 ngSn/g), Saint John, N.B. (3212 ngSn/g), and Vancouver (2525 ngSn/g). Marinas in the Georgian Bay area, notably Heritage Marina in Midland Bay, also contained high concentrations of TBT (390 ng/g). Sediments in shipyards were also heavily polluted with butyltin compounds. For example, sediment in an Algoma Steel Ship slip (Sault Ste. Marie) contained 17, 45, and 195 ng/g respectively of monobutyltin (MBT), dibutyltin (DBT) and TBT. The methyltin species were generally found near industrial locations. Whether the sources were from biological activities or from industrial usage is unknown. MBT was found in all the sewage influent (1.9-20.6 μg Sn/L) and effluent (0.7-14.5 μg Sn/L) samples. In 25 of the 36 sewage samples, significantly lower concentrations of MBT were found in the effluent samples, but in no case was there total elimination of monobutyltin after the treatment processes. A report is being prepared for publication.

Contaminant / Toxicity Relationship in an Invertebrate

The aim of this study was to relate the body burden of a contaminant to toxicity, which is considered to be a more realistic approach than the conventional practice of relating ambient concentrations to toxicity. Waterborne toxicity and bioaccumulation tests were performed to estimate the level of body burden that is lethal to the test biota. Preliminary results have been obtained from experiments using *Hyalella azteca* as test biota for bioassay for butyltin toxicity. The acute toxicity (1 week LC_{50}) for TBT has been established to be 2-3 μgSn/L solution concentration, whereas tissue concentration at LC_{50} was in the range of 50-70μgSn/g dry weight. Toxic effects were evident at tissue concentration of *ca.* 30 μgSn/g dry weight. Sn(II) did not show any toxic effect on the test biota in all the experiments. Ongoing experiments include relationship of size of *Hyalella* to accumulation, and chronic toxicity of TBT. In the exposure experiments with sediments of high TBT content, the highest uptake value was from the Wye Channel, Halifax Harbour and St. John's Harbour, with uptake values in the range 2.29-2.85 μgSn/g tissue (dry weight) respectively, which were far below the toxic level. The relationship of sediment TBT concentration to uptake by *Hyalella* can be established when the sediment analysis is complete.

Methylcyclopentadienylmanganese Tricarbonyl (MMT)

MMT is used in unleaded gasoline to replace organoleads as antiknock agents, and to enhance the octane rating. The combustion residue (Mn oxides) are known to cause Parkinsonism-like effects. MMT also apparently adversely affects the emission systems of modern cars. Last year, a ban was proposed by the Minister of Environment on its use. An extremely sensitive gas chromatography - atomic emission spectrometry (GC-AED) technique has been developed for the determination of MMT in air and in soil with an absolute detection limit of 0.5 fg (0.5×10^{-15}g) expressed as Mn. Preliminary results showed that air in underground car parks and roadside dirt near gasoline stations in Ontario contain MMT.

Publications and Presentations in FY 1995-96

Chau, Y.K. 1996. Determination of MMT and alkyllead compounds in the environment by GC-AED. Presented at the Pittsburgh Conference, Chicago, March 4-8.

Chau, Y.K. and O.T.R. Kulikovsky-Cordeiro. 1995. Occurrence of nickel in the Canadian environment. *Environ. Reviews* 3: 95-120.

Chau, Y.K., F. Yang and M. Brown. 1995. Supercritical fluid extraction of butyltin compounds from sediment. *Anal. Chim. Acta* 304: 85-89.

Chau, Y.K., R.J. Maguire, M. Brown, F. Yang and S.P. Batchelor. 1996. Organotin compounds in water, sediment and biological samples in Canada. Presented at the Workshop on Organotin Compounds in the Canadian Aquatic Environment, Sidney, B.C., February 19-20.

Chau, Y.K., F. Yang and M. Brown. Determination of methylcyclopentadienylmanganese tricarbonyl (MMT) in gasoline and environmental samples by gas chromatography with helium microwave plasma atomic emission detection. *Appl. Organometal. Chem.* (in press).

Chau, Y.K., F. Yang and R.J. Maguire. Improvement of extraction recovery for the monobutyltin species from sediment. *Anal. Chim. Acta* (in press).

Fang, Y. and Y.K. Chau. 1995. Laboratory contamination associated with supercritical fluid extraction operations. *Appl. Organomet. Chem.* 9: 365.

Hempel, M., K.K. Kwan, B.J. Dutka, D. Liu and Y.K. Chau. 1995. Risk assessment on mercury contamination sites - toxicity of organic mercury compounds. *Analyst* 120: 721-724.

Kuballa, J. R.-D. Wilken, K.K. Kwan and Y.K. Chau. 1995. Speciation and genotoxicity of butyltin compounds. *Analyst* 120: 667-670.

Liu, Y., V. Lopez-Avila, M. Alcaraz, R.R. Adam, M.K. Behlke, Y.K. Chau, J.W. Cochran, D.M. Gilvydis, D. Green, L.E. Haberger, W.W. Li, B.D. Quimby, R.H. Rieck, P.C. Uden and S.A. Wise. 1995. Capillary gas chromatography-atomic emission detection method for the determination of pentylated organotin compounds: interlaboratory study. *J. Assoc. Offic. Anal. Chem. Inter.* 78: 1275-1285.

Project: **Priority Substances**

Study Title: **Water and Sediment Ecotoxicology**

Study Leader: **B.J. Dutka**

Overview

Research was completed on the relationship of sediment preservation and bioassay responses, the relationship between direct sediment bioassays and sediment extract assays, and the toxicity/genotoxicity of road runoff. In addition, the relationship of spiked sediment toxicity to pure chemical toxicity was studied and changes were followed in the toxicity of target chemicals (PSL 1 and 2) during the biodegradation. Major activities are summarized below.

Relationship between Sediment Preservation Techniques and Bioassay Responses

Complete and unequivocal preservation of samples, whether domestic wastewater, industrial wastes, natural waters or sediments for microbiological or bioassay testing, is a practical impossibility. Regardless of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques only retard chemical and biological changes that inevitably continue after sample collection. In previous studies we have evaluated the toxicant load of inlet and outlet sediments in various stormwater ponds in the Toronto area. After these studies were completed, we developed a direct sediment genotoxicity test. Because the history of the stormwater pond sediments was known, it was believed they would provide ideal genotoxicological conditions to evaluate the direct sediment genotoxicity test *vs.* the genotoxicity of an organic extract of the sediment.

