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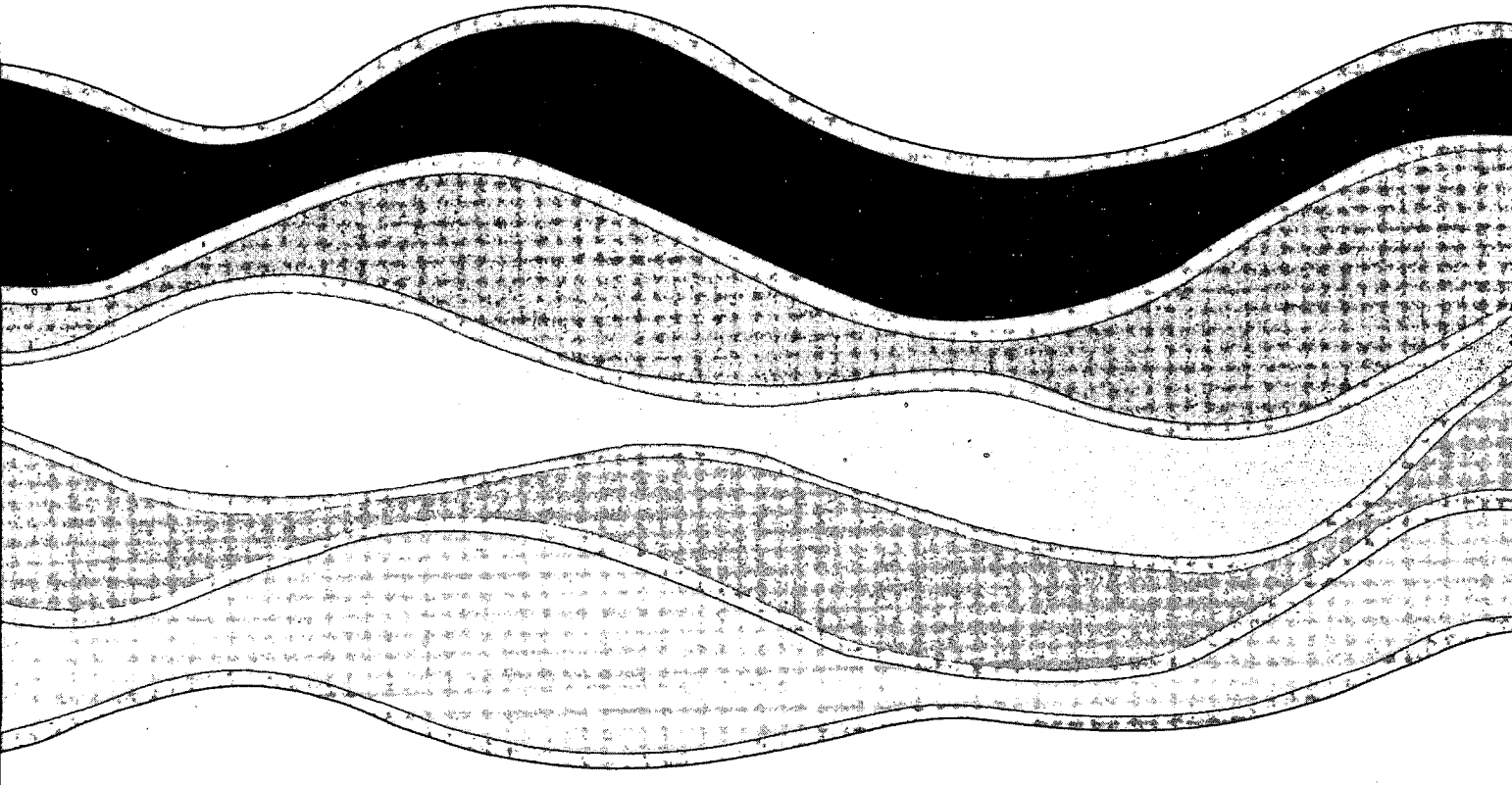

AQUATIC ECOSYSTEM PROTECTION BRANCH

RESEARCH ACTIVITIES 1994-95

NWRI CONTRIBUTION NO. 95-71

AQUATIC ECOSYSTEM PROTECTION BRANCH
RESEARCH ACTIVITIES
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National Water Research Institute
Canada Centre for Inland Water
Burlington, Ontario
Canada L7R 4A6

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MANAGEMENT PERSPECTIVE

This report presents an overview of the research carried out in 1994-95 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

Le présent rapport dresse un aperçu de la recherche effectuée en 1994-95 par la Direction de la protection de l'écosystème aquatique de l'Institut national de recherche sur les eaux. Vous y trouverez aussi plusieurs 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 servira à renseigner nos nombeux clients, visiteurs, et partenaires canadiens et étrangers.

Le Directeur de la Direction,
John Lawrence

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NWRI Contribution No. 95-71

Aquatic Ecosystem Protection Branch
Research Activities
1994-95

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Aquatic Ecosystem Protection Branch

About the Branch

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 generation of detailed knowledge and understanding of the behaviour and impacts of priority pollutants to support informed environmental decision making and sustainable management practises.

The Branch is composed of three projects:

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

Activities of the Branch include:

- identification of the patterns of behaviour of priority toxic substances in aquatic environments;
- 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 1994-95, research activities directly contributed to a number of programs related to toxic substances (*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 the St.Lawrence Vision 2000) as well as to international studies (*e.g.*, Boreal Ecosystem Atmosphere Study).

This has been a very active year for the Branch. Major accomplishments are briefly summarized below and described in greater detail in the reports of project chiefs and study leaders. The various partnerships, collaborative and cost recovery activities are also briefly summarized below.

Research Highlights

Metolachlor Research: Several reports and papers were published on metolachlor, the most heavily used agricultural pesticide in Ontario. The studies address information gaps identified in the "Canadian Water Quality Guidelines for Metolachlor" document published in 1991 under CCME. Because of deficiencies in the metolachlor toxicity database, it was only possible to establish an interim guideline for the protection of aquatic life. The recent NWRI research results will contribute to the setting of full Canadian Water Quality Guidelines for the protection of aquatic life. The results will also provide essential information for the periodic re-registration of metolachlor under the Pest Control Products Act.

St. Lawrence River RAP: Significant contributions were made in support of the St.Lawrence River Remedial Action Plan. These included: (1) Participation on the Canadian Review Panel for the Massena Superfund sites which contributed to the formulation of a Canadian position on the potential impacts of dredging contaminated sediments in the international portion of the St.Lawrence river; (2) Progress on the development of mussel monitoring protocols for the St.Lawrence River, which will include monitoring of several of the COA Tier I and Tier II substances; (3) Initiation of a study on the toxicity of sediment near an aluminum smelter plant; and (4) Report on the chemical characterization of sediment in the vicinity of an oil tank storage area.

Kingston Stormwater Pond Project: The first phase of the Kingston Stormwater Pond project was successfully completed in March 1995. The three-year project was sponsored by the Great Lakes 2000 Cleanup Fund and the Great Lakes University Research Fund. Branch staff teamed up with Queen's University scientists to demonstrate stormwater management practices and develop new remedial measures. Partnerships with municipal and provincial agencies helped to maximize effectiveness of the research and developed a general awareness of the potential benefits of stormwater quality improvements

Athabasca River: Extensive work was carried on organic contaminants in the Athabasca river system in support of NRBS. Samples from the oil sands development area and from tributaries were used to provide "fingerprint" information for tracing sources of organic contaminants to the river. The primary focus was on polynuclear aromatic hydrocarbons (PAHs) which can originate from several sources: (1) natural leaching of soils and oil sands, (2) short, medium and long

range transport of combustion products and (3) industrial effluents. Preliminary results suggest that methylated PAHs could be used as markers of industrial sources, and for differentiating them from tributary sources.

Fraser River: Work is progressing on the modelling of sediment transport in support of the Fraser River Action Plan and the Northern Rivers Basin Study. Reports were published on erosion and deposition processes of Fraser river sediments and on the effect of pulp mill effluent on the transport of suspended sediments in the Athabasca River.

Ecotoxicology: A major ecotoxicity handbook was published. The handbook contains toxicity results obtained with the Microtox® test on more than 1,200 chemicals. A licensing agreement has been signed with Microbics Corporation for the worldwide distribution of the COMPUTOX™ toxicity database. The database covers over 2,300 chemical compounds and is intended for desktop computer use.

Non-Point Source Pollution: At least 8 refereed papers were published on nonpoint source pollution from urban drainage; topics studied included methods for estimating annual loadings, methods for the control of contaminants, ecotoxicology and monitoring of stormwater ponds.

Point-Source Pollution: At least 8 papers or reports were produced on the occurrence, persistence, degradation, toxicity and/or speciation of chemicals, *e.g.*, quinoline, copper-8-quinolinate, PAHs, organotin, butyltin compounds in Severn Sound, PCBs and chlorinated pesticides in fish from the Yamaska River, and particle-associated PCBs in Lake Ontario.

Partnerships, Collaboration & International Activities

Many of the research activities outlined above are 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 1994-95.

Federal Policy on the Management of Toxic Substances : In collaboration with representatives from EPS, CWS, AES and DFO,

four AEPB staff played a significant role in an *ad hoc* Science Group on Criteria. The Science Group was responsible for developing persistence and bioaccumulation criteria for the selection of substances for virtual elimination in support of the Federal Toxic Substances Management Policy.

University Collaboration: AEPB staff worked in close collaboration with researchers at Queen's University (on contaminant removal by stormwater ponds); at McMaster University (on toxic loadings of urban runoff; marine snow and flocs characterization); and at the University of Waterloo (on migration pathways of PAHs in urban areas).

International Collaboration: During 1994-95, the Branch hosted visiting research scientists from China, Japan, Slovakia, Germany, the Netherlands and Italy. The visitors spent periods of anywhere from a few weeks to several months, in order to do collaborative research with AEPB staff.

International Conference: Two AEPB research scientists co-chaired the Fifth International Conference on Statistical Methods for Environmental Sciences held at NWRI, August 12-15, 1994. Five hundred scientists from 40 countries attended and presented over 250 papers on various aspects of environmental research and policy issues, both on a regional and global scale.

International Standards Organization: The Branch Director co-chaired the 16th Meeting of the International Standards Organization (ISO) Technical Committee 147 on Water Quality held in Vancouver, October 17-22, 1994. The meeting attracted 110 participants from government, academia and industry sectors; 18 countries were represented.

Cost Recovery Activities

Much of the Branch's expertise and facilities are also accessible to clients outside of the Department, on a cost recovery basis. Cost-recovery activities are mainly 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, organization of interlaboratory comparison studies, assessment of laboratory

performance, and the provision of reference materials (RMs) or certified reference materials (CRMs). Major clients for 1994-95 were the Canadian Association for Environmental Laboratories (CAEAL), the US Environmental Protection Agency, Health Canada, the British Columbia Ministry of Environment, Lands and Parks, and the Mine Environment Neutral Drainage (MEND) program.

***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. During the last fiscal year, six private Canadian companies, one American company and another government agency have used the facilities and/or consulted with the professional staff. These activities included hydraulics model testing, snow loading testing on a structure, and reservoir flow model testing. The laboratory was also used as a research facility backdrop for a major motion picture.

National Calibration Service: The principal function of the service is to maintain, repair, calibrate and manage an inventory of approximately 500 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. In the past year, our clients included hydro-electric companies, provincial and municipal agencies, universities and the private sector.

Priority Substances Project

R.J. Maguire, ***Project chief***

About the Project

Research in this project is done on the hazards of toxic chemicals in aquatic environments. The hazard posed by a chemical to an organism in water or sediment depends upon its toxicity, its concentration and its persistence. Research is performed on the occurrence, persistence and fate of chemicals, biomonitoring and effects on aquatic organisms, communities and ecosystems. Chemicals investigated are chosen from priority lists of the Canadian Environmental Protection Act and the Pest Control Products Act. Research highlights for 1994-95 are summarized below.

PCBs and Chlorinated Pesticides in Fish from the Yamaska River Basin

The Yamaska River has had poor water quality for many years. In 1985, an intensive study of the occurrence, persistence, fate and effects of industrial chemicals and pesticides in the basin was initiated. Part of this study was an investigation of the occurrence of these compounds in bottom-feeding fish. Fish from the mouths of the Yamaska River and its major tributary, the Noire River, were analyzed for residues of organochlorine pesticides and PCB congeners in liver, spleen, gonad, kidney, gall bladder, visceral fat and dorsal muscle. Significant quantities of target chemicals were found in the basic extracts as well as the acidic extracts of these fish tissues, suggesting that acidic digestion followed by saponification and extraction with an organic solvent may provide a more complete recovery of organic contaminants residues from biological tissues than conventional techniques. Residues were highest and least variable in fat, therefore this tissue was used to compare patterns of contamination between sites. Fish from the Noire River contained 6X as much ΣDDT and 3X as much ΣPCBs in their fat than fish from the Yamaska River (2800 vs. 440 ng/g and 1700 vs. 500 ng/g wet weight, respectively), but no differences between sites were observed for dieldrin, lindane or heptachlor epoxide. Noire River fish exhibited a less degraded pattern of PCB contamination, with proportionately more penta- (15 % vs. 4 %) and less hexa- and heptachlorobiphenyls (70 % vs. 81 %) plus nine more

congeners in their fat. They also contained a higher proportion of the toxic congeners (28% vs. 17%), had lower lipid contents and were in poorer condition. Thus, further investigation of the sources and effects of persistent organic contaminants in the Noire River basin may be warranted. This is the final report on the Yamaska River study.

Biodegradation of Metolachlor by Bacterial and Fungal Cells

Metolachlor is an important selective herbicide used for the control of several annual grassy weeds and certain broad-leaf weeds in corn, soybean, peanut, and other crops. It is the most heavily used agricultural pesticide in Ontario. An estimated 7.2×10^3 metric tons of agricultural pesticides (active ingredient) of all types were used in Ontario in 1988. Twenty-four percent of this total was metolachlor (1.7×10^3 metric tons). Metolachlor use in Ontario more than doubled from 1983 to 1988, during which period the related herbicide alachlor was withdrawn from the Canadian market. In order that an assessment can be made of the hazards of metolachlor 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 relatively little information in the open literature on the aquatic fate and persistence of metolachlor. This study was undertaken primarily to determine the biological degradation of metolachlor, the products of biodegradation, and the persistence of metolachlor in the aquatic environment.

