00 - 301 MASTER

Environment Canada Environnement Canada

Canada

NWRI PESTICIDE RESEARCH SUMMARY, FISCAL YEAR 99/00

R.J. Maguire

NWRI Contribution No. 00-301

NATIONAL WATER
H INSTITUTE
NATIONAL DE
E SUR LES EAUX

TD
226
N87
no.
00-301
c.1

National Water Research Institute Pesticide Research Summary
Fiscal Year 1999-2000

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

NWRI contribution 00-301

Abstract and Management Perspective

Unlike other chemicals, pesticides are deliberately introduced to the environment. The use of pesticides usually involves a compromise between the benefits conferred, and environmental and human health risks. Pesticides are regulated in Canada under the Pest Control Products Act and Regulations, which are administered by the Pest Management Regulatory Agency of Health Canada. Environment Canada does research and monitoring to identify unacceptable risks to the environment posed by pesticides.

This report describes the general framework for research on pesticides at the National Water Research Institute, and Institute capabilities in certain areas. In addition, the report summarizes pesticide research conducted at the National Water Research Institute in fiscal year 1999-2000, and indicates resources expended for these studies. A summary is also given of pesticide analyses conducted by the National Laboratory for Environmental Testing.

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

Résumé et sommaire à l'intention de la direction

Contrairement à d'autres produits chimiques, les produits antiparasitaires sont délibérément introduits dans l'environnement. L'emploi de produits antiparasitaires est généralement décidé à la suite d'un compromis entre les avantages prévus et les risques pour la santé humaine et l'environnement. Au Canada, les produits antiparasitaires sont régis par la Loi et le Règlement sur les produits antiparasitaires, administrés par l'Agence de réglementation de la lutte antiparasitaire de Santé Canada. Environnement Canada effectue des recherches et de la surveillance pour déceler les risques inacceptables que pourraient constituer certains produits antiparasitaires pour l'environnement.

Le présent rapport décrit le cadre général des recherches sur les produits antiparasitaires à l'Institut national de recherche sur les eaux, ainsi que les moyens dont dispose l'Institut dans certains domaines. De plus, le rapport résume les recherches sur les produits antiparasitaires effectuées à l'Institut au cours de l'année financière 1999-2000, en indiquant les ressources consacrées à ces études. Enfin, on présente un résumé sur les analyses de produits antiparasitaires effectuées au Laboratoire national des essais environnementaux.

** 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), nutrient-contaminant interactions, synergistic effects, effects of degradation products
- estimation of toxicity to aquatic organisms using quantitative structure-activity relationships and probabilistic neural network methodologies

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 99/2000, and a list of NWRI publications and reports on pesticides.

Table of Contents

Study	Page
Past chemical use and declines in wild salmon populations	7
Occurrence, fate and effects of nonylphenol and its ethoxylates.	9
Sorption and metabolism of herbicides in microbial biofilms	12
Impact of agricultural management practices on surface and ground water quality and air quality by pesticide transport	14
Persistent organic pollutants in Great Lakes Areas of Concern	18
Distribution and persistence of DDT at Point Pelee National Park	20
Fate and effects of pesticides and industrial chemicals in aquatic ecosystems	23
Biodegradation and environmental fate of biocides	25
Application of the probabilistic neural network methodology to predict toxicity to fish	28
Butyltin compounds in the Surf Scoter from the west coast of Canada	30
Occurrence and seasonal variation of tributyltin (TBT) in marinas on Lake Ontario	31
Third national survey for TBT in the Canadian environment	33
Investigation of reproductive performance in forage fish exposed to agricultural runoff in the Thames River watershed, Ontario	34
Fate of potato related agrochemicals in a calibrated watershed in New Brunswick.	36
Agricultural runoff of pesticides with potential endocrine disrupting activity.	40
Fate and persistence of pesticides in aquatic ecosystems	41
Summary of analyses on pesticides conducted by the National Laboratory for Environmental testing in 99/00	44

NWRI Pesticide Activities for FY 99/00

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:

J. Sherry and D.T. Bennie, Environment Canada, National Water Research Institute, Burlington, Ontario
K. Haya and L.E. Burridge, Fisheries and Oceans Canada, St. Andrew's Biological Station, St. Andrew's, New Brunswick
J.G. Eales, Department of Zoology, University of Manitoba, Winnipeg, Manitoba

Summary of Activities:

BACKGROUND

A joint project between researchers from Environment Canada (S. Brown) and Fisheries and Oceans Canada (W. Fairchild) 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 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, and 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 under way.

Resources: 99/00 (NWRI only) 0.1 PY 50K O&M

Publications, Reports, Conference/Workshop Presentations:

Brown, S.B., K. Haya, L. Burridge, E.O. Swansburg, J.T. Arsenault and W.L. Fairchild. Effects of Matacil on Atlantic salmon (*Salmo salar*) smolts. Presentation at 25th Annual Aquatic Toxicity Workshop, Quebec City, PQ (October 1998).

