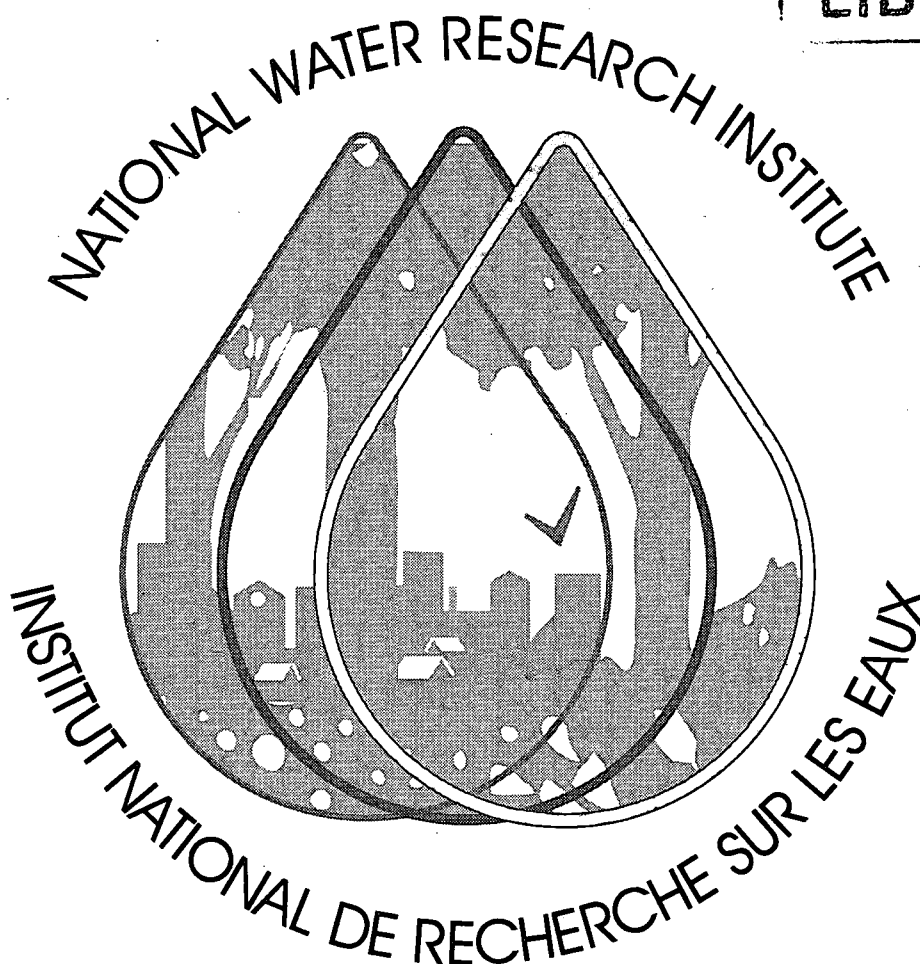


99-089
MASTER

CCIW
OCT 8 1999
LIBRARY



**NATIONAL WATER RESEARCH INSTITUTE
PESTICIDE RESEARCH, FY 1998 - 1999**

R.J. Maguire

NWRI Contribution No. 99-089

TD
226
N87
No. 99-
089

**National Water Research Institute Pesticide Research
Fiscal Year 1998 - 1999**

**Aquatic Ecosystem Protection Branch
National Water Research Institute
Burlington, Ontario L7R 4A6**

NWRI contribution 99-089

Abstract and Management Perspective

This report summarizes research on pesticides conducted at the National Water Research Institute in fiscal year 1998 - 1999.

Résumé et sommaire à l'intention de la direction

Ce rapport est un compte-rendu de la recherche sur les pesticides à l'Institut national de recherche sur les eaux durant l'année fiscale 1998-1999.

** This report is also available electronically by contacting Jenn.Dykeman@ec.gc.ca.

** On peut aussi obtenir des exemplaires électroniques de ce rapport en communiquant avec Jenn.Dykeman@ec.gc.ca.

Introduction

The National Water Research Institute (NWRI) in Burlington, Ontario and Saskatoon, Saskatchewan is Canada's largest freshwater research establishment. NWRI conducts a national program of research and development in the aquatic sciences, in partnership with the Canadian and international freshwater science communities. Research undertaken at NWRI creates knowledge, expertise and scientific leadership on water quality issues important for sustainable water resource development in Canada.

Research on pesticides at NWRI, like research on other toxic chemicals, is undertaken to elucidate fundamental principles underlying their distribution, persistence, fate and effects in aquatic ecosystems. It may also deal with "inert adjuvants" in pesticide formulations in addition to active ingredients, because there is evidence that not all "inerts" are in fact harmless to aquatic organisms. This research also addresses the more immediate concerns of the Pest Management Regulatory Agency and Environment Canada agencies that are concerned with pesticides, such as the National Wildlife Research Centre, the Commercial Chemicals Evaluation Branch, the Environmental Quality Branch (guideline development), and the Regions.

NWRI has pesticide research capability, and interests, in the following areas:

- analytical methods development (e.g., GC, HPLC, MS, AED, ICP-MS, enantiomeric determinations, immunoassays, solid-phase extraction [SPE], supercritical fluid extraction [SFE], accelerated solvent extraction [ASE], QA/QC)
- volatilization, redistribution, transport, atmospheric inputs
- chemical, photochemical and biological pathways of degradation, persistence and fate in surface waters and sediments, modeling
- groundwater movement, persistence, fate and modeling (EXPRES software for assessing the potential for groundwater contamination from pesticides)
- toxicity to aquatic/benthic organisms (battery of tests up to the level of fish, including assays for endocrine disruption), QSARs, nutrient-contaminant interactions, synergistic effects, effects of degradation products

Pesticide research at NWRI has traditionally been supported most heavily by A-Base resources. In the past it has also been supported by PESTFUND and PESTMYOP.

Attached is a summary of pesticide activities for FY 98/99, and a list of NWRI publications and reports on pesticides.

Table of Contents

<u>Study</u>	<u>Page</u>
Past chemical use and declines in wild salmon populations.....	5
Transport of pesticides through the Kenilworth sewershed to Hamilton Harbour.....	7
Distribution and persistence of DDT at Point Pelee National Park.....	9
Minimizing agricultural pesticides in the Great Lakes basin by incorporating interdisciplinary management practices.....	12
Broad spectrum analysis of pesticides in aquatic ecosystems.....	14
Fate and effects of tributyltin in fresh water.....	17
Tributyltin in Great Lakes harbours.....	19
Chronic effects of tributyltin on freshwater invertebrates.....	21
Biodegradation and environmental fate of biocides in aquatic ecosystems.....	23
Investigation of reproductive performance in forage fish exposed to agricultural runoff in the Thames River watershed, Ontario.....	26
Developing computational models for the prediction of the toxicity of pesticides, their precursors and metabolites to aquatic organisms.....	27
Sorption and metabolism of herbicides in microbial biofilms.....	28
Effects of the sulfonylurea herbicide metsulfuron methyl on the growth and reproduction of five wetland and terrestrial plant species.....	30
Persistent organic pollutants in Great Lakes areas of concern.....	32
Summary of analyses on pesticides conducted by the National Laboratory for Environmental Testing in FY 98/99.....	33

NWRI Pesticide Activities for FY 98/99

Title: Past chemical use and declines in wild salmon populations

Principal investigators: S. Brown (scott.brown@cciw.ca, TEL 905-336-6250, FAX 905-336-4420), W.L. Fairchild, Fisheries and Oceans Canada (fairchildw@mar-dfo-mpo.gc.ca), TEL 506-851-2056, FAX 506-851-2079)

Collaborators:

Sherry, J. and Bennie, D., National Water Research Institute, Burlington, Ontario; Haya, K. and Burridge, L.E., Fisheries & Oceans Canada, St. Andrew's Biological Station, St. Andrew's, New Brunswick, Canada; Eales, J.G., Department of Zoology, University of Manitoba, Winnipeg, Manitoba, Canada.