Since there is a recognized problem with sediment preservation for bioassay testing, it was decided that these sediments and bioassay procedures could also be used to evaluate one of the more common sediment preservation techniques: freezing. Simple freezing and thawing over 2 two-week cycles was incorporated into the above comparison study. In this evaluation, we studied: (a) the effects of freezing and thawing on sediments as they relate to bioassay results, (b) the relative sensitivities of direct sediment bioassays and bioassays performed on sediment extracts, and (c) the relative toxicant/genotoxicant load of inlet and outlet sediments at three stormwater ponds.

The bioassay responses to stored sediments were bioassay-specific as two bioassays supposedly measuring similar effects often produced diametrically opposite results. There is a suggestion that the two-week results are as different from the original samples as they are from the four-week results. Also four-week storage results are not predictably lower or higher than original sample results. The superior sensitivity of the direct sediment SOS-Chromotest procedure over genotoxicity tests performed on sediment extracts was well illustrated in this comparison study and confirmed earlier observations made in our laboratory.

Toxicity/Genotoxicity of Highway Runoff

In the Province of Ontario, in spite of recent improvements in point source controls through programs like MISA, it is impossible in most urbanized areas to attain water quality targets and restore

beneficial uses without some control of stormwater and combined sewer overflow discharges. Highways and associated land corridors may produce significant volumes of runoff conveying a variety of contaminants. Traditionally, the design of highway drainage focused on removing runoff to ameliorate traffic safety issues. The impact of dispersed highway runoff was rarely considered. To develop some appreciation of such impacts, we conducted a preliminary study of the toxicity of highway runoff.

For this preliminary survey of toxicant and genotoxicant in highway runoff, a section of the QEW highway (Burlington Skyway) was selected. Two runoff samples were collected, one within minutes of the onset of a heavy storm and the other after approximately 15 hours of light rainfall. These samples were tested to establish the presence of toxicants using the following battery of bioassays: *Daphnia magna* acute toxicity test, reverse electron transport (RET) submitochondrial particle (SMP) assay, forward electron transport (FET) submitochondrial particle (SMP) assay, SOS-Chromotest without S9, SOS-Chromotest solid phase test, Microtox, *Panagrellus redivivus* assay, *Spirillum volutans* assay and seed germination test using Buttercrunch lettuce seeds (*Lactuca sativa*). The water samples were concentrated 10X by flash evaporation for all samples except *Daphnia magna*. Two soil samples, one from an area directly impacted by runoff water and another from a nearby field, were collected and tested for acute toxicity using DSTTP procedure and for genotoxicants using the SOS-Chromotest solid phase test.

The data from this preliminary study using concentrated and unconcentrated runoff water suggest the presence of very low concentration of acute water soluble toxicants and greater concentration of water soluble genotoxicants in all runoffs. However the solid SMP results are the most interesting. Since SMP proteins are among the most highly-conserved in nature, only insignificant changes in their structure and function are observable across evolutionary lines. Thus, a quantitative toxic response, observed utilizing SMP from beef heart, will likely be exactly duplicated by human, fish or plant SMP, which suggests that highway road runoff may be a serious pollutant.

This preliminary bioassay study of road runoff supports the suspicion that highway runoff could be hazardous to soil organisms, plant life and freshwater aquatic life, not as an acute toxicant but as a chronic toxicant and/or genotoxicant. These data suggest the need to look at differences in toxicity in soils receiving highway runoffs *vs.* soils not receiving runoff and to establish if there is a real difference in toxicant level/effect. Also, we believe it is important to establish the role that the various road surfaces play in generating toxic runoff.

Spiked Priority Chemicals in Sediments

Although biodegradability and toxicity are intimately related in affecting the fate and persistence of a chemical, the study of its environmental persistence and toxicity is far more complicated than merely determining its biodegradability and toxicity in a laboratory setting. Once introduced into the environment, virtually all chemicals are simultaneously subjected to biological and abiotic degradation. Thus, meaningful interpretation of the toxicity data is difficult, particularly when the data have to be extrapolated to natural ecosystems. The interactions between organisms and toxicants in real environment are extremely complicated. Many processes and mechanisms, such as adsorption, biodegradation, biotransformation, and synergism, could all be involved in these interactions.

A study was carried out to illustrate the difficulties and problems encountered when assessing the effect of biodegradation processes on the toxicity potential of target chemicals in sediments. We examined the relationship between aerobic and anaerobic biodegradation of two priority organic chemicals (nonylphenol [PSL2] and aniline [PSL1]) and their environmental toxicity. The chemicals

were spiked into natural polluted sediments. Changes in toxicity/genotoxicity and concentrations of the spiked chemicals were monitored over a period of six months. From our data, the following tentative conclusions can be made:

- The original sediment data showed a wide variability in toxicant distribution in the "homogenized" sediments, therefore cautioning about basing conclusions on one or two sets of measurements;

- nonylphenol levels may have been maintained by the biodegradation of another compound whose biodegradation product is nonylphenol;

- anaerobic biodegradation appears to increase nonylphenol levels while decreasing indirect acting mutagens and increasing direct acting mutagens; DSTTP toxicity decreased with increasing anaerobic biodegradation periods, thus appearing not to be affected by the two target chemical concentrations;

- the sediments were so loaded with various unknown bioavailable toxicants, and we suspect that they effectively masked the impact of the spiked chemicals through antagonistic reactions or bonding with the spiked chemicals and therefore changing their bioavailable state;

- the results from SOS Chromotest (sediment and pore water) in anaerobic spiked samples suggest that during biodegradation some direct and indirect acting mutagens are formed, in some cases temporarily;

- DSTTP, Microtox SPT, SOS Chromotest, and SOS Chromotest solid phase with S9 values shown by the spiked sediment were not any more toxic than the original sediment. These results suggest that aniline and nonylphenol spiking had no effect in these bioassays;

- the nematode test appears to be the only bioassay in which we observe an impact after the initial spiking of the sediment (both in term of % survival and % maturation). Percent maturation in both aerobic and anaerobic sediments remained low during, and were in similar ranges over the six month biodegradation period. These data suggest that the spiking of the sediment caused the formation of genotoxic activity not directly related to aniline and nonylphenol concentrations.