This work showed that metolachlor was very stable in natural waters. No apparent biodegradation or biotransformation of metolachlor in the three test lake waters (Blue Chalk Lake, Gull Feather Lake, and Moot Lake) was observed, even after a 170-day incubation in the cyclone fermentor. Using a PAH-degrading bacterial culture as the test organism, metolachlor was judged to have an environmental persistence much greater than medium molecular weight PAHs. Only the white rot fungus *Phanerochaete chrysosporium* was found to be capable of biotransforming metolachlor. Based on the three identified metabolites, a tentative metabolic pathway of metolachlor biotransformation by *P. chrysosporium* was proposed. The pathway involved various processes including demethylation, hydroxylation, and hydrolytic dechlorination. In summary, the extensive use of metolachlor as a pesticide may have a long-lasting impact on the Canadian aquatic ecosystem.

This work fills research needs identified by the Ecosystem

Interpretation Branch of Environment Canada in the possible setting of a full Canadian Water Quality Guideline for metolachlor for the protection of aquatic life, and by the U.S. EPA in the course of pesticide re-registration.

Supercritical Fluid Extraction (SFE) of PCBs in Fish Tissues

Conventional solvent extraction of fish tissues for the determination of PCBs is a proven technique that is still practised in most laboratories. However, this method is slow, consumes a large amount of solvent and, because of the coextracted lipids, requires a lengthy cleanup. Typically, the minimum sample turn-around time is two days and it uses up to one litre of solvent per sample. We have shown that PCBs in fish tissues were quantitatively extracted by unmodified supercritical carbon dioxide at 100°C and 5000 psi pressure in less than 40 min. Fish lipids were selectively retained by activated alumina incorporated with the sample during the extraction step. The lipid content in SFE extracts was typically less than 0.5 % by weight and was removed by a Florisil cleanup. This technique eliminates the need of chlorinated solvent which is usually required in the gel permeation cleanup for the lipid removal in Soxhlet extracts. This method was also applied to the determination of hexachlorobenzene, *p,p'*-DDE and mirex, three commonly found organochlorines in fish.

This work presents a more time-efficient alternative to existing technology in which the extraction can be automated. It is also a "Green" method as it virtually eliminates the use of solvents.

Occurrence of Nonylphenol in the Canadian Aquatic Environment

Alkylphenol polyethoxylates are the most widely used nonionic surfactants in Canada. Because of slow biodegradability, nonylphenol polyethoxylates have been discontinued from use in consumer products, such as household laundry detergents, in North America. They are used for a myriad of industrial applications in coal processing, latex paint formulations, emulsifiers for greases and lubricating oils, hospital cleaning agents and as pesticide diluents. The primary Canadian users of nonylphenol polyethoxylates 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. There are three Canadian manufacturers of NPE_n with a combined total capacity for production of 17.0 kt. These facilities are located in Ontario.

Nonylphenol is a candidate chemical for CEPA-PSL2. In order to make an assessment of the possible hazards that this group of compounds might present in aquatic environments, more information is required on its occurrence in Canada, its toxicity to Canadian aquatic organisms and its persistence and fate. Very little data exist on the concentrations of NP and NPE_n in the environment in Canada. Nonylphenol polyethoxylates have been detected in the final effluents from three textile mills in Atlantic Canada and there are unpublished reports of its presence in final effluents of two Ontario pulp mills. There are some data available detailing the levels of alkylphenol polyethoxylates in water and sediments from 30 U.S. rivers, indicating that 60 to 75% of the river water samples had nonylphenol and nonylphenolethoxylate levels below the reported detection limits of 0.1 ppb (for NP, NPE_1 and NPE_2). Most comprehensive data sets on this subject originate in Europe.

During the summer of 1994, a preliminary survey was carried out for nonylphenol in several harbours and rivers draining into the Great Lakes. Nonylphenol was found in the range of <0.01 ppb to ca. 0.3 ppb in these natural waters. Octylphenol was also found in the range of <0.01 ppb to 0.08 ppb in the same samples. Later in the year, a sampling program at several sewage treatment plants within a 60 km radius of Burlington was initiated. Results from sewage plant influent are in the range of 0.8 ppb to 5.5 ppb while final effluents have concentrations of 0.4 ppb to 3.6 ppb. A trend has emerged at all facilities sampled except one - the influent concentration of NP is higher than the final effluent concentration. These concentrations are considerably less than the acute toxicity levels in the literature for freshwater invertebrates, fish and algae but appear to be on the threshold for chronic toxicity in mysid shrimp and fathead minnow embryos, larvae and juveniles. The final effluent of ten Canadian pulp mills was also analyzed. Nonylphenol concentrations of 1.1 ppb to 26 ppb were found in the final effluents of six of these mills.

LC-GC-MS Identification of Toxic Substances

D.T. Bennie, *Study Leader*

Overview

Research was initiated to study the occurrence of potential PSL-2 substances in aquatic environments across Canada. One group of compounds with which this study was concerned was nonylphenol (NP) and nonylphenol polyethoxylates (NPE_n) and their occurrence in pulp mill effluents and aquatic environments. Key findings are summarized below.

Background Information

Alkylphenol polyethoxylates are the most widely used nonionic surfactants in Canada. Because of slow biodegradability, nonylphenol polyethoxylates have been discontinued from use in consumer products, such as household laundry detergents, in North America. They are used for a myriad of industrial applications in coal processing, latex paint formulations, emulsifiers for greases and lubricating oils, hospital cleaning agents and as pesticide diluents. The primary Canadian users of nonylphenol polyethoxylates 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. There are three Canadian manufacturers of NPE_n with a combined total capacity for production of 17.0 kt. These facilities are located in Ontario.

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Occurrence of Nonylphenol in Canadian Aquatic Environments

During the summer of 1994, an extensive literature search was completed as was a preliminary survey of several harbours and rivers draining into the Great Lakes. Nonylphenol was found in the range of <0.01 ppb to 0.3 ppb in these natural waters. Octylphenol was also found in the range of <0.01 ppb to 0.08 ppb in the same samples. Later in the year, a sampling program at several sewage treatment plants within a 60 km radius of Burlington was initiated. Results from sewage plant influent are in the range of 0.8 ppb to 5.5 ppb while final effluents have concentrations of 0.4 ppb to 3.6 ppb. A trend has emerged at all facilities sampled except one - the influent concentration of NP is higher than the final effluent concentration. These concentrations are considerably less than the acute toxicity levels in the literature for freshwater invertebrates, fish and algae but appear to be on the threshold for chronic toxicity in mysid shrimp and fathead minnow embryos, larvae and juveniles. The final effluent of ten Canadian pulp mills was also analyzed. Nonylphenol concentrations of 1.1 ppb to 26 ppb were found in the final effluents of six of these mills.

Environmental Effects of Metals and Organometals

Y.K. Chau, ***Study Leader***

Overview

Significant improvements were made to the analytical methods for the speciation of organotins. The national survey of organotins is progressing. Experiments were carried out on the effects of biofilm on the fate of organotins and on the relationship between body burden of organotins in biota and its toxicity. Key findings are summarized below.

Improved Analytical Techniques for Organotin Speciation

Several significant improvements were accomplished in analytical techniques for organotin speciation. Firstly, a highly sensitive and specific gas chromatography-atomic emission spectrometry technique was developed, capable of analyzing 15 pesticidal and non-pesticidal organotin species simultaneously, with absolute detection limits of 0.5 pg. With the high excitation energy of the plasma, greatly enhanced sensitivity was achieved. The multi-channel feature of the atomic emission system further enhanced its specificity. The simultaneous use of the carbon channel and the tin channel often provides information which can differentiate the interferences due to organics which have the same retention time as the organotin species. This technique is now used in the laboratory to cover the complete range of the commonly used organotin compounds. Secondly, a supercritical fluid extraction (SFE) technique for extracting organotins from sediment was also developed. Supercritical carbon dioxide is used as the extractant, which is cleaner and faster, and is expected to significantly reduce solvent use in extractions of sediment and biological materials. By mixing a chelating agent, sodium diethyldithiocarbamate, with the sediment sample in the extraction cell, much higher recovery of the butyltin species was achieved.

Some modifications were also made in the enhancement of the extraction of the monobutyltin (MBT) species from sediment, which has historically been difficult. By using a more polar solvent,

toluene, and acetic acid in the sample digestion step, the extraction of MBT has been dramatically improved to 86%, the highest recovery so far achieved for this species. Improvement was also made in the concentration of organotin compounds from water by using C_{18} disks prior to SFE extraction. Quantitative recovery of the TBT species from water was obtained by this technique. All these improvements have been incorporated into the analytical methods for organotin species.

Occurrence of Organotin Compounds in the Canadian Environment

The results of the 1994-95 national survey of organotin compounds agreed with and confirmed the findings of the 1993-94 limited survey of harbour waters and sediment, and sewage samples. The highest concentration of butyltin compounds found was in sediment in marinas in the Georgian Bay area, notably Heritage marina in Midland Bay, with concentrations of 327, 271 and 390 ng/g of respectively MBT, DBT and TBT. Sediments in ship yards are also heavily contaminated with butyltin compounds. For example, sediment in the Algoma Steel Ship slip contained 17, 45, and 195 ng/g respectively of MBT, DBT and TBT. The methyltin species were generally found near industrial locations. Whether the sources are from biological methylation of inorganic tin or from industrial usage is not known. The analytical work is still ongoing. A full report will be written when the analysis is completed.

Influence of Biofilm on the Fate of Organotins

Biofilms are believed to be important in the removal and degradation of contaminants. A study was initiated on the fate of organotins in experimental flumes located outdoors. The biofilm growth was monitored through measurements of carbohydrate concentrations. During the course of the study, complications were encountered. Carbohydrate concentrations fluctuated during the day, suggesting interferences by other light-dependent organisms which contained carbohydrates. Another complication was the simultaneous interactions between the uptake and adsorption by bacteria, algae and particulates, as well as adsorption on container walls. The data were highly erratic. Mass balance experiments confirmed that adsorption was occurring on the glass plates, container walls, and particulate matter in the system, and that the flume was not suitable for experiments with organotin species. The study was therefore terminated, but techniques for the

estimation and quantification of biofilm growth were developed.

Contaminant/Toxicity Relationship in Invertebrates

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

Reports and Presentations

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Water and Sediment Ecotoxicology
B.J. Dutka, ***Study Leader***

Overview

Studies completed this year were on (i) the toxicity of petroleum refinery effluents, (ii) a comparison of solid phase microbial assays, macroinvertebrate assays, and *in situ* benthic community structure, (iii) the development of a direct sediment genotoxicity bioassay, (iv) the toxicity of the herbicide metolachlor to *Daphnia magna* and *Panagrellus redivivus,* and (v) the establishment of bioassay procedures for assessing hydrocarbon pollution in tropical countries.

Toxicity of Petroleum Effluent

We used a battery of toxicity tests to assess the acute toxicity, genotoxicity and chronic toxicity of effluent samples from two Ontario refineries. The test organisms included representatives of the bacterial, algal, plant, cladoceran and nematode communities. The results of this preliminary study indicated that the effluent samples had little acute toxicity to the test organisms. There were indications of some sublethal toxicity to *Ceriodaphnia dubia*, and *Panagrellus redivivus*. One of the effluents inhibited the growth of *Selenastrum capricornutum* (IC_{50} of 59.9%) and also caused a 15 percent reduction in the germination of *Lactuca sativa* (buttercrunch lettuce) seeds. The SOS-Chromotest, a commercially available test that measures the activity of a bacterial DNA repair system, detected genotoxic effects in a single effluent that had been concentrated tenfold. There was no apparent relationship between several of the chemical parameters and the observed sublethal effects. Further research is needed to establish whether or not the observed toxic effects are typical of effluents from Ontario refineries.

Microbial Assays and Benthic Invertebrate Toxicity

There have been very few comparative assessments of the relative sensitivities of microorganisms in short-term screening bioassays and

the toxicity to benthic invertebrates exposed to contaminated sediments for longer periods of time (10-28 days). In this study, the responses of four species of benthic invertebrates (*Chironomus riparius, Hyalella azteca, Hexagenia spp.* and *Tubifex tubifex*) and three microorganism bioassays (DSTTP, Microtox and ECHA biocide monitor) exposed to sediments collected from 46 nearshore sites in the Laurentian Great Lakes were compared using rank correlations.

The results indicated that the microbial screening tests, specifically the direct sediment toxicity test procedure (DSTTP) which measures growth inhibition in *E. coli*, and the solid phase Microtox test, correlate well with results from several longer term exposure tests with invertebrates. In addition, when information on the structure of the benthic invertebrate communities (Number of taxa and Number of organisms/m^2) was included in the ranking procedure, both microbial tests were strongly correlated with a decline in invertebrate taxa or abundance. The results indicate that either of these two microbial assays should be included in any "battery of tests" approach in the assessment of sediment toxicity.

Development of a Direct Sediment Genotoxicity Bioassay

A modified SOS-Chromotest bioassay using a chromogenic pad was developed to test for genotoxicity in sediments directly without extraction. This test is based on the *de novo* synthesis of ß-galactosidase enzyme by a genetically-engineered *E. coli* strain PQ37. In the bioassay, an exponential growth phase antibiotic-containing culture of the test bacterium is introduced into a series of tubes with the first tube containing 0.1 gram of sediment. Serial dilutions are then made and the tubes of sediment plus bacterial culture are incubated at 37°C for four hours, followed by placing a drop of each mixture on a chromogenic pad and incubation for 20 hours at 37°C. The solid particulates are then washed off with tap water and positive (genotoxic) activity is noted by the presence of a distinctive blue colour on the pad. The SOS-Chromotest pad procedure may be best used as a relative measure of genotoxicity by comparing results to a reference sample. In addition it can also determine sediment cytotoxicity by comparing samples spiked with a genotoxic standard (*i.e.*, 4-nitroquinoline-N-oxide). Preliminary results suggest that this new bioassay is highly sensitive, consistent and discriminating.

Toxicity of Metolachlor to Invertebrates

Research was completed to evaluate the freshwater concentrations of the herbicide metolachlor, a germination inhibitor used mainly for weed control, which would produce acute and chronic toxicity in *Daphnia magna*. Studies were carried out in hard and soft water at three trophic states: oligotrophic, mesotrophic and eutrophic. Also as part of this study, we established metolachlor concentrations which would produce acute and genotoxic effects in the soil nematode *Panagrellus redivivus*.

Daphnia magna chronic toxicity (CT_{50}) data for reproduction indicate the CT_{50} concentrations for mesotrophic water were approximately 1.14 ppm for soft water and 11.4 ppm for hard water. The four day *Panagrellus redivivus* bioassay showed that 100 ppm metolachlor produced no effect on the *Panagrellus* (100 per test) and 200 ppm started to produce a slight toxic and genotoxic effect. In this study it was found that approximately 400 ppm metolachlor was required to kill 50% of the *Panagrellus redivivus* (EC_{50} survival). These results suggest that *Panagrellus spp.* are relatively resistant to metolachlor.