Summary of Activities:

BACKGROUND

A joint project between researchers from Environment Canada (Dr. Scott Brown, National Water Research Institute, Burlington, ON) and Fisheries & Oceans Canada (Dr. Wayne Fairchild, Gulf Fisheries Centre, Moncton, NB) surveyed historical catch records and showed that application of the pesticide formulation Matacil® 1.8D to control forest damage by spruce budworm between 1975 and 1985, was linked to declines in Atlantic salmon recreational catch. The Matacil® 1.8D formulation contained the carbamate insecticide, aminocarb, and the surfactant, nonylphenol, as primary solvent. Nonylphenol and its ethoxylates are on the Canadian Environmental Protection Act (CEPA) second Priority Substances List (PSL2) and are currently undergoing CEPA assessment for their toxicity and potential to act as endocrine disrupters. After operational spraying, measured concentrations of aminocarb in water samples were well below lethal thresholds for salmon, but estimated concentrations of nonylphenol fell within a range where estrogenic effects might be anticipated. The spray programs, occurring mid-May to mid-June, coincided with the final stages of smolt development in Atlantic salmon. Smoltification is a critical time for home stream imprinting, development of hypo-osmoregulatory abilities and occurs in association with changes in the activity of several hormonal systems.

CURRENT STATUS

Preliminary results from a follow-up laboratory experiment supported by the current CEPA assessment and by the DFO Toxic Chemicals Program showed that exposures of salmon during smoltification to environmentally relevant levels of water-borne nonylphenol or estrogen compromised subsequent sea-water survival in a portion of the exposed fish. A manuscript describing the initial phases of the work has been published (See Fairchild et al. 1999). The results have also been presented at recent scientific workshops and conferences (Aquatic Toxicity Workshop; Society of Environmental Toxicology and Chemistry).

IMPLICATIONS

While Matacil® 1.8D is no longer used, the effects it exerted may be due to its estrogenic potential. Thus nonylphenol and/or estrogenic activity stemming from other sources (e.g., domestic sewage, agricultural wastes or pulp mill effluents) might influence present day salmon populations. An interdepartmental research project to verify current findings and to assess implications for present day salmon is underway.

Resources (NWRI only): 0.9 PY, 25K O&M

Publications, Reports, Conference/Workshop Presentations:

- Brown, S.B., K. Haya, L. Burrige, E.O. Swansburg, J.T. Arsenault and W.L. Fairchild. Effects of Matacil on Atlantic salmon (*Salmo salar*) smolts. Presentation at the 25th Annual Aquatic Toxicity Workshop, Quebec City, PQ, October 1998.
- Brown, S.B., K. Haya, L. Burrige, E.O. Swansburg, J.T. Arsenault, J.G. Eales; J. Sherry, D. Bennie and W.L. Fairchild. Effects of water-borne 4-nonylphenol on Atlantic salmon (*Salmo salar*) smolts. Poster presentation at the SETAC 19th Annual Meeting, Charlotte, NC, November 1998.
- Fairchild, W.L., E.O. Swansburg, J.T. Arsenault and S.B. Brown. 1998. Does an association between pesticide use and subsequent declines in catch of Atlantic Salmon (*Salmo salar*) represent a case of endocrine disruption? Environ. Health Perspect. **107**: 349-358.
- Fairchild, W.L., E.O. Taylor, J.T. Arsenault and S.B. Brown. Does an association between 4-nonylphenol use and subsequent declines in catch of Atlantic salmon (*Salmo salar*) represent a case of endocrine disruption? Presentation at the SETAC 19th Annual Meeting, Charlotte, NC, November 1998.

NWRI Pesticide Activities for FY 98/99

Title: Transport of pesticides through the Kenilworth sewershed to Hamilton Harbour.

Principal investigators: I. G. Droppo (ian.droppo@cciw.ca; TEL 905-336-4701; FAX 905-336-4420) and J. Struger (ONT-REG EHD) (John.Struger@CCIW.ca; TEL 905-336-4966; FAX 905-336-4609)

Collaborators:

Summary of Activities:

In 1993, 1.3 million kilograms of pesticides were applied to lawns in Ontario urban areas by commercial operators (this does not include the amount applied independently by homeowners). It is suggested by Struger *et al.* (1999) that this total is at least 25% of agricultural totals and, as such, represents a significant source of pesticides for the contamination of urban aquatic ecosystems through stormwater conveyance (overland or via separate or combined sewers).

The Hamilton-Wentworth Pollution Control Plan states that on average 23 combined sewer overflow (CSO) events occur each year (May through October) at each of the more than 20 outfalls in Hamilton Harbour, resulting in a total discharge of approximately 4.33 million m³ of combined sewage. The Kenilworth Sewershed, is one of the larger discharge points (by volume) to the harbour with an estimated 311,000 m³ of combined sewage discharged for a typical rainfall year. The sewershed has a contributing area of 265.5 ha, with the upper portion of the sewershed dominated by older residential, single family dwellings, with commercial ribbons along major streets. Spring, summer and fall lawn applications of pesticides is commonplace in this area. The lower portion of the sewershed (approximately 9% of the contributing area) has mixed industrial practices with steel manufacturing being the dominant industry.

Preliminary sampling began in 1998 with all samples collected at the Kenilworth outfall during combined sewer overflow (CSO) events. Sampling will continue into the fall of 1999. CSO samples were analyzed for cypermethrin, MCPP, MCPA, 2,4-D, metolachlor, diazinon, atrazine, d-ethyl atrazine, and chlorpyrifos. Table 1 provides examples of the concentrations of pesticides being delivered to Hamilton Harbour from several storm events. Both diazinon and chlorpyrifos exceeded the Ontario water quality objectives for the protection of Aquatic Life. Concentrations of pesticides from multiple storm events will be used in conjunction with the recorded rainfall record to model the loadings of pesticides into Hamilton Harbour. Results from this study will be useful for the evaluation of the source, fate and effect of pesticides in Hamilton Harbour.

Table 1. Detected concentrations ($\mu\text{g/L}$) of various pesticides from 5 different overflow events.

Date	Diazin on	chlorpyrif os	MCP P	MCP A	2,4- D	metolachi or
Jun. 12/98						1.2
Jun. 25/98	0.11		1.5		2.1	
Jun. 30/98					0.78	
Aug. 10/98			0.51	0.54		
Aug. 22/98	0.088	0.069				

Resources (NWRI only): On an annual basis approximately 0.05 PYs of support is directed to this study from each of C. Jaskot, B. Trapp and I. Droppo (total 0.15 PYs). In addition 5K O&M and 30K of capital is used in this study.

Publications, Reports, Conference/Workshop Presentations:

Struger, J., B. Ripley and G. Gris. 1999. Pesticide concentrations in urban aquatic environments. Poster presented at the International Association for Great Lakes Research Conference, Cleveland, Ohio, May 25-28, 1999.

NWRI Pesticide Activities for FY 98/99

Title: Distribution and persistence of DDT at Point Pelee National Park

Principal Investigator: A.S. Crowe (Allan.Crowe@CCIW.ca; TEL 905-336-4585; FAX 906-336-6430)

Collaborators: Parks Canada (D. Reive, Point Pelee National Park)

Summary of Activities:

Point Pelee National Park was the first National Park created in Canada based on its biological value. However, even after the Park was established in 1918, a considerable amount of commercial and residential land use and activities continued. Apple orchards occupied a large proportion of the south and central area of the Park until the late 1960's. Numerous houses and summer cottages existed in the Park until the mid-1970's. Several campgrounds and trailer parks existed within the park until the 1960's, and currently only one restricted-use campground remains. Accompanying these activities was the large scale use of the pesticide DDT between 1948 and 1967 for mosquito control in recreational areas and pest control in the apple orchards. DDT was applied within the Park primarily as a particulate spray over wide areas and also as "toss bombs" at specific sites or pools of water.

The US EPA declared DDT to be an environmental hazard because of its long residual life and its accumulation in food chains where it proved to be detrimental to certain forms of wildlife. The US EPA banned its use on January 1, 1973, and a similar ban soon followed in Canada. It was thought that DDT and its degradation products DDD and DDE would no longer exist at Point Pelee. However, during 1998, DDT was detected in the shallow soil within the Park, by researchers from the University of Windsor undertaking a wildlife survey. Reported concentrations in soil exceeded the Ontario Ministry of Environment limits for DDT for Recreational/Parkland land use of 1.6 µg/g [MOE 1997]. The highest concentrations detected were located near the Camp Henry campground. This raised concerns about the potential health risk to Park employees and visitors.