Brown, S.B., K. Haya, L. Burridge, 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 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 SETAC 19th Annual Meeting, Charlotte NC (November 1998).

NWRI Pesticide Activities for FY 99/00

Title: Occurrence, fate and effects of nonylphenol and its ethoxylates.

Principal investigator: Donald T. Bennie (don.bennie@cciw.ca, TEL 905-336-4693, FAX 905-336-4420)

Collaborators:
M. Servos and S. Brown, NWRI
P. Seto, BETO, EPB
W. Ernst and L Rutherford, EPB, Atlantic Region
W. Fairchild, DFO, Maritime Region.

This study on nonylphenol and its ethoxylates is reported here because nonylphenol has been used as a solvent in a pesticide used for forest spraying in Canada.

Summary of Activities:

1) Studies to determine the environmental occurrence and fate of nonylphenol and its polyethoxylates continued with the collection and analysis of samples of various effluent streams of municipal sewage treatment plants, textile mills and pulp and paper mills in Atlantic Canada. The alkylphenolic parameters to be determined are 4-nonylphenol (4-NP), nonylphenol ethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), nonylphenoxyacetic acid (NP1EC), nonylphenoxyethoxyacetic acid (NP2EC), nonylphenol polyethoxylates (NPnEO, where n = 3 to 17), 4-*tert*-octylphenol (4-*t*-OP), octylphenoxyacetic acid (OP1EC) and octylphenoxyethoxyacetic acid (OP2EC). Samples of effluent and sludge were collected and analyzed from 10 STPs, 6 pulp and paper mills and 3 textile mills. The sampling program was completed in December, 1999; however, the analytical results of this study will not be available until late March, 2000. This study addresses research needs identified for the CEPA PSL 2 assessment of nonylphenol and its ethoxylates as well as departmental issues regarding endocrine disrupting compounds.

2) In collaboration with other researchers at Environment Canada (EC) and Fisheries and Oceans Canada (DFO), a study was undertaken to determine the effects of water-borne 4-nonylphenol on the seawater adaptability, growth and survival of Atlantic salmon (*Salmo salar*) smolts. S. Brown and W. Fairchild have found significant relationships between historical applications of an insecticide containing 4-nonylphenol (4-NP) and catch data for Atlantic salmon populations, suggesting possible declines in catch related to effects at the smolt stage. To test the hypothesis that 4-NP impairs parr-smolt transformation (PST), Atlantic salmon smolts were exposed to environmentally relevant, pulse doses of water-borne 4-NP. To determine whether 4-NP is operating via its properties as a weak estrogen, smolts were also exposed to sustained doses of estradiol (E2). The smolts' capability to withstand sea water and their subsequent growth and survival were evaluated after exposure to nominal concentrations of 20 and 200 µg/L 4-NP, and to 100 and 300 ng/L E2. Actual tank exposure concentrations of 4-NP were also

determined and found to be significantly lower than nominal exposure concentrations. DFO and EC collaborators measured osmoregulatory (plasma and tissue ions, gill ATPase), biochemical (glucose/glycogen), and endocrine (thyroid hormones, vitellogenin, cortisol) parameters on smolts throughout the experiment. There were no treatment related increases in mortality during a sea water challenge soon after exposure. Subsequent growth and survival in sea water was impaired in about 25% of fish from the various treatment groups (5% in control). The response was bimodal, with the affected fish showing weight loss from soon after treatments. Concentrations of 4-NP in harvested Atlantic salmon smolts were determined as well. Significant uptake of 4-NP in the smolt tissues was found, especially at low nominal concentrations. If the effects exerted by 4-NP are due to its estrogenic potential, then estrogenic activity stemming from other sources (*e.g.*, domestic sewage, agricultural wastes or phytoestrogens from pulp mills) might influence present day salmon populations. Field work was conducted on the Miramichi River in north-east New Brunswick to ascertain the levels of alkylphenolic substances discharged from sewage treatment plants and pulp mills to which Atlantic salmon smolts might be exposed during the parr-smolt transformation phase. The chemical analysis work on these samples is not complete at this time. This study addresses research needs identified for the CEPA PSL 2 assessment of nonylphenol and its ethoxylates as well as departmental issues regarding endocrine disrupting compounds. As such it falls under the Clean Environment business line and the result is the prevention or reduction of the environmental and human health effects posed by toxic substances or other substances of concern.