Publications and Presentations in FY 95-96

Aoyama, I., D. Liu and B.J. Dutka. 1995. A sequential manometric technique for assessing the toxicity of chemical mixtures. *Environ. Toxicol. Water Qual.* **10**, 151-156.

Castillo, G., M.T. Martins and B.J. Dutka. 1995. Assessment of the efficiency of drinking water treatment using the coliphage, total coliform and H_2S paper strip tests. In: Proceedings of the Water Environment Federation Symposium on Environmental Laboratories - Testing the Waters, Cincinnati, OH, Aug. 13-16.

Dutka, B.J. 1995. Investigación de tóxicos en aquas naturales y sedimentos de Maquehue y Chol-Chol. International Seminar, Temuco, Chile (Proyecto CIID: Control de la calidad del aqua, a nivel communitario (Chile/Canada):92-1058 05.

Dutka, B.J. 1996. (i) Toxicity testing for public health, (ii) Adapting toxicity tests to local conditions, and (iii) Rapid assessment: immunoassays. International Workshop on the Evaluation and Management of Toxic Substances in Surface Waters, Mexico City, February 12-16.

Dutka, B.J., G. Castillo and M.T. Martins. 1995. Control de la eficiencia del proceso de desinfeccion del agua potable, mediante ensayos simplificados y metodologia convencional. International Seminar, Temuco, Chile (Proyecto CIID: Control de la calidad del aqua, a nivel communitario (Chile/Canada):92-1058 05.

Dutka, B.J., K. Teichgräber and R. Lifshitz. 1995. A modified SOS-Chromotest procedure to test for genotoxicity and cytotoxicity in sediments directly without extraction. *Chemosphere* **31**, 3273-3289.

Dutka, B.J., K. Teichgräber and R. Lifshitz. 1995. Direct solid phase test for genotoxicity using SOS-Chromotest. Presented at the 7th International Symposium on Toxicity Assessment, Santiago, Chile, May 7-12.

Dutka, B.J., J. Marsalek, A. Jurkovic, R. McInnis and K.K. Kwan. 1995. A seasonal ecotoxicological study of stormwater ponds. *Zeitschrift Angewandte Zooloogie* **80**, 361-381.

Dutka, B.J., R. McInnis, A. Jurkovic, D. Liu and G. Castillo. 1995. Water and sediment ecotoxicity studies in Temuco and Rapel River basin. Presented at the 7th International Symposium on Toxicity Assessment, Santiago, Chile, May 7-12.

Dutka, B.J., A. Jurkovic, R. McInnis, D. Liu and J. Marsalek. 1996. Ecotoxicity of highway runoff - preliminary baseline studies. Presented at the 31st Central Canadian Symposium on Water Pollution Research, Burlington, Ontario, February 6-7.

Hempel, M., Y.K. Chau, B.J. Dutka, R. McInnis, K.K. Kwan and D. Liu. 1995. Toxicity of organomercury compounds: bioassay results as a basis for risk assessment. *Analyst* **120**: 721-724.

Kwan, K.K. and B.J. Dutka. 1995. Development of reference sediment samples for solid phase toxicity tests. NWRI Contribution No. 95-61.

Marsalek, J., B.J. Dutka, A.J. McCorquodale and K. Tsang. 1995. Microbiological pollution in the Canadian upper Great Lakes connecting channels. NWRI Contribution No. 95-55.

Project: **Priority Substances**

Study Title: **Environmental Endocrine Disrupters in Water and Sediment**

Study Leader: **K.K. Kwan**

Research was started this year on the adaptation and development of an estrogenic screening assay for environmental samples. The release of chemical compounds from industries and the use of pesticides in agriculture are common in North America. The evidence of estrogenic effects of some alkylphenol, plastic monomers and some pesticides has raised concerns about environmental contamination by these chemicals. We are interested in the use of estrogenicity bioassays to assess environmental xenobiotics and to discriminate between estrogenic and non-estrogenic chemicals. Bioassays using female rodents to monitor the increase in mitotic activity in tissues of the genital tract and fish to monitor the biological hormonal and metabolic changes after administration of chemicals have been proposed. Although these tests are reliable, they are not suitable for large-scale screening of suspected estrogenic chemicals in the laboratory. Therefore, a biologically equivalent cell line test (E-Screen) was adopted in our laboratory as an estrogenic screening test for priority chemicals and environmental samples.

The E-Screen test was first developed by Dr. A. Soto of Tufts University in Boston. The test uses the human breast estrogen-sensitive MCF_7 cells and compares the cell yield achieved after a 6-day incubation of culture in medium supplemented with 5% charcoal-dextran stripped fetal bovine serum in the presence (positive control) or absence (negative control) of estradiol and with various concentrations of the chemicals suspected of being estrogenic.

The objectives for this year were to set up a laboratory to perform the E-Screen test to screen for environmental estrogenic and anti-estrogenic chemicals; to build up a database on the priority chemicals which are relevant to CEPA, PSL1 and 2, PCPA and virtual elimination programs; and to test water and sediment collected from pristine areas to establish baseline data. We have experienced many problems in adapting the test. However, with the MCF_7 cells now under control, an estradiol dose-response study was initiated. Estradiol at concentrations of $3X10^{-8}$ to $3X10^{-14}$ M was used in these evaluations. The results are encouraging but the procedure still needs some refinement. Additional experiments on estradiol are being carried out. As soon as the estradiol dose-response study is reproducible, we will start to test pure chemicals and environmental samples.

Publications and Presentations in FY 95-96

Dutka, B.J., R. Bourbonniere, R. McInnis, K.K. Kwan and A. Jurkovic. 1995. Bioassay assessment of impacts of tar sands extraction operations. *Environ. Toxicol. Water Qual.* **10**:107-117.

Dutka, B.J., Marsalek, A. Jurkovic, R. McInnis, and K. K. Kwan. 1995. A seasonal ecotoxicological study of stormwater ponds. *Zeitchrift Angewandte Zooloogie* **80**: 361-381.