In April, 1998, Parks Canada requested the assistance of the National Water Research Institute of Environment Canada in assessing the extent of DDT contamination at two areas of concern, Camp Henry and the Park's Maintenance Compound. The objectives of the field sampling/analysis program were to:

1. verify the previous reported results (from University of Windsor);
2. determine the extent of the zones of high levels of DDT, both spatially and with depth;
3. determine if other areas of high levels of DDT exist in the soils within the campground and the Maintenance Compound;
4. check the Park's groundwater supply wells in the vicinity of Camp Henry for dissolved DDT.

A subsequent computer modelling study was undertaken to assess the environmental factors controlling the persistence, and distribution of DDT within the soil and groundwater.

The results of the field and modelling study can be summarized as follows:

1. Analyses of shallow soil samples collected at Point Pelee National Park show the presence of DDT, and often in concentrations that exceed the Ontario Ministry of Environment limits for DDT in soil for Recreational/Parkland land of 1.6 µg/g.
2. Analyses of groundwater obtained from several wells show DDT is several orders of magnitude below the Canadian Drinking Water Guideline of 30 µg/L at all wells.
3. Concentrations of DDT decrease rapidly with depth, indicating that DDT is generally confined to the upper 20-40 cm of the soil. This corresponds to the organic-rich soil horizon.
4. DDT is not mobile in the soil horizon, either in its pure phase or dissolved phase;
 - properties of the soil (high organic carbon) and DDT (high K_{oc}) lead to a strong attenuation of DDT to the organic matter at the surface of the soil.
 - the low solubility of DDT and the high hydraulic conductivity of the soil lead to negligible concentrations of dissolved DDT in the groundwater.
5. Localized areas of high concentrations of total DDT at Camp Henry and the Maintenance Compound are probably due to spills or disposal.
6. Computer simulations confirm that DDT is essentially not mobile in the soil, will remain at the soil surface, and will not leach to the water table.
7. The half-life of DDT in soil in most of the soil at Point Pelee probably exceeds 40 years. In marsh sediments, the half-life of DDT is probably <10 years.

A current study is focusing on further computer analyses to determine the environmental factors leading to the persistence of DDT and its metabolites. Future research will also be undertaken to assess the persistence of Dieldrin, which was frequently found at Point Pelee National Park in locations and at levels comparable to DDT.

Resources (NWRI only):

P.Y.'s - principal investigator (0.35 PY), technical support from Tech.Ops. 0.2 PY (C. Talbot, E. Walker, T. Breedon)

10K O&M and NLET allocation (in addition 75K was recovered from Parks Canada for O&M, capital depreciation, salary recovery, field expenses, consumables, etc.)

Publications:

Crowe, A.S. 1999. The distribution and persistence of DDT at Point Pelee National Park. *in* Proceedings of The 1999 Parks Research Forum - Ontario Annual Meeting, Guelph, Ontario, April 22 and 23, 1999, 12 pp. (submitted)

** in addition, two confidential reports were prepared and sent to Parks Canada

Presentations:

Crowe, A.S. The distribution and persistence of DDT at Point Pelee National Park.
Presented at The 1999 Parks Research Forum - Ontario Annual Meeting,
Guelph, Ontario, April 22-23, 1999.

NWRI Pesticide Activities for FY 98/99

Title: Minimizing agricultural pesticides in the Great Lakes basin by incorporating interdisciplinary management practices.

Principal NWRI Investigator: H.Y.F. Ng (howard.ng@cciw.ca, TEL 905-336-4905, FAX 905-336-4420)

Collaborators: J. Gaynor (principal investigator), C.S. Tan, C.F. Drury and T. W. Welacky (Agriculture & Agri-Food Canada); I.J. vanWesenbeeck (DowElanco, Environmental Fate)

Summary of Activities:

Initiative

The Great Lakes basin is the home to 80% of Ontario's crop land. Contaminants in the Great Lakes originate from all kinds of human activities. Herbicides account for 75% of pesticide use in Ontario. Herbicides are generally applied once a year to control weeds and optimize yields in field crops. Increased public concern of the role of agriculture and associated chemical use has prompted an urgent need in obtaining information on the impact and proposed agricultural management practices on water quality.

Approach

In response to the proposed agricultural management practices on the Great Lakes water quality, an interdisciplinary, multifaceted approach to corn management, incorporating annual ryegrass intercrop, tillage, water table control, subsurface irrigation and banded application to reduce herbicide loss through surface runoff, tile discharge and the persistence of the herbicides in soil, were investigated. The investigation was conducted on plot scale of Brookston soil incorporated with two drainage systems with four tillage and intercrop treatments replicated twice. The herbicides studied included atrazine and its metabolite, metolachlor, and metribuzin.

Summary

The intent of intercrop was to increase infiltration of water and reduce runoff and accompanying herbicide loss. Conservation tillage (soil savers) combined with ryegrass intercrop has potential to decrease total herbicide loss in tile drain and surface runoff by 46 to 49% compared to conventional moldboard plow tillage without intercrop. Surface runoff was reduced by the intercrop treatment which reduced herbicides transport.

Water table control and subsurface irrigation increased herbicide transport by surface runoff but decreased loss through tile discharge so that total herbicide loss did not differ from drained treatments without subirrigation.

The banded herbicide application was half of that amount of broadcast application. In this study, maximum triazine and metolachlor loss in surface runoff and

tile discharge was 3.8 and 2.3 % respectively, of that applied. When herbicides were applied entire area, maximum losses were 6.6% for atrazine and 4.7% for metolachlor. Of the cultural practices studied, reduced herbicide input by band application will reduce herbicide loss irrespective of environmental factors.

The persistence of the herbicides atrazine (1.1 kg/ha), metribuzin (0.5 kg/ha) and metolachlor (1.68 kg/ha) in a corn management system was followed.

Ryegrass intercrop incorporated with conventional tillage system had little consistent effect on soil residues of the herbicides at 0 to 10 cm depths. Half life for atrazine ranged from 34 to 56 days, metribuzin 24 to 35 days and metolachlor 40 to 79 days with longer half life in dry years. Des-ethyl atrazine was the major metabolite of atrazine which persisted along with atrazine and metolachlor to the next planting season. Less than 10% of the original herbicide application was recovered the year following application.

The mouldboard plowed soil had higher soil residues in the 10 to 15 and 15 to 20 cm depths than conservation tillage. Herbicide residues were larger in mouldboard plows combined with intercrop than in the other treatments. Water table control significantly reduced herbicide half life, but not in drier years. On some sampling dates and depths more des-ethyl atrazine was recovered from water table controlled and subsurface irrigation system. Herbicides with high water solubility and low affinity for soil may leach to deeper depths in no-tillage than conventional tillage culture. Thus, environmental factors affect herbicide residues more than cultural practices.

Environmental factors such as organic matter, soil texture and pH affect persistence of herbicides in soil. These factors control the availability of the herbicides to microbial or chemical alteration. Other factors such as soil moisture content and temperature relate to the kinetics of persistence.

Current Status (1999-00):

The study of persistence of herbicides is ongoing. The study will be conducted on 4 ha farm-based fields with a focus on the role of compost on herbicides persistence.

Resources (NWRI only): 0.3 PY, 5K O&M, 15K capital

Publications, Report, Conference/Workshop Presentations:

Gaynor, J.D., C.S. Tan, H.Y.F. Ng, C.F. Drury, T.W. Welacky and I.J. van Wesenbeeck. 1999. Soil persistence of atrazine, metolachlor and metribuzin in controlled drainage/subirrigation corn management. *J. Environ. Qual.* In press.

Gaynor, J.D., C.S. Tan, H.Y.F. Ng, C.F. Drury, T.W. Welacky and I.J. van Wesenbeeck. 1999. Water quality from corn production using intercrop, controlled drainage/subirrigation, and tillage management with band applied atrazine, metribuzin and metolachlor. *J. Environ. Qual.* In press.