Resources:

A-base PYs in NWRI	2
A-Base O&M in NWRI	$5.0K
A-Base capital in NWRI	$69.5K
External PYs (estimate)	0
External O&M (estimate)	GL 2000: $32.5K; BETO: $210K; TSRI: $10.3K
Total External O&M (est.)	$252.8K
External capital (estimate)	0

Start date

1) 1997-98
2) May, 1998

End date

1) April, 2000
2) Ongoing

Publications, Reports, Conference/Workshop Presentations:

Bennie, D.T., Sullivan, C.A. and Servos, M.R. The fate of STP-derived alkylphenol ethoxylate metabolites in an Ontario river. Presented at the 20th Annual Meeting of the Society of Environmental Toxicology and Chemistry, Philadelphia, PA, 14-18 November 1999.

Brown, S.B., Fairchild, W.L., Haya, K., Burridge, L., Swansburg, E.O., Arsenault, J.T., Sherry, J., **Bennie, D.** and Eales, J.G. The effects of endocrine disruptors on seawater adaptability, growth, and survival of salmon smolts. Presented at the International Congress of Comparative Physiology and Biochemistry, Special Session on Endocrine Disruptors, Calgary, Alta., 25-29 August 1999.

Brown, S.B., Fairchild, W.L., Haya, K., Burridge, L., Swansburg, E.O., Arsenault, J.T., Sherry, J., **Bennie, D.**, MacLatchy, D. and Eales, J.G. Effects of water-borne 4-nonylphenol on Atlantic salmon smolts. Presented at the Wildlife Toxicology Program Science Meeting, Ottawa, Ont., 4-6 October 2000.

Fairchild, W.L., Arsenault, J.T., Haya, K., Burridge, L., Eales, J.G., Sherry, J., **Bennie, D.**, and Brown, S.B. Effects of water-borne 4-nonylphenol and estrogen on Atlantic salmon (*Salmo salar*) smolts. Presented at the 26th Annual Aquatic Toxicity Workshop, Edmonton, Alta., 2-6 October 1999.

Fairchild, W.L., Arsenault, J.T., Haya, K., Burridge, L., Eales, J.G., Sherry, J., **Bennie, D.**, and Brown, S.B. Effects of water-borne 4-nonylphenol and estrogen on Atlantic salmon (*Salmo salar*) smolts. Presented at the 20th Annual Meeting of the Society of Environmental Toxicology and Chemistry, Philadelphia, PA, 14-18 November 1999.

Fairchild, W.L., Arsenault, J.T., Haya, K., Burridge, L., Eales, J.G., Sherry, J., **Bennie, D.**, and Brown, S.B. Effects of water-borne 4-nonylphenol and estrogen on Atlantic salmon (*Salmo salar*) smolts. Presented at the Canadian Conference for Fisheries Research, Fredericton, N.B., 6-8 January 2000.

Schnell, A., Servos, M., **Bennie. D.**, Burnison, K., Wood, J. and Van Der Kraak, G. (1999). Characterization of Ontario sewage treatment plants for the occurrence, fate, release, and potential impacts of endocrine disrupting compounds. Presentation the Water Environment Association of Ontario Annual Symposium, April 12-13, 1999, Toronto, Ontario

Servos, M., Burnison, K., **Bennie, D.**, Sherry, J., Brown, S., Van Der Kraak, G., Schnell, A. and Ternes, T. 1999. Impacts of alkylphenol polyethoxylates, natural and synthetic estrogens in municipal effluents in Canada. Presentation at the Environmental Endocrine Disrupting Chemicals Conference, 7-12 March 1999, Ascona, Switzerland.

NWRI Pesticide Activities for FY 99/00

Title: Sorption and metabolism of herbicides in microbial biofilms

Principal investigator: John R. Lawrence, John.Lawrence@ec.gc.ca, 306-975-5789, FAX-975-5143

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

Summary of Activities:

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. The most important aspect of EPS is its highly reactive nature, its accumulates metals, concentration of nutrients, and a role in the sorption of toxic organics in the environment. In addition it has been shown that specific biofilm regions and EPS residues were associated with the sorption of the herbicide To understand the impact of 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. Further the nature of biofilms is influenced by nutrient availability, thus there is potential for interactions between nutrients and pesticide contaminants that may influence their fate.
In the study reported here biofilms were grown in rotating annular bioreactors with river water as inoculum; under control conditions and with additions of carbon, nitrogen, phosphorus and carbon+nitrogen+phosphorus. The resultant biofilms were then used in assays to assess the impact of nutrients on biofilm development and subsequently on sorption and metabolism of selected ^{14}C labelled herbicides. Biofilm sub-samples (1 cm^2) were incubated with radiolabelled ^{14}C atrazine and ^{14}C diclofop methyl and evolved $^{14}CO_2$ and sorbed label evaluated by scintillation counting procedures. For atrazine, there was no apparent difference in $^{14}CO_2$ evolution or sorption among biofilms grown with nutrient stimulation. Similar trends were observed for the ^{14}C diclofop methyl. The observations indicated that despite significant changes in biofilm architecture and EPS composition under nutrient treatments there were not detectable impacts on the fate of these two herbicides. This is an on going project evaluating nutrient and contaminant interactions

Resources: (0.25 PY, 10K, OM)

Publications, Reports, Conference/Workshop Presentations:

Laramée, Louise, **J.R. Lawrence**, and C.W. Greer. 2000. Molecular analysis and development of 16S rDNA oligonucleotide probes to characterize a diclofop-methyl degrading biofilm consortium. Can. J. Microbiol., 46: 133-142.