Hempel, M., Y.K. Chau, B.J. Dutka, R. McInnis, K.K. Kwan and D. Liu. 1995. Toxicity of organomercury compounds: bioassay results as a basis for risk assessment. *Analyst* **120**: 721-724.

Kuballa, J. R.-D. Wilken, E. Jantzen, K.K. Kwan and Y.K. Chau. 1995. Speciation and genotoxicity of butyltin compounds. *Analyst* **120**: 667-673.

Kwan, K.K. 1995. Direct Sediment Toxicity Testing Procedure Using Sediment-Chromotest Kit. *Environ. Toxicol Water Qual.* **9**: 193-196.

Kwan, K.K. and B.J. Dutka. 1995. Development of reference sediment samples for solid phase toxicity screening tests. NWRI Contribution No. 95-61.

Kwan, K.K. and B.J. Dutka. 1995. Comparative assessment of two solid-phase toxicity bioassays, the direct sediment toxicity testing procedure (DSTTP) and the Microtox solid-phase test (STP). *Bull. Environ. Contamin. Toxicol.* **55**:338-346.

Project: **Priority Substances**

Study Title: **Occurrence of Priority Organic Chemicals in Environmental Samples and Effluents**

Study Leader: **H.-B. Lee**

Overview

An analytical method for the determination of nitrilotriacetic (NTA), ethylenediaminetetraacetic (EDTA), and diethylenetriaminepentaacetic (DTPA) acids in sewage treatment plant and pulp mill effluents was developed. Research on the supercritical carbon dioxide extraction of trialkyl/aryl phosphates (TAPs) from sediments was completed. Work continues on the study of occurrence and degradation of 4-nonylphenol (4-NP) in environmental samples. In collaboration with the Canadian Wildlife Service (CWS), a study was initiated on the occurrence, persistence, fate and effects of acetolactate synthase (ALS) inhibitor herbicides. Major activities are summarized below.

Chelating Acids

A method for the determination of the chelating acids NTA, EDTA, and DTPA in municipal sewage treatment plant (STP) and paper mill effluents was developed. The acids were extracted by solid phase extraction cartridges packed with strong anion exchange resins and were eluted by formic acid. After conversion into their 1-propyl esters, the acids were quantified by GC/NPD and confirmed by GC/MS. The recoveries of these acids ranged from 83 to 104% in water and effluent samples fortified to levels from 1 to 1000 mg/L. All three acids were found in STP effluents, although the concentrations were relatively low for EDTA (< 100 mg/L) and DTPA (< 15 mg/L). In contrast, much higher concentrations (> 1000 mg/L) of NTA were observed for nearly all primary STP effluents. Very high levels (> 2500 mg/L) of DTPA were also found in effluents from some paper recycling mills that use this chelating acid to remove metal ions. This work presents a new and efficient method for the monitoring of potential priority substances and produces the first report for the occurrence of DTPA in the Canadian aquatic environment.

Trialkyl/aryl Phosphates

The development of a supercritical fluid extraction (SFE) method for TAPs in sediments was completed. With the exception of trimethyl and triethyl phosphates, quantitative recovery of 11 other TAPs from spiked sediments was obtained for spiking levels at 10, 1, and 0.1 mg/g. SFE of the sediments was carried out at 80°C and 5300 psi using supercritical carbon dioxide in the presence of a 1:1 mixture of water and methanol as a modifier. An octadecylsilane (ODS) trap was used for the collection of the TAPs during dynamic extraction. Extracts were quantified by GC/NPD and confirmed by GC/MS with a Mass Selective Detector. The detection limit for TAP by this method was 0.025 mg/g. This procedure has been applied to the screening of TAPs in river and lake sediments. This work provides information addressing research needs on potential priority substances.

Nonylphenol

The study on the occurrence of 4-NP, a PSL2 substance, in digested STP sludge and aquatic sediments collected across Canada was continued. With a few exceptions, the level of 4-NP in STP sludge was > 100 mg/g. In contrast, its level in aquatic sediments was generally low (< 1 mg/g). A collaborative study with B.J. Dutka on the aerobic and anaerobic degradation of 4-NP in spiked sediment was also completed. Sediment samples under the above degradation conditions were analyzed for 4-NP at various intervals. Results indicated significant degradation of 4-NP, under aerobic conditions, after an incubation period of five months. This work develops knowledge on the occurrence of 4-NP in the Canadian aquatic environment and delivers information addressing research needs on priority substances identified in CEPA's PSL2.

Acetolactate Synthase Inhibitor Herbicides

In collaboration with CWS, a study on the occurrence, persistence, fate and effects of the ALS herbicides, metsulfuron-methyl (MM), ethametsulfuron-methyl (EM) (both sulfonylurea herbicides), and imazethapyr (IZ) (an imidazolinone herbicide), was initiated. In the first phase of this work, methods development for the determination of the two sulfonylureas, MM and EM, at low nanogram levels was conducted. A GC/MS method involving the acid hydrolysis of the parent compounds followed by perfluoroacylation of the triazine moieties of the herbicides was developed and is being further validated. Supercritical carbon dioxide extraction conditions for the sulfonylureas spiked onto Celite, Empore disks, and sediments are being evaluated. Work on the determination of IZ by GC/NPD, GC/MS and HPLC as well as other potential analytical techniques for MM and EM are also being investigated. This study will extend into the next fiscal year with the collaborative determination of the toxicity of the three herbicides to non-target aquatic plants.

This study will provide information on the occurrence, persistence, fate and effects of a new class of ultra-low volume herbicide which is thought to be responsible for significant non-target crop damage as well as having great potential for damage to non-target-non-crop terrestrial and aquatic plants with consequent loss of food and habitat for wildlife.

Publications and Presentations in FY 95-96

Lee, H.-B. and D.R. Gere. 1996. Review of supercritical fluid extraction of organic contaminants in sediments. In: Manual of Physico-chemical Analysis and Bioassessment of Aquatic Sediments, A. Mudroch et al. (eds.), Lewis Publishers, New York (in press).

Lee, H.B., T.E. Peart and K.L.E. Kaiser. 1996. Determination of nitrilotriacetic, ethylenediaminetetraacetic, and diethylenetriaminepentaacetic acids in sewage treatment plants and paper mill effluents. *J. Chromatogr. A* (in press).