NWRI Pesticide Activities for FY 98/99

Title: Broad spectrum analysis of pesticides in aquatic ecosystems

Principal Investigator: J. Headley (john.headley@ec.gc.ca; TEL 306-975-5746; FAX 306-975-5143)

Collaborators: (J. Lawrence, AEPB, NWRI; A. Cessna, AAFC; L.C. Dickson, Toxicology Research Centre; J. Gandrass, GKSS, Germany; Jon Gillies, University of Saskatchewan and T.R. Neu, UFZ, Germany)

Summary of Activities:

Activities for the 1998/99 period were focused primarily on finalizing the preparation of reports on pesticide research pertaining to the four areas listed below. Activity 1 and 2 are on-going.

1. Development and application of methods for determining the uptake and transformation of pesticides, such as p,p'-DDT, diclofop-methyl, triallate, lindane, atrazine, parathion-methyl and dimethoate, thifensulfuronmethyl and methsulfuron-methyl in agricultural run-off water, riverine biofilms, amphipods, groundwater and wetland ecosystems.

Biofilms are believed to play a significant role in the fate and transport of contaminants in aquatic environments. However little is known about the rates of sorption (k) and partitioning (K_d) of contaminants to biofilms. Studies of the latter were performed using mature biofilm cultivated in a roto-torque reactor. The reactor was flushed with river water containing a mixture of tetrabutyltin, p,p'-DDT, diclofop-methyl, triallate, lindane, atrazine, parathion-methyl and dimethoate in two experiments. The first experiment was conducted at a spiked level of 1 $\mu\text{g/L}$ and the second at 10 $\mu\text{g/L}$ for each component. Apart from dimethoate, there was rapid depletion of all contaminants from the water phase within the first 5-10 minutes with sorption occurring by pseudo first order kinetics. In general, the mean values of k (10^{-4} min^{-1}) increased with water solubility and were: 8, 70, 110, 180, 230, 370 and 100 for pp-DDT, diclofop-methyl, triallate, tetrabutyltin, lindane, atrazine and parathion-methyl respectively. The values of $\log K_d$ increased linearly with $\log K_{ow}$ and decreased linearly with the log of the aqueous solubilities. In general, K_{ow} values were significantly greater than the corresponding values of K_d , indicating that partitioning of contaminants was not limited to lipophilic regions of the biofilm.

2. Treatability of Prairie natural waters containing 2,4-D, including measurement of the dependence of the rates of removal of 2,4-D on temperature, pH, and dissolved organic carbon in riverine systems.

This work is continuing in collaboration with the University of Saskatchewan. Preliminary results indicate that the 2,4-D is most rapidly degraded in natural river water at ambient pH and temperature.

3. Measurement of the distribution and flux of organochlorine pesticides in delta regions of large river basins.

There is a lack of information on of organochlorine pesticides (OCPs) in waters of Russian rivers. This hampers evaluation of their transboundary. Studies were undertaken from 1988-1994 to: (i) characterize the levels and geographical distribution of OCPs major Russian river basins, and (ii) determine trends in temporal dynamics of the water borne contaminants. Russian rivers were contaminated by OCPs to an extent similar to that found in many countries one to two decades earlier. γ -HCCH (1,2,3,4,5,6-hexachlorocyclohexane) was the most widespread pesticide, followed by: α -HCCH, DHC (2,4,5,6,7,8,8-heptachlor 4,7-endo-methylbicyclo [4,3,0] -5-nonene), HCB (hexachlorobenzene), DDT (1,1-di (4'-chlorphenyl)-2,2,2-trichlorethane), β -HCCH, DDE (1,1-di (4'-chlorphenyl)-2,2-dichlorethylene) and DDD (1,1-di (4'-chlorphenyl)-2,2-dichlorethylene) based on data from the State Network of Environmental Monitoring (SNEM). Concentrations seldom exceeded maximum allowable concentrations (MACs) and mean concentrations met National Russian ambient water quality criteria. Highest exceedence (expressed as a percentage of the number of water samples) of the MAC occurred for γ -HCCH (19%) and α -HCCH (17.3%), with lower exceedences observed for DDT (4.3%), DDE (1.3%), and DDD (0.2%). Complementary observations were made using established QA/QC protocols. The latter studies showed that much lower exceedences had occurred: γ -HCCH (2.4%), DDT (2.1%), α -HCCH (2.0%), with negligibly low exceedences observed for DDE (0.4%), β -HCCH (0.3%) and DDD (0.1%). In general, levels of OCPs in Russian inland water during 1991 -1993 was similar to that found in Western countries a decade earlier.

4. Review of methods for the determination of herbicides residues in biota

Current extraction, derivatization and clean-up techniques, and instrumental methods are reviewed for the analysis of herbicide residues in biota. Sampling procedures are shown to be an integral part of the methodology. Herbicide analysis is seldom based on analyte-specific methods but is usually integrated into multi-residue methods. Current methods generally utilize relatively small sample sizes and miniaturized apparatus to take advantage of advances in instrumental performance and detection of analytes. These methods reduce the amount of solvent used for sample preparation and help to minimize waste generation. As well as using less solvent, the resulting miniaturized methods tend to be generally cheaper, faster, and less labour-intensive than conventional methods and, furthermore, they reduce analyst exposure to hazardous materials.

Mass spectrometry, interfaced with high-resolution gas chromatography, high performance liquid chromatography and capillary electrophoresis, has become the detection method of choice for herbicide analysis. Mass spectrometry is well suited to the confirmation of target analytes and the tentative identification of unknown analytes. High performance liquid chromatography-mass spectrometers are becoming more widely available and less expensive. Capillary electrophoresis is a relatively new separation technique providing many advantages over traditional gas and liquid chromatography, including shorter analysis times and smaller injection volumes. There

have been advances in the development of immunoassays primarily for the rapid screening for herbicide residues. These methods, once optimized, can facilitate high sample throughput at relatively low cost compared to conventional approaches. To date however, development has been limited to aqueous systems and little immunoassay work has been done for the direct determination of herbicides in biota.

Resources (NWRI only): 0.3 PY (John Headley and Kerry Peru), O&M \$1.5K

Publications, Reports, Conference/Workshop Presentations:

- Headley, J.V., A. Cessna and L.C. Dickson. 1999. Herbicides residues in biota, determination. *Encyclopedia of Analytical Chemistry: Instrumentation and Applications*. (accepted as submitted)
- Headley, J.V., K.M. Peru, J. Gandrass, J. Kubella and Y. Gong. 1998. Relative uptake kinetics of pesticides in riverine biofilm. *Environ. Sci. & Technol.* **32**: 3968-3973.
- Zhulidov, A.V., J.V. Headley, D. F. Pavlov, R.D. Robarts, L.G. Korotova, V.V. Fadeav and O.V. Zhulidova. 1998. Distribution of organochlorine pesticides in Russian natural waters. *Journal of Environmental Quality* **27**: 1356 - 1366.
- Lawrence, J.R, G. Kopf, J.V. Headley and T.R. Neu. Sorption and metabolism of selected herbicides in river biofilm communities. Presented at the Annual Meeting of American Society for Microbiology, Atlanta, GA, May 22-24, 1998.

NWRI Pesticide Activities for FY 98/99

Title: Fate and effects of tributyltin in fresh water

Principal investigator: R.J. Maguire (jim.maguire@ec.gc.ca; TEL 905-336-4927; FAX 905-336-4420)

Collaborators: F. Yang

Summary of Activities:

Tributyltin (TBT) is perhaps the most toxic chemical that has ever been deliberately introduced into the aquatic environment. Although it has been used as a molluscicide in the control of Schistosomiasis in Africa, and as a general lumber preservative, it is the antifouling use of TBT that has caused the greatest environmental concern. Antifouling uses of TBT began in the 1960s and 1970s. France was the first country to restrict the use of TBT in antifouling paints. French authorities had observed a decrease in growth rates of oysters in some Atlantic coastal areas as early as 1975. Abnormal spatfall, decrease in survival rates and shell malformations had also been observed since about 1974. By the early 1980s effects on oysters in Arcachon Bay in France were linked to TBT, and in 1982 France banned the use of TBT-containing antifouling paints on vessels shorter than 25 m. Many other countries have adopted similar regulations, among them, Canada in 1989.