Beaumier, D., **J.R. Lawrence** and C.W. Greer. 1999. Community changes in a diclofop-methyl degrading consortium. Abstract, Canadian Society of Microbiologists Annual Meeting, Montreal, Quebec, Canada.

NWRI Pesticide Activities for FY 99/00

Title: Impact of agricultural management practices on surface and ground water quality and air quality by pesticide transport

Principal investigator:
Allan J. Cessna (allan.cessna@ec.gc.ca; TEL 306-975-5768; FAX 306-975-5143)

Collaborators:
Jane Elliott: jane.elliott@ec.gc.ca; 306-975-5738; fax - 306-975-5143

Laurie Tollefson, PFRA/CSIDC, Outlook, SK: tollefsonl@em.agr.ca; 306-867-5404; fax - 306-867-9656

Summary of Activities:

There were two on-going field studies in 1999-2000. The first study, in collaboration with Elliott, was initiated in 1994 under the Canada-Saskatchewan Agriculture Green Plan Agreement to investigate the impact of tillage systems on the quality of surface runoff from cropland with respect to herbicide and plant nutrient content. This field-scale study is being carried out on approximately a section of land near Biggar, SK involving four producers, each of whom farms a quarter section of land within the watershed. The four quarters of land encompass long-term zero till, short-term zero till, high inputs (fertilizer and pesticides) conventional till and low inputs conventional till. Components of each quarter drain independently so that runoff (snow melt and rainfall) volume from each tillage system is measured each year and herbicide and nutrient losses *via* the surface runoff are quantitated each year from each tillage system as a proportion of the amounts applied. Following Green Plan, the study was continued with NWRI A-Base funding. Three years of Agri-Food Innovation Fund (AFIF) funding (1999/2001) have been obtained to carry the study to a conclusion.

In the second study, the effect of sprinkler irrigation of high nitrogen and high pesticide input crops on ground water quality is being assessed. This study is being carried out on the Saskatchewan Irrigation Diversification Centre at Outlook, SK in collaboration with Elliott and Tollefson. The crop being studied is potato. The crop is grown on field-scale sites using a three-year rotation. Four fertilizer treatments reflecting fertilization practices currently used within the irrigation district are being studied on each site with the same herbicides, insecticides and fungicides being applied with each fertilization practice. Each year, ground water samples from each fertilizer treatment were collected at bi-weekly intervals from mid-May to mid-October and then on a monthly basis until the following May. Samples were analyzed for both pesticide and nutrient content. The study was begun in 1998 and was funded for the first two years under the National Soil and Water Conservation Program. An additional two years (200/2001)of funding has been obtained from AFIF. The study will continue

through 2002 such that, with the three-year rotation, potatoes will be grown twice on both sites.

Resources: (Cessna plus Elliott)

A-base PYs in NWRI - 0.25 PY
A-Base O&M in NWRI -$10 K
A-Base capital in NWRI - $3 K

External PYs (estimate) - 1.25 PY
External O&M (estimate) - $75 K
External capital (estimate) - none

Publications, Reports, Conference/Workshop Presentations:

Scientific Manuscripts:

Cessna, A.J., Waite, D.T., Grover, R. and Kerr, L.A., 1999, Duplicate sampling reproducibility of atmospheric residues of herbicides for paired pan and high-volume air samplers. Chemosphere (in press)

Jamie, Y.W., **Cessna, A.J.**, Biederbeck, V.O., Grover, R., Smith, A.E. and Korven, R.C. 1999. Effects on alfalfa of repeated applications of irrigation water containing monuron and simazine: I. Herbicide residues in soil and crop and their effects on yield. Can. J. Soil Sci. 79:639-645 (#1208)

Larney, F.J., **Cessna, A.J.** and Bullock, M.S., 1999, Herbicide transport on wind-eroded sediment. Journal of Environmental Quality 28:1412-1421.

Rosenberg, A.M., Semchuk, K.M., Helen McDuffie, H.H., Ledingham, D.L., Cordeiro, D.M., **Cessna, A.J.,** Irvine, D.G., Senthilselvan, A., and Dosman, J.A., 1999, Prevalence of antinuclear antibodies in a rural population. Journal of Toxicology and Environmental Health Part A, 57:225-236.