Assessment of Hydrocarbon Pollution in Tropical Countries

Due to increasing concern about environmental pollution caused by the petroleum refinery industry, we were approached by the *Instituto Colombiano del Petroleo* in Bucaramanga, Colombia, to assist and guide them in setting up a national toxicity screening and monitoring program. Under the first phase of the contract, we applied our battery of tests to the liquid and sediment samples collected from Colombian sites subjected to various types of hydrocarbon pollution. A report was done on the results of our analyses on the natural and concentrated samples. Recommendations were made on which bioassays they should use, taking into consideration their preference for using bioassays with organisms that can be grown in Colombia. The results and recommendations were presented in Bucaramanga, Colombia, and the staff trained on procedures specific for their type of samples.

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Supercritical Fluid Extraction and Related Techniques

H.B. Lee, ***Study Leader***

Overview

Research on the application of supercritical fluid extraction (SFE) techniques to the determination of polychlorinated biphenyls (PCBs) in fish tissues was completed. Methods for the determination of 4-nonylphenol (NP) in sewage treatment plant (STP) effluent and sludge were developed. Work continues on the study of occurrence of NP in STP samples collected across Canada. Preliminary analytical work for the development of two sediment reference materials for the Northern River Basins Study was completed. Major findings are summarized below.

SFE of PCBs in Fish Tissues

Conventional solvent extraction of fish tissues for the determination of PCBs is a proven technique that is still practised in most laboratories. However, this method is slow, consumes a large amount of solvent and, because of the coextracted lipids, requires a lengthy cleanup. Typically, the minimum sample turn-around time is two days and it uses up to one litre of solvent per sample. We have shown that, PCBs in fish tissues were quantitatively extracted by unmodified supercritical carbon dioxide at 100°C and 5000 psi pressure in less than 40 min. Fish lipids were selectively retained by activated alumina incorporated with the sample during the extraction step. The lipid content in SFE extracts was typically less than 0.5 % by weight and was removed by a Florisil cleanup. This technique eliminates the need of chlorinated solvent which is usually required in the gel permeation cleanup for the lipid removal in Soxhlet extracts. This method was also applied to the determination of hexachlorobenzene, *p,p'*-DDE and mirex, three commonly found organochlorines in fish.

This work presents a more time-efficient alternative to existing technology in which the extraction can be automated. It is also a "Green" method as it virtually eliminates the use of solvents.

Determination of 4-Nonylphenol (NP) in STP Effluent and Sludge

NP is the persistent degradation product of nonylphenol polyethoxylates, a major class of non-ionic surfactants used in Canada. This phenol is toxic to many aquatic organisms. Recently, it was also shown to be an environmental estrogen that was linked to the feminization of male fish, resulting in the lack of reproductive success. Although the use of nonylphenol polyethoxylates in household detergents has been drastically reduced, they are still employed by the paper and textile industries. While the occurrence of NP in environmental samples has been monitored in some European countries since the early 1980's, there are very few reports of the levels of NP in the Canadian aquatic environment. Recently, we have developed a selective method for the extraction and acetylation of NP in STP effluents. Under SFE conditions, NP in sewage sludge and sediments was extracted and derivatized simultaneously. The levels of NP in the STP effluents collected in Toronto and neighbouring cities varied from 0.5 to 30 μg/L. There was a 2 to 3-fold reduction in NP levels between the primary and final effluents. In contrast, very high levels (>100 μg/g) of NP were found in the sewage sludge. These concentrations of NP are similar to those reported in Europe. A related compound, 4-*tert*-octylphenol, was also detected in these samples. Studies on the occurrence, degradation and pathways of NP in environmental samples are continuing.

This work develops knowledge on the occurrence, persistence and fate of NP in aquatic ecosystems and delivers information addressing research needs on candidate substances for CEPA-PSL2.

Development of Sediment Reference Materials

One of the major objectives in the Northern River Basins Study (NRBS) is to determine how and to what extent the aquatic ecosystem has been affected by toxic chlorinated organics derived from pulp and paper mills. These compounds are the focus of several projects and large amounts of analytical data were generated for many samples including sediments. In order to obtain reliable analytical results, various interlaboratory and intralaboratory QA/QC activities were implemented in laboratories which perform the chemical analyses. Reference materials are normally developed and used to validate analytical methods and to monitor the analytical performance. However, reference materials were either not available for organic parameters such as resin acids and chlorinated phenolics or not

suitable for the NRBS work because of very different matrices and/or levels of contaminants. In response to a request from the NRBS, the development of two sediment reference materials was initiated. Two bulk sediment samples were collected from the Athabasca and Wapiti Rivers in Alberta and they were freeze-dried and homogenized. Replicate analyses were performed on these materials for PCBs, organochlorines, PAHs, resin acids and chlorinated phenolics. Preliminary reference levels for the above organics in the samples were generated and a final report is being prepared.

Reports and Presentations

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Biodegradation of Priority Contaminants

D. Liu, *Study Leader*

Overview

Research was completed on the biodegradation of metolachlor by bacterial and fungal cells, and on the volatilization of metolachlor from water. Work continues on the biological degradation of cyanazine, and the development of integrated approaches in ecotoxicity assessment. Key findings are summarized below.

Biodegradation of Metolachlor by Bacterial and Fungal Cells

Metolachlor is an important selective herbicide used for the control of several annual grassy weeds and certain broad-leaf weeds in corn, soybean, peanut, and other crops. It is the most heavily used agricultural pesticide in Ontario. Twenty-four percent of all agricultural pesticides used in Ontario in 1988 was metolachlor (*i.e.*, 1.7×10^3 metric tons of metolachlor). Its use in Ontario more than doubled from 1983 to 1988, during which period the related herbicide alachlor was withdrawn from the Canadian market. In order that an assessment can be made of the hazards of metolachlor to aquatic ecosystems, more information is required on its occurrence in water, its toxicity to aquatic organisms, and its persistence and fate. There is relatively little information in the open literature on the aquatic fate and persistence of metolachlor. This study was undertaken primarily to determine the biological degradation of metolachlor, the products of biodegradation, and the persistence of metolachlor in the aquatic environment.

This work showed that metolachlor was very stable in natural waters. No apparent biodegradation or biotransformation of metolachlor in the three test lake waters (Blue Chalk Lake, Gull Feather Lake, and Moot Lake) was observed, even after a 170-day incubation in the cyclone fermentor. Using a PAH-degrading bacterial culture as the test organism, metolachlor was judged to have an environmental persistence much greater than medium molecular weight PAHs. Only the white rot fungus *Phanerochaete chrysosporium* was found to be

capable of biotransforming metolachlor. Based on the three identified metabolites, a tentative metabolic pathway of biotransformation by *P. chrysosporium* was proposed. The pathway involved various processes including demethylation, hydroxylation, and hydrolytic dechlorination. In summary, the extensive use of metolachlor as a pesticide may have a long-lasting impact on the Canadian aquatic ecosystem.

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

Volatilization of Metolachlor from Water

Our earlier work has shown that metolachlor is fairly stable to biological, chemical and photochemical degradation, and it is commonly assumed that volatilization of metolachlor from water is not a significant pathway because of its relatively high aqueous solubility (530 mg/L at 20°C) and low vapour pressure at 20-25°C. The volatilization of metolachlor from water was studied in the laboratory and in an outdoor open-channel experiment. As expected, volatilization was not significant at temperatures less than 25°C. However, at a temperature of 30°C or above, there was significant volatilization. Such conditions may occur in Canada in the summer in small ponds or irrigation ditches. In tropical countries, such high temperatures are common, and significant losses of metolachlor from water through volatilization can be expected. Additional experiments indicated that aeration of water significantly accelerated volatilization losses. Such air-stripping may be important in turbulent streams and rivers. These experimental results demonstrate the importance of ecosystem-specific characteristics in determining the fate and persistence of aquatic contaminants.

This work generates new knowledge about the environmental behaviour and persistence of metolachlor in the aquatic environment.

Biofilm Estimation Technique

Biofilms are very common in the aquatic environment and account for much of the biomass and microbial activity in the system. Recent studies have demonstrated that biofilms are largely responsible for the

removal and degradation of contaminants. For this reason, it is important to further our knowledge of biofilm growth. However, it is difficult to properly characterize the biofilm, because it is a complex structure composed of living microorganisms as well as inorganic and organic solids. The biochemical method developed in our laboratory is based on the direct measurement of the total carbohydrate content in the biofilm which has been developing on a mini glass slide. It is highly specific and the growth of the biofilm can be detected in one hour. This method has been used for studying the effects of flow rate on biofilm development in open channels. We are planning to use this technique to investigate the mechanism of adsorption of aquatic herbicides by natural biofilms.

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Priority Substances Project

Fate of Pesticides and Industrial Chemicals in Water

R.J. Maguire, ***Study Leader***

Overview

Research was completed on the biological degradation of metolachlor, the occurrence of PCBs and chlorinated pesticides in fish from the Yamaska River basin, Québec, the occurrence of chlorinated paraffins in the St. Lawrence River at Cornwall, and an evaluation of solid phase extraction (SPE) for model compounds in organic-free water. Work continues on the national survey for pesticidal and non-pesticidal organotin compounds, the toxicity of sediment-bound tributyltin to benthic organisms, and the occurrence of nonyl phenol and trialkyl/aryl phosphates in Canadian waters. Much of this work is described in the reports of other Priority Substances Project study leaders. Other major activities are summarized below.

PCBs and Chlorinated Pesticides in Fish from the Yamaska River

The Yamaska River has had poor water quality for many years. In 1985, an intensive study of the occurrence, persistence, fate and effects of industrial chemicals and pesticides in the basin was initiated. Part of this study was an investigation of the occurrence of these compounds in bottom-feeding fish. Fish from the mouths of the Yamaska River and its major tributary, the Noire River, were analyzed for residues of organochlorine pesticides and PCB congeners in liver, spleen, gonad, kidney, gall bladder, visceral fat and dorsal muscle. Significant quantities of target chemicals were found in the basic extracts as well as the acidic extracts of these fish tissues, suggesting that acidic digestion followed by saponification and extraction with an organic solvent may provide a more complete recovery of organic contaminants residues from biological tissues than conventional techniques.

Evaluation of SPE for Model Compounds in Organic-Free Water

This work is the first stage of the implementation of a new technology, automated solid phase extraction (SPE), for the extraction and concentration of organic contaminants from natural waters. The Zymark AutoTrace™ extractor was evaluated for the solid phase extraction (SPE) and concentration of trace organic contaminants from water. Eight organochlorine compounds of environmental interest, and covering a wide range of values of octanol-water partition coefficient (K_{ow}), were dissolved in organic-free water and extracted with the AutoTrace extractor using a variety of eluents and conditions based on a survey of the literature. The eluent giving the best recoveries was 15% diethyl ether in n-pentane. Recoveries of the six mid-range log K_{ow} analytes were satisfactory, in the range 72-91%. The recovery of the highest log K_{ow} analyte, Mirex, was only 64%. Up to about 15% of the missing Mirex could be accounted for by a combination of breakthrough and retention on the SPE disk. Recovery of the least lipophilic analyte, 1,4-dichlorobenzene, was only 31%. The missing 1,4-dichlorobenzene was not accounted for by breakthrough or retention on the SPE disk. It may have been lost through volatilization during the disk drying step or in the solvent concentration step.

Reports and Presentations

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Priority Substances Project

Extraction and Separation in Environmental Analysis

F.I. Onuska, *Study Leader*

Overview

Research was initiated on the enantiospecific determination of PCBs in collaboration with the Slovak Technical University, under the sponsorship of a NATO linkage grant. Research was completed on the isotachophoresis (ITP)-capillary zone electrophoresis (CZE) of nitrophenols in water, the extraction efficiency of chlorinated benzenes from surface water using microwave extraction, and the extraction of phenols from sludges using a solvent "demixing" technique. Major activities are summarized below.

Isotachophoresis-Capillary Zone Electrophoresis of Nitrophenols

Nitrophenols are fairly toxic micropollutants that are used in the synthesis of dyes, pharmaceutical products, fragrances, explosives and pesticides. They have been found in relatively clean environmental samples like rain, cloud and fog water, in addition to industrial effluents.

In cooperation with Dr. J. Marak of Comenius University in Bratislava, Slovak Republic, a joint project on the determination of nitrophenols in water was completed. After isotachophoretic pre-concentration and cleanup, a band containing nitrophenols preconcentrated to a few microlitres was automatically transferred into the analytical capillary column. Nitrophenols were separated by capillary zone electrophoresis in an alkaline buffer at pH 10. Resolution and selectivity of the separation were improved using modifiers. Detection limits were in the ppt range. These values could be further improved by optimizing the electrostacking of slow anionic analytes forming charged molecules only at very high pH.

Extraction of Chlorinated Benzenes from Surface Water

The efficiency of microwave extraction in the determination of low ppt concentrations of individual chlorinated benzene congeners in water samples has been demonstrated. The results of this study indicate that microwave extraction is a powerful tool for sample enrichment in ultra-trace analysis of organic pollutants in water down to the ppq level. The microwave technique can achieve results that are comparable to those obtained by liquid-liquid extraction, even with large volumes, while offering the advantages of simplicity, speed and the potential for automation. The pre-concentration factors are close to 1000, and therefore the detection limits are in the pg/L range. Our previous research in this area has shown that sediment samples can easily be extracted with this technique. Special attention should be devoted to pretreatment and derivatization possibilities that could be incorporated into a one-step methodology for polar analytes, since microwave energy speeds up reaction processes and provides more selectivity for the analysis of polar compounds.

Microextraction by Demixing for the Determination of Phenols

The solubility of analytes in water often decreases upon the addition of an inorganic salt. This salting-out phenomenon can be used advantageously in the separation of an otherwise water-miscible solvent from water if the water-miscible solvent also concentrates the analyte of interest.

A protocol was developed for determining low levels of phenol, cresols and xylenols in water. The "demixing" technique uses 2-propanol and ammonium sulphate (with a small amount of monosodium phosphate) as the extractant. It has been shown that demixing of aqueous samples with 2-propanol, salt and 2,4,6-trichloroanisole as an internal standard gave quantitative recoveries of phenol, cresols and xylenols. This procedure provides far lower detection limits than the methodology currently used by the U.S. EPA. To achieve demixing of the two phases, 37.7 g of ammonium sulphate + 6.8 g of monosodium phosphate were added to a 50 mL sample of water. After dissolving the salt, 3 mL of 2-propanol was added. The sample was mixed gently and two phases were allowed to separate, then were separated and the 2-propanol extract was dried over Na_2SO_4. Analyses using this technique can be done in less then 60 minutes, with limits of detection about 0.3 μg/L. Analyses were done using high resolution gas chromatography-mass spectrometry in selected ion monitoring mode.