Niimi, A.J., H.-B. Lee and D.C.G. Muir. 1996. Environmental assessment and ecotoxicological implications of the co-elution of PCB congeners 132 and 153. *Chemosphere* (in press).

Williams, T.G., J.H. Carey, B.K. Burnison, D.G. Dixon and H.-B. Lee. 1996. Rainbow trout (*Oncorhynchus mykiss*) mixed function oxygenase responses caused by unbleached and bleached pulp mill effluents: a laboratory-based study. In: Environmental Fate and Effects of Pulp Mill Effluents, M.R. Servos et al. (eds), St. Lucie Press, Delray Beach, Florida, pp. 379-389.

Project: **Priority Substances**

Study Title: **Biodegradation of Priority Contaminants**

Study Leader: **D. Liu**

Overview

Research was completed on the degradation of cyanazine in aquatic environments, the toxicity assessment of organomercury compounds, and the study of aerobic and anaerobic biodegradation processes in sediment on the environmental toxicity of spiked priority chemicals (nonylphenol and aniline). Work continues on the volatilization of cyanazine from water, the adsorption of cyanazine and other triazine herbicides by microbial biomass/solids under anaerobic conditions, the uptake of cyanazine by natural biofilms, and the environmental persistence and biological degradation of the new antifouling compound Irgarol 1051. Major activities are summarized below.

Assessment of Cyanazine Persistence in Water

Cyanazine is an important selective herbicide used for the control of several annual grassy weeds and certain broad-leaf weeds in fields of corn, soybeans, and triazine-resistant canola. It is one of the most heavily used agricultural herbicides in Ontario. An estimated 4.2×10^3 metric tons of agricultural herbicides (active ingredients) of all types were used in Ontario in 1993. More than five percent of this total was cyanazine. Cyanazine use in Ontario declined only slightly (4%) from 222,870 kg to 213,240 kg between 1988 and 1993, while atrazine use declined drastically (41%) from 999,410 kg to 585,208 kg within the same time period. In order to make an assessment of the hazards of cyanazine use to aquatic ecosystems, more information is required on its occurrence in water, its toxicity to aquatic organisms, and its persistence and fate. There is virtually no information in the open literature on the aquatic fate and persistence of cyanazine.

This study has shown that cyanazine is a very stable compound in water. No apparent biodegradation or biotransformation of cyanazine was observed in a mixed cocktail of farmland runoff and soil leachate. In a cyclone fermentor containing a PAH-degrading bacterial culture and sewage microorganisms under aerobic conditions, and in anaerobic vials, no biodegradation was noted, even after a 195-day incubation. Using the herbicide metolachlor as a biodegradability reference compound and the white rot fungus *Phanerochaete chrysosporium* as the test organism, cyanazine was estimated to have an environmental persistence much greater than that of metolachlor. Consequently, the extensive use of cyanazine as a herbicide may have a long-lasting impact on Canadian aquatic ecosystems. Since cyanazine has a strong tendency to complex with solids, its ultimate fate in the aquatic sediment warrants further investigation.

This work fills research needs identified by the Evaluation and Interpretation Branch of Environment Canada in the possible setting of a full Canadian Water Quality Guideline for the protection of aquatic life, and by the U.S. EPA in the course of pesticide re-registration.

Toxicity Assessment of Organomercury Compounds

Mercury contamination of soil is a world-wide problem, especially in Germany where several hot spots of mercury contamination have been reported. Risk assessment of these sites must be carried out before any major cleanup operation can be planned. Using a high performance liquid chromatography - atomic fluorescence spectrometry (HPLC-AFS) technique, several organomercury compounds including methylmercury, ethylmercury, phenylmercury and some unknown organomercury species were found in soil samples collected from the site of an old mercury plant. When these organomercury compounds were tested with a battery of six short-term bioassays, the results indicated that the alkylmercury compounds were more toxic than arylmercury compounds. This was expected, because the high molecular weight of the arylmercury compounds could limit their ability to permeate through the biological membrane.

This work supports previous observations that for the toxicity of organomercury compounds, the nature of the organic portion of the molecular structures (alkyl or aryl, the degree of lipophilicity) has a profound effect on their biological activity against the test biota. The results of this work also demonstrate the usefulness of combining chemical analysis with short-term bioassays in risk assessment of contaminated sites.

Spiked Priority Chemicals in Sediments

Although biodegradability and toxicity are intimately related in affecting a chemical's fate and persistence, the study of a chemical's environmental persistence and toxicity is far more complicated than merely determining its biodegradability and toxicity in a laboratory setting. This work clearly demonstrates the problems and difficulties involved in assessing the effect of the naturally occurring biodegradation processes in sediments on the toxicity potential of certain spiked priority chemicals (nonylphenol and aniline). The results indicate that there is a wide variability in the toxicant distribution in the homogenized sediment samples, a factor that is difficult to control and that may eventually nullify efforts in the toxicity determination and chemical analysis for environmental contaminants. Another problem encountered in this study is that without a clean sediment sample as the control, it is not possible to draw a clear-cut conclusion as to the net contribution of the spiked chemicals to the observed total sediment toxicity. The sediment samples were so loaded with various unknown bioavailable toxicants that they effectively masked the impact of the spiked chemicals.

This preliminary study has clearly demonstrated that there is a need to carefully examine the environmental persistence and toxicity of priority chemicals beyond a laboratory setting. For this reason, a more rigid experiment with various controls is being planned.

Adsorption of Cyanazine and Triazine Herbicides

Most of our experiments on cyanazine have been completed in an attempt to determine whether or not adsorption was a possible mechanism for the disappearance of cyanazine observed in previous biodegradation experiments. Unanswered questions addressing the observed losses with time were investigated in order to determine whether or not the absence of cyanazine degradation products was the result of an actual degradation process (*i.e.,* short metabolite half lives or concentrations below detection limits) or the result of some sort of irreversible adsorption of the cyanazine to biomass of the biodegrading cells. The results suggested that the time-dependent irreversible adsorption of cyanazine to microbial mass/solids could have a significant impact on the fate of cyanazine in the aquatic environment. The study results provoked some interesting questions. Why do metolachlor and atrazine have little affinity for binding to the microbial mass? Atrazine and cyanazine belong to the triazine herbicides and therefore their slight difference in molecular structure is not likely responsible

for their environmental behaviour in terms of tendency for adsorption. Work will continue on this subject.