Waite, D.T., **Cessna, A.J.,** Gurprasad, N.P. and Banner, J., 1999, A new sampler for collecting separate dry and wet atmospheric depositions of trace organic chemicals. Atmospheric Environment 33:1513-1523.

Reports:

Cessna, A.J., Elliott, J.A. and Nicholaichuk, W., 1999, Herbicide and Nutrient Transport in Irrigation Runoff Water from the South Saskatchewan River Irrigation District #1 into the South Saskatchewan River. Final Report submitted to the CSAGPA Irrigation Sustainability Committee and the CSAGPA Water Quality Technical Committee.

Elliott, J.A., **Cessna, A.J.,** Hogg, T. Wahab, J., Ferguson, M., Vestre, B., Flegg, P. and Tollefson, L., 1999. Agrochemicals in the soil and ground water under intensively-irrigated crop production. Annual Progress Report to the National Soil and Water Conservation Program.

Conference/Workshop Presentations:

Cessna*, A.J., Waite, D.T., Kerr, L.A. and Grover, R., 1999, Duplicate sampling reproducibility of atmospheric residues of herbicides for paired pan and high-volume air samplers. In *Proceedings of the 34th Annual Western Canada Trace Organic Residue Analysts Workshop*, Calgary, AB, April 28 - 30

Crossley*, M., Arbuthnott, K., Semchuk, K.M., McDuffie, H., Senthilselvan, A., **Cessna, A.J.,** Dosman, J., Irvine, D., Rosenberg, A., Ledingham, D., and Snodgrass, P., 1999, Neurological effects of occupational and environmental exposure to herbicides in a prairie ecosystem study (PECOS). Presented at the International Neurological Society Meeting, Boston, MA, February; Abstract published in the Journal of the International Neuropsychological Society 5:129

Hagel*, L.M., McDuffie, H.H., Semchuk, K.M., Ledingham, D.L., **Cessna, A.J.,** Irvine, D.G., Senthilselvan, A., Crossley, M., and Dosman, J.A., 1999, PECOS: an exploration of associations between exposure to pesticides and non-fatal, unintentional injury in a rural population. Page 80 in *Abstracts of the International Congress on Ecosystem Health: Managing for Ecosystem Health*, Sacramento, CA, August 15-20.

McDuffie*, H.H., Semchuk, K.M., **Cessna, A.J.,** Irvine, D.G., Senthilselvan, A., Rosenberg, A.M., Crossley, M., Dosman, J.A., Hanke, P., Laxdal, V.A., Holfeld, L., Ledingham, D.L., Hagel, L. and Masley, M.L., 1999, The prairie ecosystem study (PECOS): Environmental pesticide exposure and human health: characterization of exposure by questionnaires. Page 88 in *Abstracts of the International Congress on Ecosystem Health: Managing for Ecosystem Health*, Sacramento, CA, August 15-20.

McDuffie*, H.H., Semchuk, K.M., **Cessna, A.J.,** Irvine, D.G., Ledingham, D.L., Hanke, P., Crossley, M.F.O., Senthilselvan, A., Dosman, J.A., and Rosenberg, A.M., 1999, Prairie ecosystem study (PECOS): Dermal and inhalation exposure to pesticides. Page 88 in *Abstracts of the International Congress on Ecosystem Health: Managing for Ecosystem Health* , Sacramento, CA, August 15-20.

McDuffie*, H.H., Semchuk, K.M., **Cessna, A.J.,** Irvine, D.G., Ledingham, D.L., Hanke, P., Crossley, M.F.O., Senthilselvan, A., Dosman, J.A., and Rosenberg, A.M., 1999, Prairie ecosystem study (PECOS): Accidental occupational dermal and inhalation exposures to pesticides between baseline (February 1996) and retest (June 1996). Page 89 in *Abstracts of the International Congress on Ecosystem Health: Managing for Ecosystem Health*, Sacramento, CA, August 15-20.

Semchuk*, K.M., McDuffie, H.H., **Cessna, A.J.,** Irvine, D.G., Ledingham, D.L., Laxdal, V.A., Dosman, J.A., Senthilselvan, A., Rosenberg, A.M., Hanke, P., Crossley, M., 1999, Herbicides in human plasma. In *Final Program & Abstracts of the Canadian Society for Epidemiology & Biostatistics*, Vancouver, BC, May 6-8 (Abstract 121).

Waite*, D.T., **Cessna,** A.J. and Grover, R., 1999, Duplicate sampling of surface films and associated pond water for herbicides. In *Proceedings of the 34th Annual Western Canada Trace Organic Residue Analysts Workshop*, Calgary, AB, April 28 - 30

NWRI Pesticide Activities for FY 99/00

Title: Persistent Organic Pollutants in Great Lakes Areas of Concern

Principal Investigator: C.H. Marvin, Aquatic Ecosystem Management Research Branch, NWRI.