The extraction method described above is comparable to, or better than, currently used methodology, while offering the advantages of simplicity, cleanliness, low cost and significant absence of interferences. The preconcentration factors obtained for a 50 mL sample are at least 400. Analytical recovery averaged yields greater than 95%.

Reports and Presentations

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Biomonitoring Techniques for Contaminants in Rivers

J.L. Smith, ***Study Leader***

Overview

Research continued on the development of protocols for the use of freshwater mussels as biomonitors for metals and organic contaminants in the St. Lawrence River, on the toxicity of sediments near an aluminum smelter on the St. Lawrence River and on the development of alternative extraction and clean-up techniques for determining residues of organic contaminants in biological samples. Studies to identify suitable biomonitoring organisms for the Niagara River, determine the occurrence of chlorinated paraffins in the St. Lawrence River near a manufacturing site in Cornwall, Ontario, evaluate zebra mussels as biomonitors for organic contaminants in the lower Great Lakes, and determine the occurrence of PCBs and chlorinated pesticides in fish from the Yamaska River basin, Québec, were completed. Highlights of several major studies are summarized below.

Environmental Occurrence of Chlorinated Paraffins

Chlorinated paraffins were on the first Priority Substances List of the Canadian Environmental Protection Act (CEPA). In Canada, these compounds are mainly used as plasticizers, high-pressure lubricants and flame retardants. Based on the information available, it was not possible to assess whether chlorinated paraffins are "toxic" as defined under Paragraph 11(a), that is, whether they have or may have an immediate or long-term harmful effect on the environment. One of the recommendations of the assessment report was to acquire additional data on levels of chlorinated paraffins in the aquatic environment around the manufacturing site. ICI Forest Products is the only producer of chlorinated paraffins in Canada, operating a plant in Cornwall, Ontario that discharges into the St. Lawrence River. The purpose of this study was to determine the occurrence of chlorinated paraffins in sediments and biota from the St. Lawrence River near the ICI plant.

Samples of sediment, native freshwater mussels, zebra mussels and

adult fish were collected from the St. Lawrence River in the vicinity of the combined Domtar/Cornwall Chemicals/ICI Forest Products outfall in Cornwall during the summer and fall of 1993. An effluent sample was collected from the ICI plant during the same period. A sample of young-of-the-year yellow perch, which had been collected immediately downstream of the combined outfall in the fall of 1992, was also obtained. All of these samples were analyzed for residues of chlorinated paraffins; for the adult fish, only the livers and fat were analyzed. To date the only sample that has been confirmed to contain chlorinated paraffins was the 24-hour composite sample of plant effluent, and the total concentration was 13 μg/L. In other countries, manufacturing and lubricant applications were found to be the two points of most concentrated release of chlorinated paraffins into the environment. Therefore, this study will be extended from the site of manufacture to major industrial areas in the Great Lakes basin where chlorinated paraffins are known to be used.

Niagara River Biomonitoring Study

A collaborative research study with MOEE's Environmental Monitoring & Reporting Branch was initiated in 1993-94. The purpose of the study was to identify suitable biomonitoring organisms for their Long-Term Sensing Sites Program. The use of caged mussels (*Elliptio complanata*) in this program had been declared unsuccessful, because these organisms accumulated levels of organic contaminants that were either undetectable or extremely variable. Samples of zebra mussels, quagga mussels, amphipods, oligochaetes, snails, crayfish, young-of-the-year spottail shiners and sediment were collected from a site on the lower Niagara River in 1993, and analyzed for Niagara River priority pollutants. Samples of caged mussels exposed for 12 week periods at the same site in the summer and fall of 1992 were analyzed for comparison. All samples were freeze-dried prior to analysis.

Results for PCBs are now available. Oligochaetes accumulated the highest concentrations of ΣPCBs (324 ng/g dry weight) and had a lipid content of 4%. Spottail shiners also accumulated high concentrations of ΣPCBs (93, 165 and 199 ng/g dry weight in three composite samples), but the data were quite variable. This may be due to the considerable variation in lipid contents among these samples (3 to 7%, dry weight basis). One sample of amphipods was analyzed, and it contained 94 ng/g ΣPCBs. Snails and crayfish accumulated concentrations ranging from 20 to 65 ng/g; snails were analyzed with their shells intact. Small zebra mussels were also analyzed with their

shells on, and were found to contain relatively low levels of ΣPCBs (8 to 18 ng/g). In other work, we determined that the shells of zebra mussels contain a negligible portion of the total body burden of organic contaminants but constitute approximately 90% of the dry whole weight. Thus, concentrations in the soft tissues would have been approximately 80 to 180 ng/g for these samples. These concentrations are comparable to levels of 39 ng/g and 171 ng/g found in the soft tissues of large zebra mussels (5% lipid) and large quagga mussels (8% lipid), respectively. The most surprising finding was that caged mussels (*E. complanata*) accumulated moderately high and very consistent concentrations of ΣPCBs. Three individual mussels exposed in July 1992 contained 97, 111 and 77 ng/g ΣPCBs, and three individuals exposed in October 1992 contained 79, 102 and 86 ng/g ΣPCBs. In previous work, MOEE's Rexdale Laboratory was unable to detect PCBs in any caged mussels from this site, using a detection limit of 20 ng/g wet weight. The soft tissues of mussels are approximately 90% moisture. Thus, if we reported our data on a wet weight basis, concentrations would have ranged from 7.1 to 11.1 ng/g. These values are well below MOEE's MRV (minimum reportable value) for ΣPCBs. These results suggest that caged mussels may, in fact, be suitable biomonitoring organisms, and that the difficulties in obtaining useful data in the past may be related to MOEE's methods of preparing and analyzing biological samples for organic contaminant residues.

Pesticides and PCBs in Yamaska River Fish

The Yamaska River has had poor water quality for many years. In 1985, an intensive study of the occurrence, persistence, fate and effects of industrial chemicals and pesticides in the basin was initiated. Part of this study was an investigation of the occurrence of these compounds in bottom-feeding fish. Fish from the Yamaska River and its major tributary, the Noire River, were analyzed for residues of organochlorine pesticides and PCB congeners in liver, spleen, gonad, kidney, gall bladder, visceral fat and dorsal muscle. Residues were highest and least variable in fat, therefore this tissue was used to compare patterns of contamination between sites. Fish from the Noire River contained 6 times as much ΣDDT and 3 times as much ΣPCBs in their fat than fish from the Yamaska River (2800 *vs.* 440 ng/g and 1700 *vs.* 500 ng/g wet weight basis, respectively), but no differences between sites were observed for dieldrin, lindane or heptachlor epoxide. Noire River fish exhibited a less degraded pattern of PCB contamination, with proportionately more penta- (15% *vs.* 4%) and less

hexa- and heptachlorobiphenyls (70% *vs.* 81%) plus nine more congeners in their fat. They also contained a higher proportion of the toxic congeners (28% *vs.* 17%), had lower lipid contents and were in poorer condition. Thus, further investigation of the sources and effects of persistent organic contaminants in the Noire River basin may be warranted.

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Contaminant Pathways & Controls Project

J. Marsalek, *Project chief*

About the Project

The main goal of this project is to develop strategies for maintaining the sustainability of large-scale aquatic ecosystems which are impacted by stresses from both point and nonpoint sources of pollution from agriculture, forestry, industry and urban developments. Knowledge generated from this research is applied in the development of water management plans for large regional ecosystems which are currently studied under the Fraser River Action Plan (FRAP), Great Lakes 2000, and the Northern Rivers Basin Study (NRBS). Research highlights for 1994-95 are summarized below.

Tracking Contaminant Sources, Pathways and Effects

The tracking of various contaminants in the Athabasca River and Lake Athabasca system helped to develop an overall understanding of contaminant sources and pathways in this system. Oil sand impacts on the Athabasca River could be traced by polynuclear aromatic hydrocarbons (PAHs) and were discernible from those of tributary sources. Impacts of bleached kraft pulp mills were tracked by odour compounds and, in the case of an existing mill, were reduced after technological process changes were implemented; contributions of a newly opened mill were hardly detectable. The history of the industrial development in this basin was reflected by contaminant distributions found in Lake Athabasca sediments. Distinct horizons with increased levels of dioxins, furans, radionuclides and arsenic corresponded to the 1960s and 1970s, and started to decline from the early 1980s on. Low-level, petroleum-related contamination from natural sources occurred over a broader time span.

Investigations of sustainable agriculture issues focused on two widely used pesticides, atrazine and metolachlor. The dissipation rates of atrazine and metolachlor were determined at both plot and watershed scales. Half-lives of atrazine in surface/subsurface runoff from Brookstone clay and Guelph loam were 27 and 42 days after

application, respectively; and for metolachlor, 20 and 52 days after application, respectively. Laboratory studies of metolachlor partitioning revealed that significant volatilization of metolachlor occurred at temperatures $\geq$ 30°C. Such conditions may occur in Canada in small ponds or irrigation ditches during the summer.

The development of adequate measurement procedures is essential for monitoring and assessing contaminant transport. Work focused on calibrations of current meters and suspended sediment samplers. For the Price current meters, an improved calibration equation, fitting extremely well the observed data, was developed. Calibrations of suspended sediment samplers (model P-63) demonstrated that individual samplers could be calibrated with a reasonable certainty. In measurements of particulate floc sizes, different results were obtained with an elutriation apparatus and the Malvern particle size analyzer. However, the comparison of data obtained yielded information on the density of flocs.

Sediment/Contaminant Interaction and Transport

Transport characteristics of fine sediments from the Athabasca River and the Fraser River were determined in the rotating flume. In the former case, the pulp mill effluent enhanced the flocculation mechanism and increased the sediment deposition rate. One of the active elements contributing to contaminant binding and flocculation are colloids which are abundant in natural systems or can be introduced into engineered systems to decontaminate water. Erosional behaviour of sediment was affected by the presence of pulp and paper effluent as well as by the duration of consolidation of fine sediment. These findings indicate that the fine sediment behaviour is site specific and requires the testing of local materials to determine their transport behaviour. This knowledge will be used in formulation of contaminant transport and bioaccumulation models for various ecosystems.

Nonpoint Source Pollution: Sources, Impacts and Controls

The first phase of a study of an on-stream stormwater pond in Kingston, Ontario was completed in cooperation with Queen's University. Observed mass balances determined removals of suspended solids, total phosphorus, nitrate, oil and grease, phenols and zinc at about 40%. Insignificant removals were observed for total dissolved solids, chloride, copper and lead. Sulphate, nitrate, ammonia and

Total Kjeldahl Nitrogen were produced in the pond through transformations. Much of the reported removal was accomplished by sedimentation, occurring at a rate of about 0.02 m/yr. Settled sediments, composing mostly silt (35%) and clay (61%), contained metals exceeding the lowest effect level of the Ontario sediment quality guidelines, defined as 16, 31 and 120 μg/g for Cu, Pb and Zn, respectively. The fate of contaminants in stormwater detention ponds was further studied in four Toronto stormwater ponds. Among heavy metals, the highest levels were found for Zn, Pb, Cu, Cd, Ni and Cr. Ammonia concentrations in the water column frequently reached and exceeded the chronic toxicity threshold of 300 μg/L.

Natural Organic Matter & Organic Contaminants in Ecosystems

R.A. Bourbonniere, ***Study Leader***

Overview

Our work is continuing on dissolved organic matter (DOM) dynamics in the northern boreal forest in support of BOREAS; on the impacts of oil sands development upon the lower Athabasca River downstream of Fort McMurray, Alberta; and on contaminant deposition and environmental change on Lake Athabasca, Great Slave Lake and Reference Lakes in support of the Northern River Basins Study (NRBS). Key findings are summarized below.

Dissolved Organic Matter Dynamics - BOREAS

Our research efforts under this study are part of the Boreal Ecosystem-Atmosphere Study (BOREAS), a joint Canada/U.S. study concerned with the interactions among the terrestrial, aquatic and atmospheric components of the boreal forest and their implications for global climate change. Both fire and beaver activity are natural disturbances that result in deforestation in boreal ecosystems. Our work examines the biogeochemical processes which occur in the burned soils and beaver ponds.

DOM geochemistry was studied in two beaver ponds near Thompson, Manitoba, throughout the ice-free season. Soil sampling in forest plots which have undergone varying degrees of recovery from fire was initiated to study leachates from soil. The soil leachate project is funded by the U.S. National Research Council to study the geochemistry of organic matter resulting from forest fires.

Seasonal changes in the character of DOM in beaver ponds are more evident in the humic acid, hydrophobic neutral and strong hydrophilic acid fractions. The overall character of DOM in pond water is similar to that of the major inflow and regional groundwater. Summer stratification, and particularly the development of an anoxic bottom layer, has a major influence on the character of the DOM pool.

Ongoing work will determine the influence of DOM character on photoproduction of CO, microbial utilization and their influence on nutrient cycling.

In conjunction with results from other researchers studying the fluxes of green house gases, our chemical and microbial characterization of DOM will support modelling work, and thus provide information on the biogeochemical processes that influence cycling of trace gases in the boreal forest biome.

Oil Sands Organic Contaminants - Athabasca River and Tributaries

This work is in collaboration with B.G. Brownlee and W.G. Booty, who are building a model for contaminant transport and degradation on the lower Athabasca River. Ancillary samples from the oil sands development area and others from tributaries are used to provide "fingerprint" information for tracing sources of organic contaminants to the river.

Extensive analysis was done on the transect samples from the Athabasca River, river mouth samples from tributaries, and effluent samples from oil sands operations collected last year. The primary focus was on polynuclear aromatic hydrocarbons (PAHs) which can originate from several sources: (1) natural leaching of soils and oil sands, (2) short, medium and long range transport of combustion products and (3) industrial effluents.

Concentrations of phenanthrene, methylated naphthalenes and pyrene, determined by fluorescence HPLC, were found to be about one to two orders of magnitude higher in industrial effluents than in tributaries or mine drainage, both during the high flow period in spring and low flow in summer. These results suggest that methylated PAHs could be used as markers of industrial sources, and for differentiating them from tributary sources. Similar work is underway to determine these same components in suspended sediments. Results on suspended sediments should indicate whether this medium is more important for transport of PAHs in the riverine environment and whether dissolved and sediment bound PAHs come from the same sources.