Attempts have been made in several countries to assess the effectiveness of their TBT regulations. In general it appears that the regulations have resulted in reduced TBT contamination of water and some organisms, and recovery of populations of some organisms, particularly those close to marinas. However, in general, such reductions have not been observed in areas frequented by large vessels that continue to be painted legally with TBT-containing antifouling paints. In addition, many researchers have noted little or no reduction in TBT concentrations in sediments several years after TBT regulations were enacted, and this has been attributed to the appreciable persistence of TBT in sediments. TBT-contaminated sediments may continue to pose a hazard to benthic organisms and to organisms in the water column, either indirectly through eating benthic organisms, or directly, after sediment resuspension.

This year, work continued on the determination of the persistence of TBT in sediment cores from several major harbours across Canada. In conjunction with the University of Waterloo, research was initiated on the toxicity of tributyltin to freshwater invertebrates. That work will continue next year. In addition, work will start on the third national survey for organotin compounds, including TBT, in the Canadian environment. An assessment of whether TBT can be considered a TSMP Track 1 substance will also be made in FY 99/00.

Resources (NWRI only): PY: 1.6 (0.5 PY for S.P. Batchelor, 1.0 PY for F. Yang, 0.1 for R.J. Maguire), 84K O&M, 0K capital

Publications, Reports, Conference/Workshop Presentations:

- Liu, D., R.J. Maguire, Y.L. Lau, G.J. Pacepavicius, H. Okamura and I. Aoyama. Microbial adsorption of cyanazine and metolachlor. *J. Environ. Sci. Health* **B33**: 1-15.
- Day, K.E., R.J. Maguire, D. Milani and S.P. Batchelor. 1998. Toxicity of tributyltin to four species of freshwater benthic invertebrates using spiked sediment bioassays. *Water Qual. Res. J. Canada* **33**, 111-132.
- Thompson, J.A.J., S. Douglas, Y.K. Chau and R.J. Maguire. 1998. Recent studies of residual tributyltin in coastal British Columbia sediments. *Appl. Organometal. Chem.* **12**: 643-650.
- Yang, F., Y.K. Chau and R.J. Maguire. Occurrence of butyltin compounds in beluga whales (*Delphinapterus leucas*). *Appl. Organometal. Chem.* **12**: 651-656.
- Liu, D., G.J. Pacepavicius, R.J. Maguire, Y.L. Lau, H. Okamura and I. Aoyama. Mercuric chloride - catalyzed hydrolysis of the new antifouling compound Irgarol 1051. *Water Res.* **309**: 155-163.
- Allan, L.M., D.K. Verma, F. Yang, Y.K. Chau and R.J. Maguire. Evaluation of extraction procedures for the analysis of butyltin compounds in air. NWRI Contribution 98-030, 12+ pp.
- Maguire, R.J. Assessment of the tributyltin situation in Canada. 215th American Chemical Society National Meeting, Dallas, TX, U.S.A., March 29 - April 2, 1998, Division of Environmental Chemistry **38** (1), 124-126.
- Maguire, R.J. Assessment of the tributyltin situation in Canada. Society for Environmental Toxicology and Chemistry (Europe) 8th Annual Meeting, Bordeaux, France, April 14-18, 1998, Abstract 2E/001, p. 42.
- Okamura, H., D. Liu, R.J. Maguire, I. Aoyama, G.J. Pacepavicius and L. Lau. Photodegradation of Irgarol 1051 in water. 19th Biennial Conference of the International Association on Water Quality, Vancouver, B.C., June 21-26, 1998.
- Yang, F., Y.K. Chau and R.J. Maguire. Occurrence of butyltin compounds in Beluga whales (*Delphinapterus leucas*). European Union "Speciation 21" Workshop on Environmental Issues - 2. Analytical Methods for Organometallic Compounds. Amsterdam, The Netherlands, September 24-26, 1998.
- Champ, M.A., T.J. Fox, H.E. Guard, R.J. Maguire, K.H. Pannell, P.F. Seligman and G.W. Swain. The structure and function of an international, independent Marine Coatings Board for assessing the risks of alternative antifouling products and technologies. 10th International Congress on Marine Corrosion and Fouling, Melbourne, Australia, February 7-12, 1999.

NWRI Pesticide Activities for FY 98/99

Title: Tributyltin in Great Lakes harbours

Principal Investigator: F. Yang (Fan.Yang@cciw.ca; TEL 905-336-6412; FAX 905-336-4420)

Collaborators: R.J. Maguire

Summary of Activities:

Pesticidal organotin compounds have been found in the Canadian environment. The organotin compound of most concern is tributyltin (TBT), because of its extremely high toxicity to aquatic organisms. The antifouling use of TBT has been regulated 10 years ago in Canada, but it still occurs in aquatic environment today. Research was carried out on (1) monitoring of butyltin compounds in marinas and their seasonal variations, (2) biomonitoring study with caged mussels at polluted harbour sites in southern Ontario.

(1) Monitoring of TBT in marinas and seasonal variations

In order to find out the sources of TBT in water, the concentration of TBT in six marinas were monitored for nine months. The concentration of TBT in water was found to increase with the increasing boating activities in marinas. The concentration of TBT was up to 14 ng Sn /L in summer season, and lower than 2 ng Sn/L in winter time. Water samples with various depth in middle of lake Ontario were also collected, and TBT was only found in the water samples obtained from a depth of 0.5 m, and was not determined in deeper water samples at two locations. The results indicated that small amount of TBT was still released from antifouling paint and not from resuspended sediment in water.

(2) Biomonitoring study with caged mussels at selected harbors in southern Ontario

The mussels (*Elliptio complanata*) were collected from Balsam Lake and were directly used to study the bioaccumulation of TBT. Caged mussels were placed in six selected harbour sites. Four mussels from each cage and 4L water samples were collected at each site monthly and analyzed for butyltin compounds. The exposure experiment lasted one year in the harbours. Another 100 mussels were used to study the uptake of organotin compounds in water spiked TBT in the lab. Preliminary results showed that bioaccumulation of TBT in mussel was not only related to the exposure time but also related to mussel size. After exposure for several months in the harbours, the high concentrations of butyltin compounds were determined in caged mussels.

Resources (NWRI only): PY 1.0, 23K O&M

Publications:

Yang, F., Y.K. Chau and R.J. Maguire.1998. Occurrence of butyltin compounds in Beluga whales (*Delphinapterus leucas*). Appl. Organometal. Chem. 12: 651.

Allan, L.M., D.K. Verma, F. Yang, Y.K. Chau, and R.J. Maguire. 1998. Evaluation of extraction procedures for the analysis of butyltin compounds in air. National Water Research Institute Contribution No. 98-030.

Yang, F., Y.K. Chau and R.J. Maguire. 1998. Determination of butyltin compounds in biological samples. The workshop of the analysis of organotin compounds, Vrije University, Amsterdam.

NWRI Pesticide Activities for FY 98/99

Title: Chronic effects of tributyltin on freshwater invertebrates

Principal investigator: A. Bartlett (Univ. Waterloo graduate student in AEPB/NWRI)
(adrienne.bartlett@cciw.ca, TEL 905-336-4405, FAX 905-336-4420)

Collaborators: U. Borgmann, R.J. Maguire

Summary of Activities:

This project started in FY 98-99. The purpose of this project is to examine the chronic effects of TBT in native freshwater invertebrates. Marine research on TBT has been quite extensive since the early 1970s, primarily because of the prominent, widespread effects on marine populations and the devastating economical impact on commercial fisheries. The effects of TBT in freshwater are not as well defined or as economically important, and as a result, the research on freshwater impacts of TBT has not had the incentive to expand to the extent of marine research. There have been few, if any, full life-cycle studies on the impacts of TBT in freshwater invertebrates, there is a lack of methodology needed in order to fill in some of these deficiencies in the data, there has been no environmental risk assessment performed, and yet TBT is still used in the Great Lakes and is present in the environment at concentrations known to cause biological effects. In order to address these concerns, the following objectives are proposed.