Volatilization of Cyanazine from Water and Adsorption of Cyanazine by Biofilm

A U.S. EPA study in 1988 concluded that cyanazine is not volatile, but literature data indicated this herbicide has been detected in the rain water from 11 states. Therefore, experiments were initiated to examine the volatility of cyanazine at room temperature (22-25°C) and at 35°C from water in 1-L beakers, and at 35°C from water in an 150-L indoor flume. The beaker experiment lasted for 60 days and the flume test continued for 106 days. The results indicated that, unlike metolachlor where significant losses were observed at 35°C, only minimal losses of cyanazine was observed at the elevated temperature. Apparently, only a modest amount of cyanazine in the water was taken up by the biofilm mass. Additional experiments are being carried out to find out the reasons for this discrepancy.

Environmental Persistence and Biological Degradation of Irgarol 1051

Irgarol 1051 is a new triazine antifouling agent which has been registered for use in some countries, and which may be registered in Canada. It is fairly persistent, and it has been found along some coasts in Europe. In the event that it is registered in Canada, we intend to examine its environmental occurrence, persistence and toxicity. Preliminary experiments have been initiated to determine the biodegradability of Irgarol 1051 by the white rot fungus, *Phanerochaete chrysosporium*. Appropriate agar plates containing Irgarol 1051 have been prepared, inoculated, and the degradation process is being monitored over time. In addition, a set of experiments using Hamilton Harbour water that has been spiked with Irgarol 1051 has also been set up in an attempt to gain some preliminary insight into the environmental persistence of this chemical in natural water.

Publications and Presentations in FY 95-96

Dutka, B.J., R. McInnis, A. Jurkovic, D. Liu and G. Castillo. 1995. Water and sediment ecotoxicity studies in Temuco and Rapel River basin. Presented at the 7th International Symposium on Toxicity Assessment, Santiago, Chile, May 7-12.

Dutka, B.J., A. Jurkovic, R. McInnis, D. Liu and J. Marsalek. 1996. Ecotoxicity of highway runoff: preliminary baseline studies. Presented at the 31st Central Canadian Symposium on Water Pollution Research, Burlington, Ontario, February 6-7.

Hempel, M., Y.K. Chau, B.J. Dutka, R. McInnis, K.K. Kwan and D. Liu. 1995. Toxicity of organomercury compounds: bioassay results as a basis for risk assessment. *Analyst* **120**: 721-724.

Lau, Y.L., D. Liu, G.J. Pacepavicius and R.J. Maguire. 1995. Volatilization of metolachlor from water. *J. Environ. Sci. Health B* **30**:605-620.

Liu, D. 1995. Chemical biodegradation and study methodology. In: Proceedings of the Mini-International Seminar on Ecotoxicology and Management of Chemicals, I. Aoyama (ed.), Research Institute for Bioresources, Okayama University, Kurashiki, Japan, pp. 13-17.

Liu, D., R.J. Maguire, G.J. Pacepavicius and I. Aoyama. 1995. Microbial biotransformation of metolachlor. Presented at the 7th International Symposium on Toxicity Assessment, Santiago, Chile, May 7-12.

Liu, D., I. Aoyama and B.J. Dutka. 1995. Enhancement of toxicant release from sediment by sonication and

sodium ligninsulfonate. Presented at the 7th International Symposium on Toxicity Assessment, Santiago, Chile, May 7-12.

Pacepavicius, G., D. Liu, R.J. Maguire, H. Ng, J.D. Gaynor, H. Okamura and I. Aoyama. 1996. Assessment of cyanazine persistence in water. *Environ. Toxicol. Water Qual.* 11: 27-36.

Okamura, H., L. Rong, I. Aoyama and D. Liu. 1995. Ecotoxicity assessment on the aquatic environment around Lake Kojima - Japan. Presented at the 7th International Symposium on Toxicity Assessment, Santiago, Chile, May 7-12.

Okamura, H., L. Rong, M. Omori, T. Mitsui, I. Aoyama and D. Liu. 1995. Ecotoxicity assessment of agricultural effluent and surface water during the application of paddy pesticides. Presented at the 6th International Conference on the Conservation and Management of Lakes - Kasumigaura '95, Tsuchiura, Japan, October 23-27.

Project: **Priority Substances**

Study Title: **Analysis of Priority Organic Chemicals in Aquatic Environments**

Study Leader: **F.I. Onuska**

Overview

Research was initiated on the application of a previously-developed demixing technique of two miscible solvents for extracting anilines and benzidines from water, sewage and sediment samples. Work continues occurrence of amino-PAHs in coal dust from Stelco and Dofasco coal storage facilities and on the biodegradation and analytical characterization of atropisomers of PCBs. Major activities are summarized below.

Analysis and Occurrence of Benzidine and 3,3'- Dichlorobenzidine

A method for the extraction and determination of benzidine and 3,3'-dichlorobenzidine (PSL1 chemicals) using high resolution gas chromatography with mass spectrometry was optimized at the 1 $\mu g/L$ level. It was found that HRGC/MS method requires a thick phase coating to reduce physical adsorption on the inner wall of the capillary column. The optimum film thickness was established for the above limit of detection. This detection limit, however, can be achieved only after a derivatization step using trifluoroacetic anhydride. This method is relatively time consuming due to the derivatization step and destruction of the excess of TFA reagent. For this reason, we developed a direct high performance liquid chromatography (HPLC) technique using an amperometric detector. This type of detection provides much higher sensitivity than HRGC/MS (low picogram level) when a glassy carbon electrode is employed.

A study was initiated to collect and analyze wastewater samples from the Humber River STP in Toronto. This STP was chosen because the only industry that uses 3,3'-dichlorobenzidine in Canada discharges to the Humber STP. The extraction procedure was evaluated, and the selectivity of determination of benzidines in sludges from the Humber STP and from Hamilton Harbour was tested. Preliminary results indicate the presence of low concentrations of 3,3'-dichlorobenzidine in STP influent. This work is continuing.