Collaborators:

E.T. Howell and E. Reiner, Ontario Ministry of the Environment
B.E. McCarry, McMaster University
G.G. Leppard, B. Scott, D. Bennie, N. Rukavina, M. Skafel and M. Charlton (NWR)

Summary of Activities:

Hamilton Harbour monitoring.

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 have shown a downward trend in concentrations of POPs in material collected in sediment traps; however, these data also indicated that POPs were problematic in both bottom sediments and the water column. The most recently published data report 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 from Hamilton Harbour using sediment traps. We have now completed analyses of these samples and have contemporary data for levels of HCHs, chlordanes, DDT-related compounds and other COA priority compounds.

Lake Erie and Lake Ontario surveillance.

A component of surveys conducted in Lake Erie (1997) and Lake Ontario (1998) was 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. Data from these analyses are 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. COA tier 1 organochlorine pesticides are included in the data sets reported.

Detroit River - Lake St. Clair - St. Clair River Corridor monitoring program.

AEMRB initiated a five-year program in the corridor in 99/00 to monitor contaminant burdens in suspended sediments sampled using sediment traps. This program was designed to evaluate suspended sediment contaminant loads prior to the commencement of remedial activities. COA tier 1 organochlorine pesticides are included in the analysis protocols.

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

Publications, Reports, Conference/Workshop Presentations:

Marvin, C.H., Leppard, G.G., Stern, G., Boden, A.R. and McCarry, B.E. Characterization of contaminants on size-fractionated suspended flocs from Hamilton Harbour. *Abstracts of the 82nd Canadian Society for Chemistry Conference and Exhibition*, Toronto, Ontario, 1999.

Marvin, C., Thiessen, L., Fox. M., Charlton, M., Milne, J. and McCarry, B. Persistent organic pollutants in Hamilton Harbour: Current status and temporal trends. *Program and Abstracts of the 43rd Conference on Great Lakes and St. Lawrence River Research.* Cornwall, Ontario, 2000.

McCarry, B., Leppard, G., Marvin, C., Leppard, Boden, A., and Stern, G.G.G., Stern, G. Contaminant-suspended particle relationships in Hamilton Harbour water. *Program and Abstracts of the 43rd Conference on Great Lakes and St. Lawrence River Research.* Cornwall, Ontario, 2000.

Scott, B.F., Muir, D.C.G., Spencer, C., Marvin, C.H., MacDonald, R., Fisk, A. and Witter, A. Comparison of trifluoroacetic acid in freshwater and marine systems. *Abstracts of the 20th Annual Society of Environmental Toxicology and Chemistry*, Philadelphia, PA, 1999.

NWRI Pesticide Activities for FY 99/00

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

Principal investigator: Allan Crowe (allan.crowe@cciw.ca, TEL 905-336-4585, FAX 905-336-4400)

Collaborator: Dale Van Stempvroot (dale.vanstempvoort@cciw.ca, TEL 905-336-6917, FAX 905-336-4585)

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, numerous commercial land use and activities continued. Apple orchards occupied a large proportion of the Park until the late 1960's. Numerous summer cottages and houses existed in the Park until the mid-1970's and only one restricted-use campground remained after the 1960's. 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 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. Given the persistence of DDT, it would be expected that the 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 at several locations within the Park by researchers from the University of Windsor while undertaking a wildlife survey.

Because of the potential health risks to the campground visitors and staff, as well as the extensive media coverage, Parks Canada made an emergency request for the assistance of the National Water Research Institute of Environment Canada. NWRI was required to (1) confirm the previously reported high concentrations of DDT, (2) determine the extent of the area contaminated, (3) check other areas and the groundwater for possible contamination, and (4) determine the reasons for the persistence of DDT. Following the confirmation of the high levels of DDT, as well as determining that high levels are found at Camp Henry and the Maintenance Compound, Park's Canada closed both of these areas to visitors and staff. Negligible concentrations of DDT were detected in the Park's groundwater..

The maximum concentration was >5 μg/g, which exceeds the MOE Guidelines of 1.6 μg/g. Analyses of DDT, DDE and DDD in soil with depth indicated that these compounds were restricted to the upper 0-30 cm of the soil profile which has a high organic content, with essentially nothing detected in the lower sorted aeolian sand having essentially no organic carbon content. Computer simulations of DDT fate and persistence in the subsurface verified that the highly adsorptive nature of these compounds (the log K_{oc} values of DDT, DDD, DDE are 6.19, 5.00 and 5.69) and their low solubility (3, 20 and

40 ppb for DDT, DDD and DDE), caused attenuation in the organic-rich portion of the soil profile and prevented leaching downward to the water table. In fact, DDT, DDE and DDD concentrations in the groundwater were <0.0001 µg/L, or several orders of magnitude below the Canadian Drinking Water Guidelines limit of 50 µg/L. The estimated half-life of DDT in soil within the former orchard area using computer analysis was >45 years which is much greater than reported literature values of approximately 10 years. However, in the wetter areas of the park, such as in marsh sediments, the half-life of DDT is probably < 10 years.