1. A chronic spiked sediment bioassay for *H. azteca* will be developed in order to determine the effect of TBT on survival, growth, reproduction, and sex ratio over two generations of amphipods. Concentrations of TBT will be measured in tissue, overlying water, pore water, and sediment. The results will be compared over two generations to determine if there are cumulative effects (i.e. if the second generation is more sensitive than the first), and the most sensitive endpoint of toxicity will be determined. Additional studies will determine the rate of depuration of TBT, and the route of uptake of TBT from the environment. Optional experiments to determine the effect of salinity and pH on the bioavailability and/or toxicity of TBT may be conducted using freshwater and salt-tolerant *H. azteca*.
2. A chronic, multi-species, spiked sediment bioassay based on the results obtained from the *H. azteca* experiments will be developed. Test organisms include *H. azteca* (amphipod), *C. riparius* (midge larva), *H. limbata* (mayfly larva), *Daphnia magna* (water flea), *T. tubifex* (oligochaete worm), *Physella gyrina* (snail), and Sphaeriidae (fingernail clams). The experiments will be carried out in aquaria containing control, low, medium, and high concentrations of TBT based on the results of the *H. azteca* experiments. The sensitivity of each species relative to *H. azteca* will be determined based on general population effects such as numbers of adults surviving, numbers of young produced, and tissue concentrations.
3. A detailed chronic spiked sediment bioassay will be developed for one organism, and studies similar to those on *H. azteca* will be performed. The choice of organism

will be the most sensitive species as determined from the results of the multi-species experiments. An optional experiment would involve collecting tissues and investigating the effects of TBT on the invertebrate endocrine system.

4. In order to validate the laboratory component of this project, a field component on selected species will be incorporated. Animals will be collected from various sites, tissue concentrations will be measured, and the results will be interpreted using the results of the spiked sediment experiments. Sediments will be collected from various sites, bioassays will be conducted using laboratory animals, and the results can be used to interpret the significance of environmental levels of TBT. Optional experiments include benthic community surveys of contaminated sites and a mesocosm study, both of which would be collaborative efforts.

Resources (NWRI only): 0.8 PY (0.1 U. Borgmann, 0.1 W. Norwood, 0.5 S.P. Batchelor, 0.1 R.J. Maguire), 25K O&M, 0K capital.

Publications, Reports, Conference/Workshop Presentations:

NWRI Pesticide Activities for FY 98/99

Title: Biodegradation and environmental fate of biocides in aquatic ecosystems

Principal investigators: D. Liu (Dickson.Liu@cciw.ca; TEL 905-336-4576; FAX 905-336-4989) and L. Lau (lam.lau@cciw.ca; TEL 905-336-4897; FAX 905-336-4420)

Collaborators: R.J. Maguire, H. Okamura and I. Aoyama (Okayama University, Japan)

Summary of Activities:

Irgarol 1051 (a triazine related to atrazine) is a new antifouling pesticide that is being used in a number of countries, and is presently being considered for registration under the Pest Control Products Act in Canada. Evidence is accumulating in some countries that ambient concentrations may be high enough to have an effect on sensitive phytoplankton in coastal waters. Research in our laboratory has been geared toward the persistence and effects of Irgarol 1051. In addition, surveys have been done in major Canadian ports in advance of the anticipated Canadian registration in order to determine baseline concentrations that at this stage could only have resulted from leaching from vessels painted in other countries. Since Irgarol is a new chemical, there is no information in the open literature on its environment persistence, fate, pathway and degradation products, which would hinder the Irgarol's risk assessment.

Chemical degradation of Irgarol 1051 was studied and the results showed that mercuric chloride was capable of rapidly catalyzing the hydrolysis of Irgarol in distilled water and buffer solutions. The degradation appeared to follow the reaction of a catalyzed hydrolysis and was not significantly affected by the pH tested (5 to 9). The mechanism for the catalyzed hydrolysis was primarily due to the formation of bidentate chelation through nitrogen (No. 5) on the ring and the nitrogen on the cyclopropylamino side chain in Irgarol 1051 with the mercuric ion. The resulting four-member chelate complex would weaken the cyclopropyl-amino bound considerably, thus facilitating the hydrolysis reaction. Ultraviolet spectroscopy of the reaction mixtures and the identification of Irgarol hydrolysis product M1 (2-methylthio-4-tert-butylamino-6-amino-s-triazine) provided the basis for the proposed mechanism on the mercuric-catalyzed hydrolysis of Irgarol 1051. M1 appeared to be more stable than the parent compound Irgarol, thus implying its possible accumulation in the environment. This hypothesis has been positively verified in the Seto Inland Sea (Japan) recently, thus further reinforcing our belief that metabolite and degradation product identification is critical in the assessment of a pesticide's ultimate impact on the environment.

Photodegradation of Irgarol 1051 by natural sunlight in the aquatic environment was studied and the rates of Irgarol degradation in sea water and river water were found to be much higher than those in pure water and buffer solutions (pH 5, 7, and 9). Certain unknown organic photosensitizers in the natural waters were found to be responsible for the observed accelerated photodegradation. Three significant photodegradation products were also observed in the reaction mixtures, with one being

identified as M1 by GC-MS analysis. Thus, M1 appeared to be a common degradation product during the microbial and photodegradation of Irgarol 1051.

Although Irgarol 1051 is generally considered to be non-volatile, there are no data in the published literature on its volatility. Volatility is one of the major mechanisms for the removal of many pesticides from the aquatic environment. Therefore, experiments were conducted in our laboratory to test the volatility of this herbicide. The results showed that Irgarol 1051 could not always be considered as non-volatile. When the water temperature is high and/or the water motion is rapid, significant losses can occur through volatilization. These results will assist in the assessment of the fate and pathway of Irgarol 1051 in the aquatic environment.

The widespread occurrence of Irgarol 1051 in the European aquatic environment has been established. However, no data are currently available in the open literature on the ambient levels of this pesticide in North American and Asian aquatic environments. Consequently, a joint long-term monitoring study between Canada and Japan was initiated to determine whether Irgarol 1051 is present in the Canadian (i.e., via leaching from ships painted in other countries) or Japanese aquatic environment. Six large trade ports (Vancouver, Toronto, Montreal, Halifax, Mizushima and Kobe), 73 marinas and 13 fishery harbours were surveyed. Irgarol 1051 was not detected in the Canadian aquatic environment. Among the 6 trade ports surveyed, only the Mizushima Port had low levels of Irgarol, up to 19.5 ng/L. Approximately 27% of the marinas surveyed in the Seto Inland Sea were found to have been contaminated by Irgarol 1051, ranging in concentrations between 12.5 and 264.2 ng/L. Irgarol 1051 was found more frequently in fishery harbours than in marinas, indicating that besides marinas and trade ports, fishery harbours can also be a significant source of contamination for the aquatic environment. Irgarol has been reported to be highly toxic to non-target marine algae with the observable growth inhibition at a concentration as low as 50 ng/L, which is well within the ambient concentration levels found in some localities of the Seto Inland Sea. Works are continuing on Irgarol monitoring and its ecotoxicity assessment.

Sea-Nine 211 (4,5-dichloro-2-n-octyl-isothiazolin-3-one) is a new alternative antifouling biocide. Being a new chemical, there is virtually no information in the open literature on its environmental persistence, fate and pathway. Preliminary study in our laboratory indicated that this biocide is easily biodegradable with a half life less than a day in the aquatic environment. Work will continue to determine its pathway and degradation product.

Resources (NWRI only): (estimate PYs for NWRI staff: 2.1 [D. Liu = 1.0, R.J. Maguire = 0.1, G. Pacepavicius = 1.0], O&M = 20 K, and capital = 10K)

Publications, Reports, Conference/Workshop Presentations

Liu, D., G.J. Pacepavicius, R.J. Maguire, Y.L. Lau, H. Okamura and I. Aoyama. 1999. Mercuric chloride-catalyzed hydrolysis of the new antifouling compound Irgarol 1051. *Wat. Res.* **33**: 155-163.