Depositional History of Contaminants & Natural Organics

The history of natural changes and contamination events which occur

in drainage basins are recorded in the sediments of depositional zones. The study of sediment cores in these areas can provide an understanding of recent trends in river-borne industrial and atmospherically transported contamination, a comparison of modern contaminant deposition with the magnitude of past events, the relative magnitude of natural and anthropogenic changes, and an indication of how changes in the hydraulic regime can influence the distribution of sediment-bound contaminants.

In Lake Athabasca sediments, components that are definitely tied to anthropogenic activities, appear in the 1960s and 1970s horizons, and there are some indications that they were already on the decrease in the early 1980s. This is the case for dioxins, furans, radionuclides and arsenic. All four classes of contaminants exhibit significant increases over background levels at times which are reasonable considering the multitude of possible sources. Petroleum-related contamination, as inferred by several indirect measures, has occurred over a much broader interval of time and is characterized by irregular, low amplitude peaks. Such a pattern suggests that petroleum contamination is caused by a multitude of small sources overlaid, in this area, by natural sources leaching from exposed oil sand deposits.

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Contaminant Transport in Rivers

B. Brownlee, *Study Leader*

Overview

In support of the Northern River Basins Study (NRBS), two studies were completed: a chemical/sensory study of odour compounds in the Athabasca River and a study on contaminant distribution in river bottom sediments of the basins. Work is continuing on a contaminant fate and food chain model for the Athabasca River. For the Program on Energy Research and Development (PERD) project on the lower Athabasca River, a working version of a two-dimensional contaminant model will soon be available and ecotoxicological studies are ongoing. Key findings are summarized below.

Athabasca River Odour Compound Study

At the beginning of 1993, the Athabasca River received effluents from one bleached kraft pulp mill (Mill A), three chemithermomechanical pulp and paper mills, one oil sands extraction and upgrading plant, and a number of municipal sewage treatment plants. Later in 1993, a second bleached kraft pulp mill (Mill B) was scheduled to begin operation midway along the river.

Following a preliminary study on odour compounds in the Athabasca River in 1991, a more extensive study was carried out in collaboration with the University of Alberta in 1993 and 1994 to characterize the odours in the river water. Chemical and sensory methods were used in a pre- and post-operational study for Mill B. Samples were collected by Alberta Environmental Protection during low flow under ice-covered conditions. The samples were analyzed by gas chromatography-mass spectrometry (GC-MS) after extraction by closed-loop stripping (CLS). Sensory analysis of CLS extracts was performed by olfactory gas chromatography (OGC) of CLS extracts and flavour panel analysis of river water and effluent samples.

For the pre-operational samples, all methods confirmed that compounds/odours characteristic of bleached kraft mill effluent were

detectable for more than 1000 km downstream from Mill A and that this effluent was the major source of odour to the Athabasca River. Post-operational samples indicated a decrease in the contribution of Mill A effluent on the odour of the river water compared with the pre-operational survey. The observed decrease is accounted for by process changes, *i.e.*, 100% chlorine dioxide substitution for bleaching and upgrading of the condensate recovery system. The contribution by Mill B effluent was difficult to discern over the background odour from the Mill A effluent, located upstream.

Odour compounds in extracts of bleached kraft pulp mill effluent (BKME) were characterized by OGC and GC-MS. A variety of sulfur odours was detected by OGC in addition to woody and pulp mill-like odours. Three sulfur compounds were identified by comparison of retention times and partial mass spectra with authentic standards: dimethyl disulfide, 3-methylthiophene and thioanisole. Typical concentrations in BKME are 1, 0.05, and 0.5 μg/L, respectively. The odour intensities were relatively low, however, and they were not detected by OGC. Dimethyl trisulfide was tentatively identified by comparison of its partial mass spectrum with a literature (library) spectrum. Its concentration in BKME was estimated at 0.5-2 μg/L. It corresponds to a skunky odour in the OGC profiles. Efforts to identify another odour peak eluting just after 3-methylthiophene and with a pronounced alkyl sulfidic odour have thus far been unsuccessful.

Lower Athabasca River Ecotoxicological Studies

Our previous studies in the lower Athabasca River, within the area of oil sands deposits, showed that natural sources are responsible for the toxic responses observed. The biological significance of these results was unclear since the tests were done on organic solvent extracts of suspended sediments. In 1994, we collected a large suspended sediment sample just upstream of Fort McMurray. This sample exhibited high toxicity for *Tubifex tubifex* when tested directly. Since the sediment from this area is eventually deposited further downstream, this may have biological significance and further sampling over a wider geographical area is planned for 1995.

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Sustainable River Development

P. Engel, ***Study Leader***

Overview

Research was initiated on the behaviour of cohesive sediments in support of the Fraser River Action Plan (FRAP). Work continues on the determination of critical shear stress for deposition and erosion, hydraulic resistance of alluvial streams and evaluation of performance characteristics of current meters and sediment samplers used by Environment Canada. Key activities are summarized below.

Erosion and Deposition of Cohesive Sediments in the Fraser River

Parameters such as settling velocity, critical shear stresses for erosion and deposition are required in order to model the transport of fine sediment in rivers. Presently, these parameters cannot be estimated from the literature and hence have to be measured for site specific sediments. NWRI's rotating flume was used to determine critical shear stresses for the deposition and erosion of fine sediments from the Fraser River. Preliminary tests have shown that a mathematical model can be used as an operational tool to determine the bed shear stresses and therefore, only direct measurements of sediment concentration as a function of time need to be made.

Tests on cohesive sediment suspensions, from the Fraser River and the Nechako River near their confluence, were also conducted. Sediment concentration, size distribution of suspended sediment flocs as a function of time, and critical shear stresses for deposition and erosion were measured. It was shown that the Fraser River sediment exhibits transport characteristics peculiar to cohesive sediments and that pulp mill effluents enhance deposition and inhibit erosion. This work was done in support of FRAP.

Resistance to Flow in Alluvial Rivers

The total shear stress exerted by the flow on a bed of sand waves is

due to the sand-grain roughness and the roughness due to the shape of the sand waves. Sediment transport is due to the sand-grain shear stress only and therefore, it is important to have a reliable method of determining this component of the total shear stress.

Using theoretical and dimensional analysis together with available experimental data, several methods of partitioning the total shear stress exerted by open channel flow over a bed composed of triangular elements, simulating sand waves, were examined. It has been shown that the concept of isolated roughness flow is valid. Analysis indicates that partitioning is most readily accomplished by using the slope-separation method when sand wave steepness is less than 0.07. When the steepness is greater than 0.07, the slope separation method can be used with an adjustment factor. The results provide basic information for mathematical modelling of sediment transport processes in addressing the sediment issues of the FRAP.

Calibration of Current Meters

Increased awareness of river pollution and the importance of water quality monitoring has made it necessary to reexamine the accuracy of discharge measurements. One of the factors contributing to the error in flow velocity measurements is the uncertainty in the current meter calibration itself. Present practice is to calibrate each current meter individually. An alternative approach would be to develop an average calibration equation, known as a group calibration, based on a large number of current meters of the same type.

Thirty nine rod suspended Price current meters were calibrated individually. It was shown that for the meters tested, the uncertainty of group calibrations was substantially greater than that of individual meters. The uncertainty was attributed to manufacturing variances in the fabrication of meter rotors. The largest errors occurred when a calibration for a particular meter was used with another meter. Tests are continuing.

Calibration of Suspended Sediment Samplers

Suspended sediment concentration in river is an important indicator of water quality. To ensure that reliable data are obtained, the Water Survey of Canada is developing a quality assurance program for the 500 samplers of various types currently in use by Environment Canada. We are assisting in the development of a calibration strategy for

suspended sediment samplers used in the national program.

Tests of five P-63 suspended sediment samplers have shown that individual samplers can be calibrated with reasonable certainty, but there can be large performance variabilities from sampler to sampler. In addition, the P-63 sampler over-samples at low velocities and under-samples at medium to high velocities. As a result, each sampler should be tested in a towing tank and adjusted to bring its performance within acceptable tolerances. Normal fabrication variances in nozzle geometry do not affect the sampler performance. This means that nozzles can be replaced in the field without further calibration.

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Transport Parameters and Flocculation Characteristics

B.G. Krishnappan, ***Study Leader***

Overview

The transport characteristics of fine sediments from the Fraser and Athabasca rivers were investigated in NWRI's rotating flume. The transport parameters and the knowledge gained from this study will be used in contaminant transport and bioaccumulation models that are being developed for both rivers, in support of the Fraser River Action Plan and the Northern River Basin Study. Key findings are summarized below.

Fine Sediments - Fraser and Athabasca Rivers

Fine sediments in rivers are known to adsorb and transport many toxic contaminants and hence play an important role in determining the health of the river ecosystem. The transport characteristics of the fine sediment, are therefore essential parameters required for modelling the transport, fate and bioaccumulation of contaminants in river system.

In this study, sediments from the Fraser River near Prince George, B.C., and the Athabasca River near Hinton, Alberta, were tested in the rotating flume and their transport parameters measured. Sediment and water samples from both rivers were tested for erosion and deposition characteristics.

Deposition Process

In the deposition tests, sediment-water mixture was thoroughly mixed in the flume initially with a mechanical mixer and then was subjected to different bed shear stresses. During the deposition process, concentration and size distribution of sediment in suspension were measured as a function of time. From these measurements, it was possible to quantify the critical condition for complete deposition of the sediment and the steady state concentration of sediment that would stay in suspension forever for a particular bed shear stress. Size

distribution data showed that the particles flocculated as they were deposited and the equilibrium size distribution of the sediment flocs is a function of bed shear stress.

The effect of the pulp mill effluent on the deposition process was tested by repeatedly adding known quantities of the effluent to the flume. The results showed that the pulp mill effluent enhanced the flocculation mechanism and increased the sediment deposition rate. This is the first time that the effect of pulp mill effluent on the transport of sediment has been quantified.

Erosion Process

The erosional characteristics were studied by allowing the sediment to deposit completely on the flume bed and then applying bed shear stresses in steps. As in the deposition tests, concentration and size distribution of the eroded sediment were measured at different shear stresses. From these measurements, it was possible to determine the critical shear stress for the erosion of deposited sediment and the erosion rate function for different shear stress steps. The effect of the consolidation time and the pulp mill effluent were investigated and it was found that both of these factors affected the erosional behaviour of the sediment.

Comparison of the Two Rivers

A comparison of the transport parameters obtained for the sediments from the two rivers showed that they are substantially different. It is therefore concluded that the fine sediment behaviour is site specific and that transport characteristics must be determined for each site. The transport parameters and the knowledge gained from this study will be used in contaminant transport and bioaccumulation models that are being developed for the Fraser and the Athabasca river basins under the Fraser River Action Plan (FRAP) and the Northern River Basins Study (NRBS) respectively.

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Sediment/Contaminant Transport in Rivers

Y.L. Lau, ***Study Leader***

Overview

A study on the volatilization of metolachlor from water and a comparative study of two sampling instruments were completed. Experiments on the growth of biofilms on artificial substratum were carried out. Work is continuing on a study of frazil and anchor ice formation in rivers. These activities are summarized below.

Volatilization of Metolachlor from Water

The herbicide metolachlor is the most heavily used herbicide in Ontario, accounting for about 25 % of all herbicides used, on a weight basis. Information on its occurrence, persistence, fate and toxicity in water is required to assess hazards on aquatic ecosystems.

Volatilization of metolachlor from water is usually not considered a significant pathway because of its relatively high aqueous solubility and low vapour pressure at 20-25°C. We studied the volatilization of metolachlor from water, in the laboratory and in an outdoor open-channel. As expected, volatilization was not significant at temperatures $\leq$ 25°C. However, at temperatures $\geq$ 30 °C, there was significant volatilization (*e.g.*, half-life of 20 days at 40°C in unstirred solutions). Such conditions may occur in Canada in the summer in small ponds or irrigation ditches. In tropical countries, such high temperatures are common, and significant losses of metolachlor from water through volatilization may be expected. Additional experiments indicated that aeration of water significantly accelerated volatilization losses. Air-stripping may be important in turbulent streams and rivers. Our experiments show that ecosystem-specific characteristics should be taken into consideration when studying contaminant persistence. Our research results are used for the establishment of full Canadian Water Quality Guideline for metolachlor and for consideration in the periodic re-registration of pesticides.

Cohesive Sediment Sampling - Comparison of Two Instruments

Contaminants are transported through the aquatic system in soluble and particulate forms. Because of the characteristic of cohesive sediment flocs to adsorb chemicals, the majority of the contaminants may sometimes be transported as particulates. The physical characteristics of these flocs are important for the modelling of contaminant transport.

This study compared the results of floc size distributions measured by two different instruments. The Malvern Particle Size Analyzer, based on the principle of light diffraction, provides information on the *in situ* floc size. The other instrument, a water elutriation apparatus, fractionates the sediment based on its settling velocity. Data from the two instruments produced quite different distributions. However, the combined sets of results produced information on floc density which would have been unknown. We concluded that the elutriation apparatus can be a simple and relatively inexpensive instrument for river sediment sampling.

Biofilm Growth in Open Channel Flows

In many shallow streams, the uptake of contaminants by biofilms on the river bed is the principal pathway for the disappearance of contaminants from the water column. It is therefore important to investigate the various factors controlling biofilm growth in order to improve our understanding of contaminant pathways.

We investigated the relative importance of two hydraulic variables, *i.e.*, bottom shear stress and mean velocity, on biofilm formation in channel flows. The experiments were carried out in two identical channels located side by side. Both had the same water supply and were subjected to the same weather conditions. Ceramic balls were used as bottom roughness elements and the accumulation of biofilms on the balls was monitored. Differences in the rate of biofilm accumulation was related to differences in hydraulic conditions.

Frazil and Anchor Ice Formation

Frazil and anchor ice can greatly affect the hydraulics of river flows. However, we know relatively little about their formation and growth. A better understanding of these processes would lead to more efficient

water resources management and power production as well as protection of the shorelines.

During the past two years, 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 are still ongoing and are planned for completion in June 1995.

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Characterization of Physically Unstable Colloids

G.G. Leppard, ***Study Leader***

Overview

Research was done on the characterization of selected aquatic colloids and colloid systems. Key findings are summarized below.

Background Information

Colloids are active in contaminant binding and in flocculation. They consist of submicrometre particles ranging from bacterial size to large molecule size. Aquatic colloids include humic substances, polysaccharides, the matrix polymers of biological flocs and biofilms, picoplankton, viruses, the oxyhydroxides of iron and manganese, biogenic silicates, finely-dispersed clay minerals and decay residues of microbial cells. Such particles are abundant in aquatic ecosystems accounting for more than 30% of the organic carbon mass in surface waters, and for most of its surface area for interactions with contaminants.