Chiral PCBs

The growing awareness of the importance of chirality in biochemical and biological systems and recognition that enantiomers can possess different biological activities has led to our attempts to separate atropisomers of PCBs and to investigate their biodegradability. In co-operation with the Slovak Technical University (STU) in Bratislava, we were awarded a NATO linkage grant for this study. We first evaluated the effectiveness of a commercially-available chiral capillary GC column (permethylated β-cyclodextrin stationary phase) for the resolution of PCB atropisomers. The results showed that this stationary phase is not selective enough. In conjunction with STU, 6 different stationary phases were synthesized: heptakis-(2,3-di-O-methyl-6-O TBDMS)-β-cyclodextrin; heptakis-(6-O-TBDMS-2,3-di-O-methyl)-β–cyclodextrin; heptakis-(2-O-benzyl-3-O-methyl-6-O-TBDMS)-β-cyclodextrin; permethyl-γ-cyclodextrin; perpentyl-γ-cyclodextrin; and permethyl-β-

cyclodextrin; these stationary phases were used for the preparation of fused silica columns. The approach was used to prepare a suitable column in varying proportion to the siloxane stationary phases containing various ratios of a particular cyclodextrin in OV-1701, SE-54 and SE-30 polysiloxanes using deactivated fused silica tubing. This work was performed at our laboratory in co-operation with Dr. E. Benicka and Prof. J. Krupcik. The optimized coatings allowed the separation of the individual enantiomers. Results of ensuing experiments confirmed that due to the enthalpy-entropy compensation of the particular cyclodextrin - solute interactions, the influence of the polysiloxane polarity on enantioselectivity depends upon temperature and the proportion of the cyclodextrin phase. This work will continue next fiscal year with the determination of chiral PCB congeners in environmental samples.

Publications and Presentations in FY 95-96

Krupcik J. and F.I. Onuska. 1995. On the interconversion energy barriers obtained for atropisomers of some PCBs by AM1 semi-empirical quantum chemistry method and gas chromatography on modified cyclodextrin stationary phase. *Fresenius Zeitschrift Anal. Chem.* **352**: 696-598.

Onuska, F.I. 1995. Microextraction by demixing of two miscible solvents for determination of pollutants in industrial waste water. Presented at the 6th International Conference on Separation of Ionic Solutes. Piestany Spa, Slovak Republic, May 10.

Onuska, F.I. 1995. Chiral recognition mechanisms in gas chromatography. Presented at the 78th Canadian Chemical Society for Chemistry Conference, Guelph, Ont., May 28.

Onuska, F.I. 1996. Evaluation of novel techniques for sample preparation in environmental analysis. Presented at COLACRO 6 - Latin American Congress on Chromatography, Caracas, Venezuela, January 18-24.

Onuska, F.I. and K.A. Terry. 1995. Microwave extraction in analytical chemistry of pollutants. 1. Polychlorinated biphenyls. *J. High Resolut. Chromatogr.* **18**: 417-421.

Onuska, F.I. and K.A. Terry. 1995. Microwave extraction in analytical chemistry of pollutants. 2. Chlorinated benzenes. *J. Microcolumn Sep.* **7**: 319-329.

Onuska, F.I. and K.A. Terry. 1995. Microextraction by demixing of two miscible solvents for the determination of phenol and its derivatives in water. *J. High Resolut. Chromatogr.* **18**: 564-568.

Onuska, F.I. and K.A. Terry. 1995. Microwave extraction in analytical chemistry of pollutants. Presented at the 78th Canadian Chemical Society for Chemistry Conference, Guelph, Ont., May 28.

Project: **Priority Substances**

Study Title: **Biomonitoring Techniques for Assessing Contamination and Stress in Aquatic Invertebrates**

Study Leader: **J.L. Smith**

Overview

Research continued on the development of protocols for using freshwater mussels as biomonitors for metals and organic contaminants in the St. Lawrence River, and to determine recoveries of organic contaminants from wet and freeze-dried biological tissues using Soxhlet *vs.* mechanical methods of extraction. Studies to determine the toxicity of sediments near an aluminum production plant on the St. Lawrence River, with an emphasis on fluoride, were completed. A study on the biodiversity of freshwater mussels in the lower Great Lakes and their major Canadian tributaries was initiated. Highlights of two major studies are summarized below.

Caged *vs.* Resident Mussels as Biomonitors for Metals in the St. Lawrence River

Freshwater mussels (*Elliptio complanata*) from Balsam Lake, Ontario, were caged for 12 weeks at three sites of differing pollution status in the St. Lawrence River. Upon retrieval of cages, resident mussels of the same species were also collected. Ten caged and 10 resident mussels per site, plus 10 pre-exposure animals, were individually analyzed for residues of 10 metals in their soft tissues. Caged mussels adjusted their body burdens of several metals (*e.g.*, Al, Cd and Ni) to resemble those in resident mussels from the same sites. For example, Ni increased from a pre-exposure concentration of 1.7 μg/g dry weight to 3.5-5.3 in caged *vs.* 3.5-5.0 in resident mussels. In contrast, Cr did not increase (6.4 μg/g pre-exposure *vs.* 6.3-7.9 in caged and 11.0-28.0 in resident mussels). Several other metals (*e.g.*, Fe, Zn) did not vary significantly among Balsam Lake, caged or resident mussels. Data on caged mussels suggested that differences in contamination among the three study sites were minimal and involved only three metals (Al, Cd and Cu). However, data on resident mussels showed that there were significant differences between one or more pairs of sites for 8 of the 10 tested metals. For most metals, pre-exposure and caged mussels differed in the variability of their individual body burdens, whereas caged and resident mussels were more similar. This provides further evidence that caged mussels attempted to adjust their body burdens of metals to reflect pollution conditions at the exposure sites. These results suggest that caged mussels would be less sensitive than resident mussels as biomonitors of spatial trends in metal pollution in the St. Lawrence River.