- Okamura, H., I. Aoyama, D. Liu, R.J. Maguire, G.J. Pacepavicius, and Y.L. Lau. 1999. Photodegradation of Irgarol 1051 in water. *J. Environ. Sci. Health*. **B34(2)**: 225-238.
- Liu, D., G.J. Pacepavicius, R. J. Maguire, Y.L. Lau, H. Okamura and I. Aoyama. Survey for the occurrence of the new antifouling compound Irgarol 1051 in the aquatic environment. *Wat. Res.* (in press).
- Lau, Y.L., D. Liu and G.J. Pacepavicius. 1998. Volatility of Irgarol 1051. *NWRI Contribution No. 98-178*.

NWRI Pesticide Activities for FY 98/99

Title: Investigation of reproductive performance in forage fish exposed to agricultural runoff in the Thames River watershed, Ontario

Principal investigator: M. Hewitt (mark.hewitt@cciw.ca; TEL 905-319-6924; FAX 905-336-6430)

Collaborators: M. McMaster, G. Van Der Kraak (University of Guelph)

Summary of Activities:

This work involves regular assessments of the reproductive performance of forage fish in the Middle Thames and Flat Creek tributaries within the Thames River watershed in southern Ontario. Regular fish collections using backpack electrofishing techniques have been initiated in the summer of 1998 and are continuing. Small numbers of both sexes of creek chub, blacknose dace and johnny darters are collected and measurements of length, weight and gonad weight and liver weight performed. Gonadal tissues are fixed and sectioned for histology as well as incubated for production of gonadal sex steroids which are measured by radioimmunoassay. The objective of these studies is to determine if runoff is adversely affecting reproductive performance in these species. A secondary objective is to obtain knowledge of the background reproductive physiology of these species as little is known about them.

Resources (NWRI only): total estimated 0.1 PYs between L. Luxon and N. Jones

O&M: \$4K for histology and fishing supplies.

Capital: purchase of electrofisher from minor cap (\$9.5K)

Publications, Reports, Conference/Workshop Presentations:

A presentation is being made in FY 99/00.

NWRI Pesticide Activities for FY 98/99

Title: Developing computational models for the prediction of the toxicity of pesticides, their precursors and metabolites to aquatic organisms.

Principal investigator: K.L.E. Kaiser (klaus.kaiser@cciw.ca; TEL 905-336-4756; FAX 905-336-6430)

Collaborators: K.M. Gough (Winnipeg), S.P. Niculescu (Burlington), G. Schüürmann (Germany), W. Klein (Germany), J. Dearden (UK), T.W. Schultz (USA), P.J. Jurs (USA), various staff at CCEB.

Summary of Activities:

Traditional methods in Quantitative Structure-Activity Relationships (QSARs) are based on comparatively small sets of chemicals with relatively small, easily described variations in substituents. In contrast, the applied environmental field deals with a broad spectrum of substances arising from many sources. For example, the OECD list of High Production Volume Chemicals, many of which are pesticides, contains over 4000 substances. As these substances encompass all kinds of materials, traditional QSAR methods to estimate their toxicities are generally not applicable because these are limited to well defined congeneric sets. Therefore, different methods need to be explored for the simultaneous modelling and prediction of the effects of a great variety of structures. Neural networks and genetic algorithms have recently gained much attention and initial applications have proven very promising.

Our investigations of the applicability and usefulness of neural networks include: the comparative study of linear regression and probabilistic neural network (PNN) models for fathead minnow and *Vibrio fischeri* bacteria toxicity data, the use of feed forward backpropagation neural networks for fathead minnow toxicity data and the influence of data pre-processing and kernel selection on the quality of the predictions of PNN models for both fathead minnow and *Vibrio fischeri* toxicity data.

Resources (NWRI only): PY 0.2; O&M 10K

Publications, Reports, Conference/Workshop Presentations:

K.L.E. Kaiser, S.P. Niculescu and K.M. Gough, "Neural network modeling of *Vibrio fischeri* and fathead minnow acute toxicity data with molecular indicator variables and physico-chemical bulk parameters", Poster, **Workshop on Computational Methods in Toxicology**, Dayton, OH, April 20-22, 1998.

K.L.E. Kaiser, J.C. Dearden, W. Klein, T.W. Schultz, "A note of caution to users of ECOSAR", **Water Qual. Res. J. Canada**, **34**: 179-182 (1999).

NWRI Pesticide Activities for FY 98/99

Title: Sorption and metabolism of herbicides in microbial biofilms

Principal investigator: J.R. Lawrence (John.Lawrence@ec.gc.ca; TEL 306-975-5789; FAX-975-5143)

Collaborators: J.V. Headley, W. Manz, TUB, Berlin, Germany, T.R. Neu, UFZ, Magdeburg, Germany, C.W. Greer, BRI, Montreal

Summary of Activities:

Agricultural watersheds throughout Europe and North America are heavily impacted by the use of agricultural chemicals including fertilizers and pesticides. In any year more than 300 million kg of herbicides are applied in North America. Under normal growing and environmental conditions from 0.2 to 3% of this herbicide application will migrate to surface or ground waters. To understand the impact of these herbicides on the aquatic environment we need to understand how they are transported, whether they persist, in short, what their fate is in the natural environment. The behaviour, transport and degradation of herbicides in aquatic environments may be significantly influenced by interactions with microbial biofilms. All submerged surfaces are covered by a biological layer, a biofilm which may present a highly reactive, extensive surface area for sorption of contaminants. One of the dominant components of microbial biofilms is the exopolymer matrix which has been suggested to have a wide range of important functions. (Lawrence et al. 1995). Extracellular polymers (EPS) play an important role in microbial competitiveness and reproductive success, such as the formation of micro-colonies (Allison and Sutherland 1987), attachment to surfaces (Marshall et al. 1989), and increased resistance to antimicrobial agents (Costerton 1984). The most important aspect of EPS is its highly reactive nature, for example, certain microbial species accumulate metals (Brown and Lester 1982; Mittleman and Geesey 1985; Rudd et al. 1988) and it was suggested that they play a role in the concentration of nutrients (Freeman et al. 1995; Freeman and Lock 1995). It has also been shown that they play a role in the sorption of toxic organics in the environment. Chlorinated aromatic molecules were concentrated in the EPS of a microbial community and could be used as a carbon source during starvation (Wolfaardt et al. 1994; Wolfaardt et al. 1995). In addition it was shown that specific biofilm regions and EPS residues were associated with the sorption of the herbicide (Wolfaardt et al. 1998).

In the study reported here biofilms were grown in rotating annular bioreactors with river water as inoculum and sole source of nutrients. The herbicides atrazine and diclofop were applied to the bioreactors at 1 ppb and 10 ppb levels while an identical reactor acted as a control. Biofilm structure was visualized using fluorescent probes specific for nucleic acids and carbohydrates/glycoconjugates (lectins) in conjunction with CLSM. Antibody techniques were used to visualize the location of atrazine in the biofilm structure. Water was analyzed using GC-MS and biofilms were analyzed using DIP-MS/MS. The concentration of both herbicides in the bulk phase followed the pattern of application. Atrazine and metabolites were detected in biofilm samples and

only trace levels were detected after the addition phase. In contrast, diclofop and metabolites reached a maximum level in the biofilm at the end of the addition phase and persisted in the biofilm. Thus both herbicides were sorbed and metabolized by the biofilm community and detected in biofilms when they were not detected in the bulk water phase. These results indicate that biofilms may be a significant sink for specific herbicides and that this should be taken into account in terms of both sampling and studies of the environmental chemodynamics of these chemicals.

River biofilms are also a critical food resource for many invertebrate grazers. Additional studies have indicated that at the levels applied (1-10 ppb) these herbicides do not influence the grazing of various invertebrates such as snails, mayflies and ostracods on river biofilms. This indicates that the invertebrates would not exhibit any avoidance of contaminated biofilm materials.

Resources (NWRI only): 0.5 PY (G. Swerhone), 10K OM

Publications, Reports, Conference/Workshop Presentations:

Refereed Publications

Wolfaardt, G.M., J.R. Lawrence, R.D. Robarts and D.E. Caldwell. 1998. In situ characterization of biofilm exopolymers involved in the accumulation of chlorinated organics. *Microbiol. Ecol* 35:213-223.