Our research is focused on applied and basic aspects of colloids and colloid systems (aggregates of colloids), in relation to:

- water decontamination systems;
- riverine contaminant transport;
- transport of organic carbon to sinks in the ocean and its implications for climate change;
- biogeochemical mechanisms limiting functions in large-scale aquatic ecosystems;
- fundamental processes of flocculation/coagulation.

Technology to Enhance Decontamination at Water Treatment Facility

In collaboration with other partners, a new technology was developed to characterize the colloid structure of suspended biological flocs. The technology provides a cost-effective mechanism for operators of water treatment facilities to create "designer flocs" by manipulating the

colloid structure in order to optimize decontamination. Research on this technical innovation is continuing in collaboration with university colleagues and is being sponsored through an NSERC Strategic Research Grant. The Wastewater Technology Centre is currently working out the procedures for the creation of the "designer flocs".

Marine Snow in the Adriatic Sea

The marine snow consists of flocculated particles which are considered to be the principal vector for the transport of organic carbon and any associated nutrients and contaminants in the ocean. We have demonstrated that the colloidal organic fibrils produced by algae and bacteria are the major structural component of marine snow. In the summer, the fibril systems at our principal research site in the Adriatic sea are responsible for 40% of the new organic production. The marine snow is implicated in what is known as the mucilage phenomenon and in oceanic buffering of excess atmospheric carbon. This research received an international award for applied science from a Japanese industrial consortium.

Importance of Colloidal Structure

In collaboration with a major European laboratory, we have demonstrated that any characterization of contaminant-particle associations in natural waters must consider the colloidal structure of the particles for all particles smaller than 10 micrometers. When not considered, inappropriate procedures tend to be chosen for the characterization and may result in the production of erroneous data for contaminant dispersion models. This basic research has been funded, over the last ten years, by major grants from the Swiss National Research Foundation and one grant from the Sandoz Foundation.

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Prevention/Remediation of Urban Non-Point Source

J. Marsalek, *Study Leader*

Overview

Two research studies of ecosystem protection against urban diffuse pollution were completed, *i.e.*, one on contaminant removal in an on-stream pond and a laboratory assessment of an oil/sediment separator. Major findings from the completed research activities are summarized below.

Contaminant Removal by an On-Stream Pond

Cumulative impacts of urban runoff, including increased flows, erosion and discharges of contaminants, cause degradation of receiving waters. Such impacts are well recognized in many Areas of Concerns (AOCs) in the Great Lakes Basin. These impacts can be partly or fully prevented by the recently proposed Best Management Practices (BMPs) which need to be assessed in the field. To respond to this need, the NWRI in cooperation with Queen's University, and with financial support from the Great Lakes Action Plan Cleanup Fund and the GLURF Program, undertook a three-year study of contaminant removal by an on-stream stormwater pond located in Kingston, Ontario.

The Kingston stormwater pond was built in 1982 to reduce stormwater peak flows from a 12.6 ha parking lot of a shopping mall. The two-cell pond consists of a permanent wet cell and a dry cell, which floods when the water level in the wet pond exceeds the normal water level by 0.2 m. The pond was instrumented and continuous measurements of rainfall, inflow, outflow and pond water level were taken, supplemented by bottom sediment surveys, velocity measurements, and sampling of inflows, outflow, suspended particulates and submerged plants.

Flow patterns in the pond were simulated by a commercial software and the modelling results, partly verified by dye tracing and current meter measurements, indicated that a large recirculation zone was formed in the pond which reduced its effectiveness in sediment

removal. Effective sedimentation can be achieved by inducing good mixing of the influent at the pond inlet, a uniform flow velocity distribution in the pond (no short-circuiting), and prevention of sediment resuspension by high flow velocities or secondary currents. Improvements of flow patterns will be achieved by installing flow baffles in the next study phase.

The thickness of bottom sediments varied from 0.15 to 0.2 m, accumulated over a 10-year period, with an average rate of accretion of about 0.02 m/year. These sediments were composed mostly of silt (35%) and clay (61%). Metals in the sediment exceeded the provincial sediment quality guideline, at the lowest effect levels of 16, 31 and 120 μg/g for Cu, Pb and Zn, respectively. Thus, this sediment would be classified as "marginally-significantly" polluted and its disposal would require certain precautions. Chemical fluxes were monitored at two inflow points and the outflow point.

Mass balances were used to establish removals for various constituents, during baseflow and event flow regimes. The highest removals were for suspended solids, total phosphorus, nitrate, oil and grease, phenol and zinc (about 40%). Removals were insignificant for total dissolved solids, chloride, copper and lead. For sulphate, nitrite, ammonia and TKN, there were negative removals, as these constituents were produced by transformations. Another factor reducing removals was the flushing of pollutants by baseflow. The removal of chemicals by biota was insignificant. Further improvements in pond outflow quality can be achieved by effluent polishing, *i.e.*, biofiltration and wetland treatment, which were also studied at the pond site.

These research results support the development of Remedial Action Plans in several Canadian AOCs. Control and/or treatment of urban stormwater and combined sewer overflows (CSOs) are required for delisting in several AOCs, *e.g.*, Toronto Waterfront, Hamilton Harbour, Bay of Quinte.

Support to the Canadian Environmental Industry

Two studies were conducted in support of the development of technology for delisting AOCs with urban diffuse pollution. Both were done on a cost recovery basis and support the Canadian Environmental Industry Strategy.

The final phase of testing a sediment/oil separator developed by

Stormceptor Canada, Inc. was completed and a final report produced. In cooperation with the Environmental Technologies Advancement Division, EP, a proposal was prepared to use this demonstration project as a pilot for the National Environmental Technology Certification Program.

A field demonstration of dynamic separators for treatment of combined sewer overflows (CSOs) was initiated in cooperation with the Wastewater Technology Centre, the lead agency, and several funding partners. The first year results indicated a disappointing performance of the separator in that it did not meet the effluent quality needed for UV disinfection. A major study redirection is planned for next year.

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Fate and Transport of Inorganic and Organic Contaminants

T. Mayer, *Study Leader*

Overview

Research was carried out on the fate of nutrients and heavy metals in stormwater management ponds. An investigation was initiated on the role of sediments in the eutrophication of marshes at Point Pelee National Park. Key findings are summarized below.

Status of Contaminants in Urban Stormwater Management Ponds

Urban areas contribute an important fraction of the non-point sources of pollution to aquatic ecosystems. Stormwater runoff, in particularly, contains significant loads of contaminants such as heavy metals, nutrients and organic substances, many of which are associated with the particulates. Stormwater management ponds, initially designed as flood control structures, have recently been constructed to retain the particulates and therefore attenuate pollutants loadings to receiving waters. These structures are important for the control of urban pollution.

Although numerous studies have been done to estimate loadings from urban sources, little is known about the fate and transport of contaminants in stormwater management ponds. This information is essential to ensure proper maintenance of the ponds and for the evaluation of their effectiveness as pollutant control measures.

Our work provides information on nutrients and heavy metal levels in different compartments of stormwater management ponds located in the Toronto area. Ponds from a variety of urban settings were selected to represent different land uses, and therefore different chemical composition. Our results showed that the pond receiving runoff primarily from industrial and commercial sites had the highest relative levels of heavy metals (Zn, Pb, Cu, Cd, Ni, Cr) contamination in its suspended and bottom sediments. Suspended sediments from the pond in the residential catchment had elevated Pb, Cu, and Cd concentrations relative to sediments in the reservoir in the open space

catchment. In the ponds receiving runoff from the residential and industrial areas, ammonia concentrations in the water column frequently reached and exceeded the chronic toxicity threshold of 300 $\mu g/L$.

This work contributes to departmental priorities related to pollution prevention and restoration, providing information for the restoration and delisting of Areas of Concern in the Great Lakes basin.

Role of Sediments in Water Quality - Point Pelee National Park

Over the past few years, excessive nutrient loadings resulted in the deterioration of water quality in marshes of Point Pelee National Park. A multi-disciplinary study was initiated to identify the sources of nutrients to the marsh. The purpose of this study was to assess the importance of nutrient loadings from internal sources. Under certain conditions, in-place sediment may act as nutrient sources in absence of or long after any input from external sources. Bottom sediments were collected at the pond with the highest nutrient concentrations and at the pond located closest to the septic system site. Interstitial water samplers were also deployed in the most effected pond to estimate fluxes of phosphorus in overlying water. High concentrations of nutrients in interstitial waters, resulting from mineralization of organic matter, implicate the bottom sediments as an important nutrient source in the most effected pond. This work is done in support of the Great Lakes 2000 program.

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Agricultural Non-Point Sources of Pollution

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

Overview

A study on the transport of the herbicides, atrazine and metolachlor, in agricultural runoff was completed. Work continues on the effects of controlled drainage/subirrigation on tile drainage water quality and crop yields, and on-farm demonstrations of the subirrigation and controlled drainage systems to determine their economic benefit to the producer. Three techniques for the extraction of metolachlor residues in runoff water were compared. Key findings are summarized below.

Fate of Atrazine and Metolachlor

Eighty percent of Ontario's cropland is located in the Great Lakes basin. Agricultural activities and the chemicals used in crop-protection and crop-production are important sources of contaminants to the Great Lakes. Atrazine and metolachlor are the major herbicides used in Ontario's agricultural cropland, representing about 75% of all pesticide use. Whenever a herbicide is applied, a portion is lost to the soil and it is important to know its subsequent fate, *e.g.*, its persistence in the soil, losses to runoff and irrigation waters, volatization, photodegradation and biodegradation.

Our research focuses on answering the following questions: How much of the applied pesticide is lost to surface and subsurface waters? How are pesticides transported between the application point and receiving waters? and what is the timescale? The results will provide the information required for the fine-tuning of agricultural practices and the protection of water quality.

This study was carried out in field plots and in an agricultural watershed. The field plots were on poorly-drained Brookston clay loam while the agricultural watershed consisted of well-drained Guelph loam and Embro silt loam. Our results show that the dissipation rates in runoff waters were faster in the field plots than in the watershed. For atrazine, half-lives in combined surface and subsurface runoff water,

were estimated at 27 days in the field plots and 42 days in the watershed; the values for metolachlor were 20 and 57 days. The applied atrazine and metolachlor losses in combined surface and subsurface runoff were respectively 1.81% and 0.33% for field plots, and 1.18% and 0.15% for the watershed.

Factors Influencing Herbicide Transport

Herbicides are most susceptible to overland and subsurface transport in runoff events soon after their application. Our research has focussed on small plot and simulation studies to characterize the factors influencing herbicide transport. Herbicide formulation and application rate, soil type and tillage, and incidence of rain after application are major factors related to herbicide loss. Herbicide concentrations in receiving waters are generally, at least, an order of magnitude smaller than those measured in runoff from simulation or small plot studies. Parameters required to model herbicide loss have been derived primarily from field scale or simulation studies and the results extrapolated to the watershed scale.

Our work showed that herbicide loss is independent of spatial variation. Soil organic carbon, water table depth, soil moisture content, soil texture, days prior to application and time after application are the primary factors to be considered in the dissipation and loss of atrazine and metolachlor after application. These results are used to fill knowledge gaps in modelling of herbicide transport.

Comparative Study of Metolachlor Analysis

The determination of herbicide residues in treated fields is required for various environmental management purposes. However, current analytical methods are often time-consuming, expensive and require specialized instrumentation. For this reason, a study was initiated to compare three different methods for the determination of metolachlor residue, *i.e.*, solid-phase microextraction (SPME) followed by GC-EC, solvent extraction followed by GC-MSD, and immunoassay. Field runoff samples collected from Woodslee were split and analyzed by study collaborators at the University of Manitoba, Agriculture and Agri-Food Canada's Research Station, Harrow, Ontario, and NWRI's National Laboratory for Environmental Testing. Preliminary results indicate that the methods compare favourably. Evaluation is still underway.

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Environmental Standards & Statistics Project

K.L.E. Kaiser, *Project Chief*

About the Project

In support of departmental and institute programs, the objectives of the Project are to use environmental statistics and quality assurance principles to ensure that the right data are collected with known, acceptable confidence levels; to provide advice on the nature and extent of sampling programs, calibration procedures, blind audits, interlaboratory comparisons, reference materials and statistical interpretation of data; to provide maintenance and calibration services for current meters; and to undertake research in environmental statistics and pathways and effects of toxic substances.

Interlaboratory Quality Assurance Performance Evaluation Studies

Quality assurance studies to support departmental programs such as Great Lakes 2000, LRTAP, FRAP and CEPA are provided to assess performance of laboratories for a wide variety of constituents. These include toxic organics in water, sediments and sediment extracts as well as for major ions, nutrients, physical parameters and trace metals in water. Some special studies addressing arsenic, selenium, bismuth and total phosphorus have been provided. There are now several hundred laboratories participating in these studies.

Reference Materials

Numerous reference materials (RMs) prepared from natural lake and river waters, precipitation, and sediments have been developed over the past twenty years. These have included waters for major ions, nutrients and physical parameters and sediments for a variety of toxic organics, including a naturally contaminated sediment for dioxins and furans. These RMs are currently used in many national and international environmental programs for methods validation and calibration control. Some of the RMs have also been employed for special blind audit studies in national and international programs.

Research on Organic Contaminants

Historic and recent collections of lamprey ammocoetes from various Great Lakes and St. Lawrence River tributaries have been analyzed for organic contaminants to establish temporal and spatial trends. Zebra mussel samples from several sites are also being analyzed for these compounds and investigated for their potential use in biomonitoring programs. Structure/activity and inter-species correlations of contaminants are being developed with the COMPUTOX™ toxicity database and toxicities of chemicals are determined with the Microtox™ test system in support of CEPA, Great Lakes 2000 and other programs. Seasonal and temporal variations of major ions, nutrients, and physico-chemical parameters in Lake Erie are being collated and analyzed for a Lake Erie water chemistry atlas.

Statistics and Modelling

New statistical techniques and algorithms are being developed for improved separation of short- and long-term trends in environmental data, for detecting and assessing the impact of effluents on rivers and lakes, with emphasis on the Niagara River and on pulp mill effluents. The work also involves reviewing and developing robust methods for trend analysis of water quality assessment methodologies. Novel ranking procedures developed at NWRI in recent years are being applied to rank environmental hazards of contaminants including pesticides in different soil and climatic conditions. In addition, new methods for visualization of limnological data are being developed for Remedial Action Plans in several of the Great Lakes Areas of Concern, including Hamilton Harbour.