Hence, unless the soils are remediated, these toxic residual pesticides pose a significant hazard to human and wildlife health for many years to come. Current methods for the remediation of soil and sediment contaminated by DDT and dieldrin typically involve either excavation and removal from the Park, or excavation and treatment on site in biopiles or bioreactors. However, both of these methods would cause widespread destruction of the Park by removal of vegetation, soil and wildlife. We are currently working on the development of an in-situ remedial technique designed to remove DDT and dieldrin from the soil at ground surface, without the destruction of the Park. Initial laboratory tests undertaken during FY 99/00, using samples from an area at Camp Henry, within Point Pelee National Park, known to have elevated concentrations of DDT showed a large portion of the DDT was apparently rapidly degraded through dechlorinated to DDE, and the data suggest that some was converted to DDD. These result are encouraging and indicate that the pesticide residues at Point Pelee are largely accessible dechlorination. Further laboratory and field tests are planned for FY 00/01

Resources:

A-base PYs in NWRI	none
A-Base O&M in NWRI	2K
A-Base capital in NWRI	none
External PYs (estimate)	none
External O&M (estimate)	none
External capital (estimate)	none

Start date
1998

End date
Publications:

Crowe, A.S. 1999. Distribution and persistence of DDT at Point Pelee National Park, Ontario. *in Proceedings of the 3rd Annual Parks Research Forum - Ontario.* April 22-23, 1999, Guelph, Ontario, (in press).

Presentations:

Contamination of Soil and Groundwater by DDT at Point Pelee National Park. At the 35th Central Canadian Symposium on water Pollution Research. February 7, 2000, Burlington, Ontario.

Distribution and persistence of DDT at Point Pelee National Park, Ontario. at the 3rd Annual Parks Research Forum - Ontario. April 22-23, 1999, Guelph, Ontario.

NWRI Pesticide Activities for FY 99/00

Title: Fate and effects of pesticides and industrial chemicals in aquatic ecosystems

Principal investigator: R.J. Maguire (905)336-4927; Jim.Maguire@ec.gc.ca

Collaborators: University of Waterloo, Department of Biology (Prof. D.G. Dixon) - collaborative research through Ph.D. student Adrienne Bartlett on the toxicity of tributyltin to freshwater invertebrates (co-supervisor, along with U. Borgmann of NWRI).

Summary of Activities:

Accumulation of tributyltin (TBT) in *Hyalella azteca* as an indicator of chronic toxicity: survival, growth, and reproduction

Body concentrations of contaminants have been shown to be more reliable indicators of toxicity than water or sediment concentrations. There are numerous advantages to this approach: body concentrations are independent of variable test/field conditions (*e.g.*, pH, complexing agents), comparisons of sensitivity can be made between species, and only the amount of bioavailable contaminant is measured. Previous studies have determined the body concentration:toxicity relationship for TBT in *Hyalella azteca* collected from laboratory bioassays, and have used this relationship as a tool to predict TBT toxicity to amphipods exposed to sediments collected from the field. However, these were water-borne exposures, while exposure to TBT in the field occurs *via* sediment as well as water. Furthermore, the exposures were only 4 weeks in duration, which is too short a time to measure reproduction, a key endpoint in TBT toxicity. In order to address these deficiencies, spiked-sediment experiments were carried out over two generations of *H. azteca*. The validity of each method was evaluated by comparing: 1. 4-week LC50s of water and sediment bioassays, 2. body concentrations at the end of 4- and 10-week exposures, and 3. body concentrations of first generation (F0) and second generation (F1) animals. This work is on-going.

Resources:

A-base PYs in NWRI - 0.4 PY
A-Base O&M in NWRI - 30K
A-Base capital in NWRI - 0K

External PYs (estimate) - 1.1 PY
External O&M (estimate) - 15K
External capital (estimate) - 0K

Start date

April 1, 1999

End date

March 31, 2002

NWRI Pesticide Activities for FY 99/00

Title: Biodegradation and environmental fate of biocides

Principal investigator: D. Liu (Dickson.Liu@cciw.ca; TEL 905-336-4576; FAX 905-336-4989)

Collaborators: R.J. Maguire, Y.L. Lau (NWRI), H. Okamura and I. Aoyama (Okayama University, Japan), H. Lee (University of Guelph)

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 that is presently being considered for registration under the Pest Control 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 very little information in the open literature on its environment persistence, fate, pathway, degradation products and ecotoxicity, which would hinder the Irgarol's risk assessment.