Published Abstracts

Lawrence J.R., B. Scharf, C. Podemski, J.M.Culp, and T.R. Neu. 1998. Effect of invertebrate grazing on the distribution of algae, bacteria and exopolymer in river biofilms. *Microbial Ecology of Biofilms: Concepts, Tools and Applications*. Lake Bluff, Illinois, Oct 8-10. 0

Mohamed, M.N., C.W. Greer, L. Laramée, B. Aßmus, A. Hartmann, and J.R. Lawrence. 1998. Effect of carbon source on biofilm species composition. Canadian Society for Microbiologists, Annual Meeting, Guelph, ON.

Lawrence J.R., G. Kopf, J.V. Headley and T.R. Neu. 1998. Sorption and Metabolism of Selected Herbicides in River Biofilm Communities. ASM Annual Meeting, Atlanta,

NWRI Pesticide Activities for FY 98/99

Title: Effects of the sulfonylurea herbicide metsulfuron methyl on the growth and reproduction of five wetland and terrestrial plant species

Principal NWRI investigator: H.B. Lee (Bill.Lee@cciw.ca; TEL 905-336-6266; fAX 905-336-4420)

Collaborators: C. Boutin (principal investigator) (NWRC), T.E. Peart, S.P. Batchelor, and R.J. Maguire.

Summary of Activities:

Context of work:

Many sulfonylureas have been registered in several countries in the last 15 years and the extent of their use has increased considerably, largely due to their low toxicity to animals and their low level of application. Metsulfuron methyl, a sulfonylurea herbicide released in Canada in 1988 by Dupont de Nemours, is no exception although precise data on the amount used are difficult to obtain. It is commercialized under the trade name Ally™ and is recommended for use on wheat (spring and durum) and barley in the Prairie provinces and Peace River Region of British Columbia in Canada for the control of several broad-leaved species, i.e. 27 species from nine families. The industrial formulation, named Escort™ is used to control or suppress several plant species (14 species from five families) in pasture, rangeland, rough turf and non-crop areas. Ally is applied at 4.5g-ai/ha while Escort can be sprayed at up to 18 g-ai/ha in Canada, both with ground equipment only.

Abstract

Methods for the determination of sulfonylurea herbicides such as metsulfuron methyl (MM) and ethametsulfuron methyl (EM) in water and soil samples have been developed. For water samples, a solid phase extraction (SPE) technique using Empore-C₁₈ disks was adopted for the preconcentration of the herbicides. The extracts were analyzed by HPLC using a diode array detector (DAD). With the detector operating at 225 nm (signal) and 450 nm (reference), a detection limit of 0.1 µg/L was achieved. Recoveries at the detection limit were 92 ± 4 % and 94 ± 5 % for MM and EM, respectively. Alternatively, the herbicide extracts could be analyzed by GC/MS after derivatization with pentafluoropropionic anhydride. For soil samples, the herbicides were first extracted by a KHCO₃ solution, then the acidified extract was processed by the same SPE procedure. At the detection limit of 0.1 µg/g using HPLC and DAD, the recoveries were 88 ± 6 % and 105 ± 7 % for MM and EM, respectively. Direct extraction of the ureas from soil with methanol-modified supercritical carbon dioxide produced lower recoveries than the base extraction procedure, particularly for EM.

Two wetland species, *Mimulus ringens* and *Bidens cernua*, two terrestrial species, *Sinapis arvensis* and *Phaseolus vulgaris*, and one species found in both wet

and dry habitats, *Echinochloa crusgalli*, were exposed to 1% (0.045 g-ai/ha) and 10% (0.45 g-ai/ha) of recommended label rate of metsulfuron methyl, a sulfonylurea herbicide widely used in western Canada. The objective of the study was to investigate the effect of metsulfuron methyl on the vegetative growth and reproductive parts of these plant species and to determine the most sensitive phenological stage. Chemical analyses of the amount of herbicide sprayed were performed using Gas Chromatography (fiber glass papers) and High Performance Liquid Chromatography (tank mix). There is a good correspondence between the quantity measured in the tank mix compared to that detected on fiber glass papers, the latter representing the dose reaching the plants during the spray event. All species exhibited marked effects on the vegetative growth and reproductive performance when sprayed at 10% label rate. Less pronounced but significant effects were shown at 1% label rate on all species except for *E. crusgalli* where only slight visible injury was noted. Seed weight was reduced for *B. cernua* and *S. arvensis*. Species belonging to the Fabaceae and the Brassicaceae families, represented by *P. vulgaris* and *S. arvensis*, would be notably at risk from small doses of metsulfuron methyl drifting away from the sprayed areas although the two wetland species also exhibited substantial sensitivity to metsulfuron methyl. Several endangered species belonging to these two families are found in or near potholes of the prairies in western Canada. The seedling stage was the most sensitive period for all species tested although surviving plants sprayed at later stages showed considerable effects on the reproductive parts. This study highlights the shortcomings of the current testing schemes required prior to pesticide registration.

Resources (NWRI only): 0.5 PY, 8 K O&M, no capital.

Publications, Reports, Conference/Workshop Presentations:

Boutin, C., Lee, H.B., Peart, T.E., Batchelor, S.P., and Maguire, R.J., "Effects of the sulfonylurea herbicide metsulfuron methyl on the growth and reproduction of five wetland and terrestrial plant species", submitted to Environmental Toxicology and Chemistry for publication.

NWRI Pesticide Activities for FY 98/99

Title: Persistent organic pollutants in Great Lakes Areas of Concern

Principal Investigator: C.H. Marvin (chris.marvin@cciw.ca; TEL 905-319-6919; FAX 905-336-6430)

Collaborators: E.T. Howell (OME), E. Reiner (OME), B.E. McCarry (McMaster University), M. Diamond (University of Toronto), G.G. Leppard, N. Rukavina, M. Skafel, M. Charlton

Summary of Activities:

1. Hamilton Harbour. Two focal points of the Hamilton Harbour RAP on the issue of toxic contamination are: 1. remediation of severely contaminated areas of sediment, and; 2. acquisition of additional information on spatial distribution and loadings of POPs, including organochlorine pesticides. The most recent data has shown a downward trend in concentrations of POPs in material collected in sediment traps, however, this data also indicated that POPs were problematic in both bottom sediments and the water column. The most recently published data reports results from analyses of water samples collected in 1990-1991 and sediment trap samples collected in 1992. The paucity of more recent data has been identified as a serious knowledge gap. Work begun in FY 98/99 included collection of suspended sediment and surface waters from Hamilton Harbour; analyses of these samples is ongoing and is expected to be completed in FY 99/00.
2. Lake Erie. A component of the Lake Erie survey undertaken in 1997 was the collection of sediment samples as part of ongoing research to assess the importance of and changes in the past of priority organic pollutants (including organochlorine pesticides) in the Great Lakes. Chemical analyses of the sediment samples is expected to be completed in FY 99/00. Data from these analyses will be compared with previous surveys to investigate temporal trends in sediments on a lake-wide basis in addition to areas of historically elevated areas of contamination.

Resources (NWRI only): 1.5 PY and 20K O&M.

Publications, Reports, Conference/Workshop Presentations: N/A

NWRI Pesticide Activities for FY 98/99

Summary of analyses on pesticides conducted by the National Laboratory for Environmental Testing in FY 98/99.

Interim Director: N.D. Warry (dave.warry@cciw.ca, TEL 905-336-4563)

ANALYSES	MATRIX		STUDY LEADER	# SAMPLES
Organochlorine PCB	Pesticides,	Chlorobenzenes, Water	Tanya Mayer	16
Organochlorine PCB	Pesticides,	Chlorobenzenes, Sediment	Allan Crowe	42
Organochlorine Toxaphene	Pesticides,	Congener PCB, Water - LVX	Derek Muir	138
Organochlorine Toxaphene	Pesticides,	Congener PCB, Biota	Derek Muir	251
Organochlorine Toxaphene	Pesticides,	Congener PCB, Sediment	Derek Muir	127
Organophosphorous Pesticides		Water	Derek Muir	80
			TOTAL	654

Environment Canada Library, Burlington



3 9055 1017 7253 0



**National Water Research Institute
Environment Canada
Canada Centre for Inland Waters**

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

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

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



Environment
Canada

Environnement
Canada

Canada