National Calibration Service

The National Calibration Service provides maintenance and calibration of current meters for numerous monitoring and research activities within and outside the department.

Inorganic Quality Assurance for Regional Systems

H. Alkema, ***Study Leader***

Overview

Interlaboratory quality assurance (QA) studies are important for ensuring that analytical measurements are of good and comparable quality. Seven interlaboratory studies were completed for a wide variety of inorganic parameters. In addition to the QA studies, the Branch develops and markets a variety of certified reference materials (CRMs) to help laboratories verify the quality of their data. Several new CRMs, including a new certified rainwater, were added to our inventory of water standards.

Quality Assurance Studies

The interlaboratory QA studies for surface waters provide extensive data quality reports for several national and international environmental programs, *e.g.*, the Federal-Provincial Agreements on Water Quality, the Great Lakes 2000 (GL 2000), and the Prairie Provinces Water Board. The seven studies conducted during this year provided data quality and performance reports to public, private and university laboratories involved in these programs. The reports address various groups of constituents such as major ions, nutrients and many trace metals and provide data quality assessments in terms of systematic bias and imprecision. Performance ratings are tabulated for each laboratory in order to estimate data quality and to identify areas where corrective measures and improvement are required.

A major effort has been made to provide a wide selection of trace metals samples. As each study needs a unique set of 10 samples, new sets of spiked samples were prepared to meet requirements for ambient and contaminated effluent concentrations. Samples were also prepared to meet specific requirements identified by participating laboratories, *e.g.*, for verifying the accuracy of arsenic, selenium and uranium analyses. Preparation of these new samples also requires that sample stability be investigated.

Certified Reference Materials (CRMs) for Natural Waters

In recent years, a greater awareness has grown in the environmental testing community for the use of CRMs and their role in establishing the accuracy and traceability of chemical measurements. In the area of natural water CRMs, the Branch has developed and marketed two series of reference standards, one for natural waters containing major ions and nutrients, and another for samples with up to 20 different metals.

CRMs can also be used as audit materials. Series of CRM samples may be submitted as "blind" samples to estimate laboratory performance and demonstrate the validity of analytical results. In the past year, the Branch has provided Health Canada with three blind audit studies to monitor and assess five contract laboratories which generated results for the Drinking Water Safety Program for native peoples. The audit studies and an assessment report quantified the performance of each contract laboratory. The BC Ministry of Environment is also using our CRMs to monitor the performance of their contract laboratories.

Through the development and distribution of its water CRMs, Environment Canada contributes significantly to the validity of chemical measurement in Canadian freshwater ecosystems.

LRTAP Interlaboratory Quality Assurance

N.M. Arafat, *Study Leader*

Overview

Interlaboratory performance evaluation studies are effective tools for monitoring the capabilities and performance of laboratories providing information for environmental programs. This year, three interlaboratory studies were prepared, delivered and completed in support of the Canadian Acid Rain Program.

LRTAP Interlaboratory Studies

Three interlaboratory studies were completed. Ten different soft surface water and rainwater samples were distributed at four-month intervals to more than 50 laboratories in Canada and the United States. Samples were analyzed for approximately 22 different constituents.

Bias in laboratory data sets was identified using the nonparametric techniques of Youden. Individual results that deviated significantly from target values were assigned flags. The participating laboratories that had a low number of flags and with data that were seldom biased were defined as satisfactory.

Over the years, more than 130 laboratories have participated in this soft water program. Many of which have participated in all studies. Overall laboratory performance, based on inaccuracy (a systematic error in the calibration) and imprecision (based on the frequency of flagged data) continues to show ongoing improvement.

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Quality Management and Coordination for Regional Ecosystems

K.I. Aspila, ***Study Leader***

Overview

During 1994-95, work has progressed on the production of a Quality Manual to meet the International Standards Organization (ISO) criteria for certification as producer of certified reference materials (CRMs). Liaison with regional staff was maintained. Progress continues on the development of computer software to define laboratory performance. Major activities are summarized below.

Quality Management and Coordination

The provision of quality assurance activities, to support environmental monitoring programs, requires good coordination of interlaboratory performance evaluation studies, the development of reference materials, sound assessment techniques for evaluation of data and an internal infrastructure that documents compliance to national and international standards.

Work has progressed on the preparation of a Quality Manual on the preparation of certified reference materials (CRMs). The manual includes documentation on the computerised assessment techniques for data evaluation, documentation describing the quality system for our QA group and documentation on the techniques required for the preparation of stable reference waters. Documented procedures are essential to meet the ISO criteria for certification as producer of (CRMs) in the international marketplace.

Liaison with regional staff was maintained. Reports from several performance evaluation studies provided feedback to laboratories and program managers on the quality of their data for a wide variety inorganic and organic constituents as described in reports by Alkema, Arafat and Stokker, in this section. Progress continues on the development of computer software that will define the performance of departmental and contract laboratories.

We were able to address quality assurance requirements and provide support to clients outside of the department, *e.g.*, the Canadian Association for Environmental Analytical Laboratories (CAEAL), the US Environmental Protection Agency, Health Canada, the British Columbia Ministry of Environment, Lands and Parks and the MEND program. Two reports were completed on the comparability of analytical data in a MEND project.

Reports and Presentations

K.I. Aspila and H. Alkema. 1994. On the Comparability of Laboratory Data for Water Samples Exchanged between ASL and UBC, Anderson Lake (Winter and Summer Surveys) MEND Project 2.11. June 1994.

K.I. Aspila and E. Kokotich. 1994. On the Comparability of Laboratory Data for Water Samples Exchanged Between ASL and UBC, Buttle Lake (Fall Survey) MEND Project 2.11. December 1994.

Statistical Modelling of Environmental Impacts

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

Overview

Research was undertaken to develop a systematic approach for detecting, estimating and predicting water quality changes, *i.e.*, trends and seasonality, in the Niagara River Monitoring data sets. Work was also done on the appropriate data analysis for the detection and estimation of the impacts of pulp mill effluents.

Water Quality Changes in the Niagara River

The Declaration of Intent between Canada and the United States requires that the target load reductions of the contaminants of concern be demonstrated by 1996. The data set generated by the Canadian upstream/downstream monitoring program has been identified by both countries as the most reliable for demonstrating achievement of the target. It was not possible to use commonly available techniques for detecting, estimating and predicting trends, because the data set contains missing and censored *(i.e.*, data that are below detection limits) observations, seasonality and serial dependence. Adequate and efficient methods for overcoming the inherent difficulties of the traditional methods have been developed and demonstrated on a subset of the Niagara River data set. Current activities are focused on transferring the methodology to Canadian and U.S. managers; developing user-friendly software for the implementation of these methods; and preparing a technical monograph on trend assessment.

Detection and Estimation of the Impacts of Pulp Mill Effluents

Studies conducted at NWRI for evaluating the impacts of pulp mill effluents on fish are designed to test for differences among several treatments. Our activities focused on finding the most appropriate data transformation for performing the statistical analysis. Then the results were translated onto the original measurement scale, in order for the results to be more easily understood by users and decision makers.

Reports and Presentations

El-Shaarawi, A.H. and T. Saha. 1994. Testing for Autodependence in a Sequence of Ordered Censored Observations. Presented at the Conference on Environmetrics, Burlington, Ontario, August 11-15.

Niculescu, S.P. and A.H. El-Shaarawi. 1994. Testing for Liniar Trend in Univariate Time Series with stationary m-Dependent or ARMA Residuals. Presented at the Conference on Environmetrics, Burlington, Ontario, August 11-15.

Elliot, J.R. and A.H. El-Shaarawi. 1994. Time Series Models of Sediment Load: Niagara River, 1986-1992. Presented at the Conference on Environmetrics, Burlington, Ontario, August 11-15.

El-Shaarawi, A.H. and J.R. Elliot. 1994. Environmental Monitoring: A Tool for Protecting Ecosystem and Human Health. Invited presentation at the session "Applying ecosystem health concepts as a management tool" co-sponsored by the International Association of Great Lakes Research & Aquatic Ecosystem and Management Society, Windsor, Ontario, June 9.

Elliot, J.R. and A.H. El-Shaarawi. 1995. Sediment lead loads in the Niagara River, 1986-1992. J. Great Lakes Res. *(In press)*

El-Shaarawi, A.H. 1994. Proving causality is not always necessary or sufficient for regulatory action. J. Great Lakes Res. 20(3): 593-596.

Elliot, J.R. and A.H. El-Shaarawi. 1994. Time series models of sediment lead concentration and load in the Niagara River at Fort Erie and Niagara-on-the-Lake, 1986-1992. NWRI Contribution 94-71.

El-Shaarawi, A.H. 1995. Trend detection and estimation with environmental applications. Mathematics and Computer Simulation. *(In press)*

Statistical Methods for Water Quality Studies

S.R. Esterby, ***Study Leader***

Overview

Environmental assessments are often complex since changes in indicators of environmental quality may be due to many factors. Because of this, it is important that the research or monitoring programs and statistical analysis be designed to permit the identification and characterization of the sources of variability. In 1994-95, our research results contributed to advance our knowledge of tools that can be used for obtaining defensible conclusions about environmental conditions/changes; and provided the information about present status and changes in environmental quality. Both are essential for running efficient programs. Major research activities are summarized below.

Exploratory Techniques for Structure-Toxicity Modelling

Modelling can be used to predict the toxicity of a chemical from its structure. There is a large body of toxicity data in the literature which can be used for developing such models. We have developed a new technique for identifying sets of similar compounds. It uses a similarity measure based upon the type of relationship between toxicity and structural indicators for compounds of known similar structure. Evaluation on a subset of the COMPUTOX™ database shows that the technique is promising and has potential for use in other applications. Techniques for structure-toxicity modelling are directly relevant to CEPA and other programs dealing with toxicity.

Trend Assessment

Over the years, extensive data sets were collected on water quality in the Great Lakes. It is therefore important to analyze the data, not only for assessing changes in water quality, but also to evaluate the relevance of the methods used. Lake Ontario temperature, TP and SRP data from 1977 to 1984 have been used to evaluate methods for

characterizing seasonal volumes throughout the year. This approach concentrates on characterizing sources of variation and builds on the previous work of others. The analysis of the March-April cruises shows that there is a variable year-to-year contribution from the deep central waters to the total SRP content prior to overturn. This provides an explanation for the year-to-year differences found in the availability of nutrients and resuspended contaminants.

Research and monitoring programs are generating data sets either designed for, or at least to be used for answering questions about changes in environmental quality over time. A paper reviewing methods for the detection and estimation of trends has been completed. Examples from water quality and acid deposition studies are used to argue for the use of methods that provide a comprehensive analysis of data. This is required in order to draw stronger conclusions and to more fully use the data which are often collected at great expense. Methodological and program issues of importance to scientists and managers are also raised in the paper.

Reports and Presentations

Esterby, S.R. and K.L.E. Kaiser. 1994. Exploratory techniques for structure-toxicity modelling. Presented at the Statistical Society of Canada Meeting, Banff, Alberta, May 8-11.

Esterby, S.R. 1995. Temporal-spatial patterns in lake water quality data. Presented at the International Biometric Society, Eastern North American Region Spring Meeting, Birmingham, Alabama, March 26-29.

Esterby, S.R. 1995. A review of methods for the detection and estimation of trends with emphasis on water quality applications. Hydrological Processes. *(In press)*

Esterby, S.R. 1995. Estimation of quantiles with application to regulations. *In*: Proceedings of Stochastic and Statistical Methods in Hydrology and Environmental Engineering, K.W. Hipel and L. Fang (Eds.), Vol. 4: 103-112, Kluwer, Dordrecht, The Netherlands.

Delorme, L.D., S.R. Esterby, L.J. Turner and N.S. Harper. 1994. *Salsola* (Russian Thistle) fossil pollen distribution on the Canadian Prairies. NWRI Contribution 94-135.

Visualization and Hazard Ranking of Toxic Contaminants

E. Halfon, ***Study Leader***

Overview

Progress has been made on the development and utilization of a scientific visualization software and on another software for the environmental assessment of toxic contaminants in groundwater. Major activities are summarized below.

Visualization of Hamilton Harbour and Cootes Paradise Data

Scientific visualization is a new and rapidly expanding field of research. A new powerful, easy-to-use, scientific visualization package for personal computers has been developed. The package called Data Animator generates animations, in FLC format, from two- and three-dimensional data sets. Geographical references, *e.g.*, shorelines, bathymetry information, may be added for clarity. Data Animator is user-friendly and it can be learned in about an hour. A graphic user interface (GUI) allows the computer operator to choose a viewpoint, fonts, colour palette and data. Point-and-click mouse operations allow manipulation of all features, with immediate on-screen feedback. This GUI allows the user to design quickly an attractive animation to specifications.

Data Animator is able to display environmental data in a clear, concise way using colours to represent ranges of data values. Computer imaging is useful to visualize the movement of water masses, the development of algal blooms, and episodes of oxygen depletion. Data Animator has been used to display research results on aquatic environments to the general public as well as to specialized scientific audiences.

In collaboration with McMaster University, animation and digital video are also being used in a prototype interactive CD-ROM on Hamilton Harbour and Cootes Paradise. Animations for all water quality parameters for several years have been performed.

Assessment of Toxic Contaminants

A second topic of research was on environmental assessment of toxic contaminants in groundwater. In collaboration with Dr. R. Brüggemann, a software package was developed under the sponsorship Canada-Germany Science and Technology agreement. The software ranks toxic contaminants according to their physical-chemical characteristics and their use. This computer program uses graphics tools and Hasse diagrams to determine which chemicals are the most hazardous to the environment, and outlines the rationale for their selection. The software has been tested with data sets from Canada, Germany and Italy.

Reports and Presentations

Brüggemann, R. and E. Halfon. 1994. Sensitivity analysis of partially ordered sets and ranking objects of environmental interest. NWRI Contribution 94-95.

Brüggemann, R., B. Münzer and E. Halfon. 1994. An algebraic/graphical tool to compare ecosystems with respect to their pollution. The German River "Elbe" as an example. I: Hasse diagrams. Chemosphere 28: 863-872.

Halfon, E. 1994. Visualization of temperature and oxygen concentrations in Hamilton Harbour, Lake Ontario. NWRI Contribution 94-79.

Halfon, E., G. Tartari, M. Howell and A. Binelli. 1994. Visualization of pH changes due to liming treatments in Lake Orta, Italy, using computer generated animations. *In* G. Guariso and B. Page (eds.) Computer Support for Environmental Assessment, Elsevier Science. pp: 37-48.