Influence of Species and Sex on Accumulation of Organic Contaminants by Mussels

Biological factors may significantly influence the accumulation of environmental contaminants by mussels, and must therefore be controlled to achieve good sensitivity and precision in "mussel watch" programs. This study examined the influence of species and sex on concentrations of organochlorine pesticides, chlorobenzenes, PCBs and PAHs in *Elliptio complanata* and *Lampsilis radiata radiata* from 12 sites on the St. Lawrence River. In contrast to earlier findings for metals, differences in bioaccumulation among the species and sexes were not significant for any organic compound. There

was, however, substantially more unexplained variation associated with data on organic contaminants than metals. Site ranks based on tissue concentrations were compared among males and females of both species for nine groups of organic compounds, and found to be significantly correlated for ΣPCBs and ΣPAHs, and also for ΣBHC except for comparisons involving female *L. r. radiata*. Ranks for Σaldrin, ΣDDT and ΣCBs agreed between male and female *E. complanata* only, and there was no agreement for Σchlordane, Σendosulfan or mirex. Lipid content is a major factor influencing the bioaccumulation of organic contaminants by organisms, and variation in lipid content is known to be a primary cause of variation in tissue residues among individuals. Lipid contents were higher and less variable in *E. complanata* than *L. r. radiata*. This may explain why male and female *E. complanata* indicated similar spatial trends for six of the nine tested compounds, whereas male and female *L. r. radiata* agreed for only two.

Based on tissue residues in female *E. complanata*, compounds of industrial origin (PCBs, PAHs, CBs) had similar spatial distributions, whereas the pesticides were generally associated with each other and best represented by ΣBHC. Mussels living downstream of known PCB sources contained more PCB congeners and higher proportions of mono- to tetrachlorobiphenyls than those living upstream, with all species and sexes clearly indicating the fresh input of PCBs to the river. These findings suggest that freshwater mussels have potential as biomonitors of organic contaminants in the St. Lawrence River. As trends were more consistent for *E. complanata*, this species would be recommended for use. Within-site variation in tissue residues was greater for organic compounds than metals and could not be systematically accounted for by species and/or sex. Sources of this variation must be identified and accounted for if mussel monitoring programs are to be successful.

Publications and Presentations in FY 95-96

Abrajano, Jr., T.A., A. Stark, L. Winsor, V. O'Malley, J. Hellou and J.L. Metcalfe-Smith. 1995. $^{13}C/^{12}C$ ratios in individual hydrocarbons as tracers of sources and pathways. Presented at the 38th conference of the International Association for Great Lakes Research, East Lansing, MI, May 28-June 1.

Hodson, P.V., J.L. Metcalfe-Smith, K.E. Holtze, K. Argudin, M. Baker and L. King. 1995. MFO induction in fish exposed to contaminated sediments from the St. Lawrence River near Massena, NY. Presented at the 22nd Annual Aquatic Toxicity Workshop, St. Andrews, NB, October 1-5.

Metcalfe-Smith and M. Villella. 1995. Organochlorine pesticides and PCBs in mussel samples collected from Environment Canada, Ontario Region's 15 routine mussel monitoring stations in 1993. Report to the Restoration Programs Division, Environmental Conservation Branch, August.

Metcalfe-Smith, J.L. and M. Villella. 1995. Influence of species and sex on concentrations of organic contaminants in freshwater mussels from the St. Lawrence River, with implications for biomonitoring programs. Presented at the 22nd Annual Aquatic Toxicity Workshop, St. Andrews, NB, October 1-5.

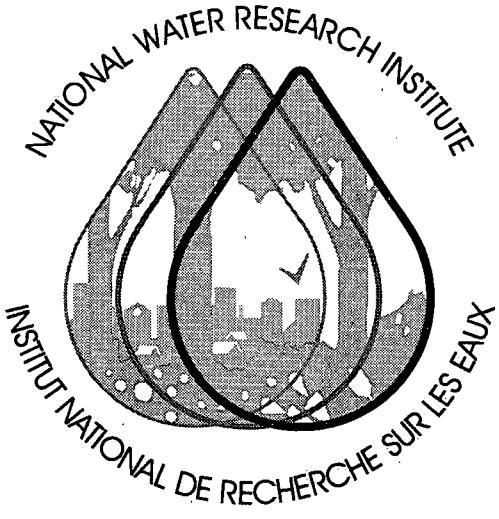
Metcalfe-Smith, J.L., G.R. Sirota, K.E. Holtze and J.J. Reid. 1996. Toxicity of sediments near an aluminum production plant on the St. Lawrence River to freshwater organisms, with emphasis on fluoride. Part I: Toxicity of sediments and elutriates, Phase I TIE, and preliminary assessment of the toxicity of sediment-associated fluoride. NWRI Contribution No. 96-172.

Metcalfe-Smith, J.L., G.R. Sirota, K.E. Holtze and J.J. Reid. 1995. Toxicity of sediments near an aluminum smelter on the St. Lawrence River to freshwater organisms. Presented at the 2nd Annual Conference on the St. Lawrence River Ecosystem, Cornwall, Ont., May 10-12.

Metcalfe-Smith, J.L., J. Biberhofer and G.M. Pieczonka. 1995. Caged *vs.* resident mussels (*Elliptio complanata*) as biomonitors of metal pollution in the St. Lawrence River. Poster presented at the Second SETAC World Congress, Vancouver, November 5-9.

Richman, L., J.L. Metcalfe-Smith, R. Santiago, J. Biberhofer and J. Anderson. 1995. Chemical characterization of the St. Lawrence River sediments in the vicinity of the oil tank storage area, Cornwall, Ontario. Presented at the 2nd Annual Conference on the St. Lawrence River Ecosystem, Cornwall, Ont., May 10-12.

Stark, A., T.A. Abrajano Jr., J. Hellou, V.P. O'Malley and J.L. Metcalfe-Smith. 1995. Source identification of polycyclic aromatic hydrocarbons in sediments from the international segment of the St. Lawrence River. Poster presented at the annual meeting of the European Association of Organic Geochemists, September 1-4, 1995, San Sebastian, Spain, and published in the proceedings: *In* J. Grimalt and C. Dessonsoro (eds) Organic Geochemistry, AIGOA, Donostia, Spain, pp.606-610.



National Water Research Institute
Environment Canada
Canada Centre for Inland Waters

P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario
Canada L7R 4A6

Institut national de recherche sur les eaux
Environnement Canada
Centre canadien des eaux intérieures

Case postale 5050
867, chemin Lakeshore
Burlington, Ontario
Canada L7R 4A6

Environment Canada Environnement Canada

Canada