Münzer, B., R. Brüggemann, E. Halfon. 1994. An algebraic/graphical tool to compare ecosystems with respect to their pollution: II: Comparative regional analysis. Chemosphere 28: 873-879.

Brüggemann, R. and E. Halfon. 1995. Comparative Analysis of Nearshore Contaminated Sites in Lake Ontario: Ranking for Environmental Hazard. Toxic and Hazardous Substance Control. *(In press)*

Halfon, E. (ed) 1995. Special issue on the use of computer graphics and visualization. J. Biological Systems. Vol. 2.

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Halfon, E., N. Schito and R.E. Ulanowicz. 1995. Energy flow through the Lake Ontario food web: Conceptual model and an attempt to mass balance, Ecological Modelling. (*In press*)

Mackay, D., E. Halfon and A. Di Guardo. 1995. Problems and perspectives of regional fate modelling of xenobiotics: A Strategy for Enhancing the Role of Multimedia Mass Balance Models for the Stewardship of Chemicals, Proceedings of a Workshop held at Hillerrød, Denmark, January 30 - February 1.

Toxicity - Organic Contaminants

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

Overview

Work is continuing on toxicity determinations and on the development of structure-activity and inter-species relationships for the estimation and prediction of toxic effects. A major ecotoxicity handbook was completed and published in 1994. We are collaborating with the Canadian Museum of Nature, on the investigation of historic and current levels of organochlorine contaminants in sea lamprey larvae and their potential use as biomonitors. Work on the production of water quality atlas for Lake Ontario and Lake Erie is progressing.

Our research is done in support of the development of new legislation, of lakewide management plans and remedial action plans in areas of concern in the Great Lakes.

Toxicity Estimation and Prediction

An estimated 60,000 to 100,000 chemicals are in worldwide commerce, of which only a small fraction has adequate toxicological, material safety, and/or environmental effect/risk data. In many cases, even very basic information is missing and assessments, *e.g.*, those under the Canadian Environmental Protection Act (CEPA), are difficult because of lack of information.

Using the Microtox test, we are continuing toxicity determinations on representative contaminants and model compounds. The data are used to develop structure-activity and inter-species relationships for the estimation and prediction of toxic effects. Research is focusing on the improvement of these relationships by narrowing confidence intervals and by broadening applicability to different parameters, chemical structures and biological endpoints.

Recent findings include the identification of a large number of erroneous toxicity data found in the published literature. The data, in some instances incorrect by several orders of magnitude, were identified with the use of quantitative inter-species toxicity data

correlations developed from our COMPUTOX™ database. The use of these data in decision making and legislation can have significant repercussions.

The Handbook on the Ecotoxicity of Chemicals to *Photobacterium phosphoreum* was published in collaboration with the *Centre de Traitement de l'Information Scientifique*, Lyon (France). This handbook collates the results of several years of in-house toxicity testing as well as literature data published to date. The handbook will be a valuable reference for those interested in the toxic effects of chemicals.

Biomonitoring of Organic Contaminants in the Great Lakes

In collaboration with the Canadian Museum of Nature, Ottawa, the analysis of sea lamprey, *Petromyzon marinus*, ammocoetes (larvae) continued with several archived samples from upper Great Lakes tributaries. Sea lamprey larvae live for several years in the sediments of creeks and rivers before they mature and move downstream into the lakes where they are parasites of fish, primarily trout and salmon. Therefore, the lamprey ammocoetes can be used as biomonitors for bioaccumulating substances in the lower part of the foodchain, similar to mussels and spottail shiners. Because of the existence of historic ammocoete collections, it is of interest to compare them with more recent samples as well as those from other tributaries. Specifically, this work provides spatial and temporal information on levels of individual PCB congeners and major organochlorine pesticides in the St. Lawrence River basin and in selected Lake Huron and Lake Superior tributaries in the late 1940's to 1990's.

Ammocoetes from the St-François and Ste-Anne rivers, St. Lawrence basin, have been analyzed. In most cases, the historic samples show higher concentrations of organochlorine pesticides, *i.e.*, chlordane and DDT group compounds, as well as PCBs. The DDT/DDE ratio has also changed significantly over the years, reflecting decreased inputs of DDT and relatively higher proportions of the metabolite DDE.

Sea lamprey ammocoetes and native mussels were compared in terms of their potential for use as biomonitors for organochlorine contaminants. Both can be sampled in similar locations. However, in some areas the indigenous mussels species are endangered. Therefore, the possible substitution of mussels with lamprey larvae could be desirable and provide protection measure for indigenous mussels in

affected areas.

Zebra mussels, *Dreissena polymorpha*, were introduced to the Great Lakes in the late 1980's, and are now widely distributed, especially in Lake Erie. As the mussels develop from mobile veligers, they become sedentary and attach themselves to structures such as navigation buoys. The fact that they filter enormous amounts of water makes them suitable biomonitors for contaminants associated with particulates. This study has taken an early lead in the investigation of the potential usefulness of zebra mussels for monitoring purposes. Research is continuing on various aspects of sample preparation and data interpretation.

Water Atlas for Lake Erie and Lake Ontario

Work is continuing on the update of the Lake Ontario water atlas published in 1984. Similar work was initiated with Lake Erie data to determine long-term seasonal and temporal trends. The information required for this work is retrieved from the various limnological database files available at CCIW. However there are gaps in the data series, with missing data for specific seasons or years.

Reports and Presentations

Kaiser, K.L.E. and J. Devillers. 1994. Ecotoxicity of Chemicals to *Photobacterium phosphoreum*. Vol. 2 in series of Handbooks on Ecotoxicity of Chemicals, J. Devillers, ed., Gordon & Breach, USA, x +879 pp.

Kaiser. K.L.E. Letter to the Editor-in-Chief of "SAR and QSAR in Environmental Sciences". (*In press*)

Renaud, C.B., K.L.E. Kaiser and M.E. Comba. Historical versus recent levels of organochlorine contaminants in lamprey larvae of the St. Lawrence River basin, Quebec. Can. J. Fish. Aquat. Sci. (*In press*)

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Kaiser, K.L.E, M.B. McKinnon and V.S. Palabrica. 1995. Erroneous toxicity data: Their identification and elimination using a standardized notation and inter-species correlations. Presentation at 30th Central Canadian Symposium on Water Quality Research, Burlington, Ontario, February.

CEPA Quality Assurance Program

W.C. Li, *Study Leader*

Overview

In support of the Canadian Environmental Protection Act (CEPA), a quality assurance (QA) program was established to ensure the reliability and comparability of analytical data on priority toxic contaminants. This was accomplished through interlaboratory QA studies and through the development of reference materials (RMs) for toxic organics. Major activities are summarized below.

Interlaboratory Studies

Final reports were completed for two interlaboratory studies on the determination of dioxins and furans in sediment extracts. Although analyses of dioxins and furans in sediment extracts require more complicated and tedious sample preparation procedures than other organic parameters, *e.g.*, PCBs, PAHs and OCs, the interlaboratory results indicated that the performance of most laboratories was satisfactory.

Reports were completed for two interlaboratory studies on the determination of octachlorostyrene (OCS), hexachlorobutadiene (HCBD) and chlorobenzenes (CBs) in standard solutions, sediment extracts and sediments in support of a QA/QC program for contaminated sediments as part of Great Lakes 2000. The results were satisfactory for standard solutions, but were less satisfactory for sediments for the majority of participating laboratories. This suggests the need for improved procedures for the extraction, concentration and cleanup of sediment samples.

Development of Reference Materials

Five sediment extract RMs for dioxins and furans have been developed for the CEPA QA program. Based on the results obtained from two interlaboratory studies, the preliminary reference values of dioxins and furans in the RMs were established. These RMs are suitable for use as

in-house quality control (QC) samples, for interlaboratory studies and for other long-term quality assurance applications. A sediment extract RM for OCS, HCBD and CBs was developed with the reference values obtained from in-house analysis using GC-ECD and GC-MSD analysis. In addition, the stability of OCS, HCBD and CBs in this RM under cold storage was monitored over 15 months. The results showed that no degradation occurred during the storage period.

Reports and Presentations

Li, W.C. and A.S.Y. Chau. 1994. Preparation and stability of chlorophenols in sediment extracts. NWRI Contribution 94-62.

Li, W.C., A.S.Y. Chau, S. Humphrey and I. Orchard. 1994. Interlaboratory study No. G-2: Analysis of selected chlorinated hydrocarbons in sediments. NWRI Contribution 94-63.

Li, W.C., A.S.Y. Chau, S. Humphrey and I. Orchard. 1994. Interlaboratory study No. G-3: Analysis of selected chlorinated hydrocarbons in sediments. NWRI Contribution 94-73.

Li, W.C. and A.S.Y. Chau. 1994. CEPA national interlaboratory comparison study (CP-3): Analysis of dioxins and furans in sediment extracts. NWRI Contribution 94-81.

Li, W.C. and A.S.Y. Chau. 1994. CEPA national interlaboratory comparison study (CP-4): Analysis of dioxins and furans in sediment extracts. NWRI Contribution 94-84.

Organic Quality Assurance for Regional Ecosystems

Y.D. Stokker, ***Study Leader***

Overview

Four organic interlaboratory quality assurance studies were completed and a fifth is nearing completion. Research efforts continued to be directed to the monitoring and certification of the sediment reference materials for PAHs, PCBs and chlorobenzenes, and to the development of reference materials for dioxins and furans. 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 focused on conducting interlaboratory QA studies to ensure organic analytical data in programs such as the Great Lakes 2000 (GL 2000), Fraser River Action Plan (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 of measurements are determined for each laboratory when blind duplicates and reference materials are included among the samples distributed. Laboratory managers can therefore use the information provided to initiate corrective actions in order to improve their laboratory measurement process. 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 Canadian Association for Environmental Analytical Laboratories (CAEAL) certification program for organic analyses. Two studies were completed on the analysis of OCs and PCBs in water for the CAEAL certification program C6, and two studies on the analysis of PAHs in

water were completed for the CAEAL certification program C7.

A National Dioxin Interlaboratory QA Study was initiated to support a partnership agreement with Cambridge Isotope Laboratories (CIL) and Fisheries and Oceans Canada on the development of three fish reference materials for coplanar PCBs, dioxins and furans. This work fills research needs identified by the department 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 burgeoning field of environmental analysis. Furthermore, the interlaboratory study itself 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 GL 2000 and FRAP.

Reference Materials

The effectiveness of interlaboratory QA programs, intralaboratory quality control and research on analytical methods 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 in-house quality control 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 despite storage times of between ten and fifteen years.

Preliminary reference values for the dioxin and furan homologue totals in two sediment RMs (EC-2, EC-3) were compiled. The acquisition of high resolution GC/MS congener data for dioxins and furans in these two RMs was initiated. 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 private sector laboratories at no charge in exchange for a small quantity of the materials for their own in-house quality control.

Reports and Presentations

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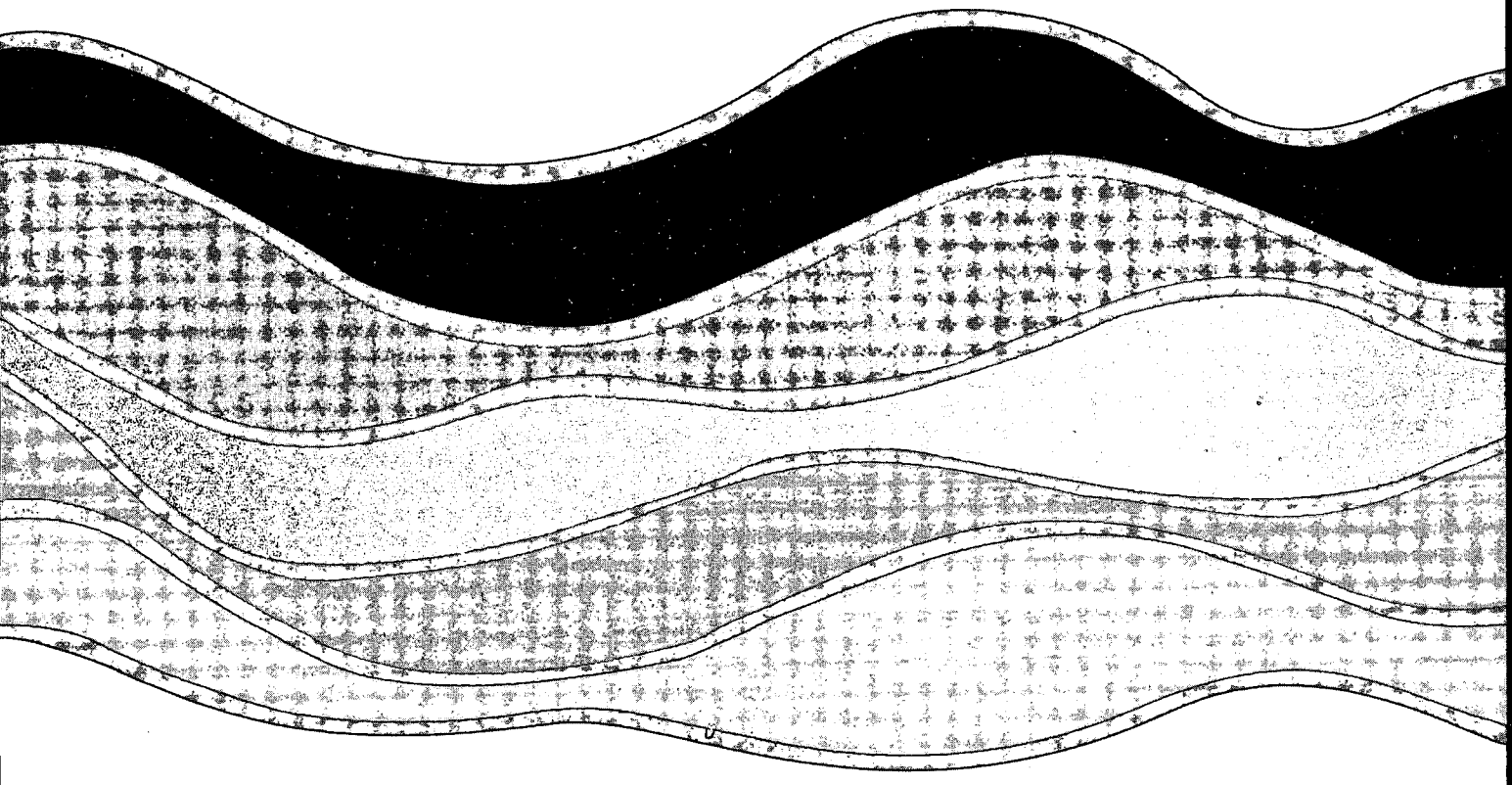

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