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 in 1996 and continued into 1999 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), and many marinas and fishery harbours were surveyed. Irgarol 1051 was not detected in the Canadian aquatic environment. However, for the first time, the stable Irgarol degradation product M1 was positively identified in environmental samples collected from the Seto Inland Sea, with concentrations of M1 (up to 1866 ng/L) being generally higher than those of Irgarol.

Ecotoxicity testing revealed that Irgarol 1051 and M1 were moderately toxic to a marine bacterium and four crustaceans tested, but were highly toxic to some algae and higher plants. In the root elongation inhibition bioassay, M1 showed a phytotoxicity at least 10 times greater than that of Irgarol and six other triazine herbicides (terbutryn, terbutylazine, terbumeton, simetryn, atrazine and simazine). These results strongly suggest that both Irgarol and its persistent degradation product M1 may potentially affect and/or damage the primary producer community in aquatic ecosystems. To

safeguard the aquatic ecosystem from the damaging impact of micro contaminants, it is recommended that, besides monitoring for the target parent compound, major degradation products should also be included in environmental surveys. Otherwise, there is a risk of underestimating the ultimate impact of a particular toxicant on the environment.

The phytotoxicity of Irgarol and M1 was systematically evaluated using a battery of bioassays with marine and freshwater species. Both compounds at low concentrations affected aquatic plant species such as the red macroalga *Porphyra yezoensis* conchospores, the brown macroalga *Eisenia bicyclis* gametophytes, the freshwater green microalga *Closterium ehrenbergii*, the floating macrophytes *Lemna gibba* G3 and *Lemna minor* 1769. The toxicity of Irgarol was higher than that of M1 for all the aquatic plant species tested, but M1 showed a higher toxicity to root elongation of a terrestrial plant. The NOEC (0.3 ug/L) of Irgarol to the brown seaweed was identical to the maximum concentration (0.296 ug/L) detected in Japanese coastal waters. The phytotoxicity study further indicate the possibility that both Irgarol 1051 and M1 may influence the primary producer community in the aquatic environment.

Resources: 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. Survey for the occurrence of the new antifouling compound Irgarol 1051 in the aquatic environment. Water Res. 33:2833-2843.

Okamura, H., M. Omori, R. Luo, I. Aoyama and D. Liu. 1999. Application ofshort-term bioassay guided chemical analysis for water quality of agricultural land run-off. Sci. Total Environ. 234:223-231.

Knoke, K., T.M. Marwood, M.B. Cassidy, D. Liu, A. Seech, H. Lee and J.T. Trevors. 1999. A comparison of five bioassays to monitor toxicity during bioremediation of pentachlorophenol-contaminated soil. Wat. Air, Soil Pollut. 110:157-169.

Phillips, T.M., D. Liu, A.G. Seech, H. Lee and J.T. Trevors. 2000. Monitoring bioremediation in creosote-contaminated soils using chemical analysis and toxicity tests. J. Industrial Microbiol. Biotechnol. 24:132-139.

Okamura, H., I. Aoyama, R.J. Maguire, D. Liu, G.J. Pacepavicius and Y.L. Lau. Fate and ecotoxicity of the new antifouling compound Irgarol 1051 in the aquatic environment. Water Res. (in press).

Okamura, H., I. Aoyama, T. Takami, T. Maruyama, Y. Suzuki, M. Matsumoto, I. Katsuyama, J. Hamada, T. Beppu. O. Tanaka, R.J. Maguire, D. Liu, Y.L. Lau and G.J. Pacepavicius. Phytotoxicity of the new antifouling compound Irgarol 1051 and a major

degradation product. Mar. Pollut. Bull. (in press).

T.M. Phillips, A.G. Seech, D. Liu, H. Lee and J.T. Trevors. Monitoring biodegradation of creosote in soils using radiolabels, toxicity tests, and chemical analysis. Environ. Toxcol. (in press).

Phillips, T.M., D. Liu, A.G. Seech, H. Lee and J.T. Trevors. Bioremediation in field box plots of a soil contaminated with wood-preservatives: A comparison of treatment conditions using toxicity testing as a monitoring technique. Water, Air, Soil Pollut. (in press).

D. Liu, R.J. Maguire, Y.L. Lau, G.J. Pacepavicius, H. Okamura and I. Aoyama. Factors affecting the rate of biodegradation. Presented at the 9th International Symposium on Toxicity Assessment, Pretoria, South Africa, 26 September - 1 October, 1999.

Okamura, H., I. Aoyama, D. Liu, R.J. Maguire, G.J. Pacepavicius and Y.L. Lau. Fate and ecotoxicity of the new antifouling compound Irgarol 1051 in the aquatic environment. Presented at the 9th International Symposium on Toxicity Assessment, Pretoria, South Africa, 26 September - 1 October, 1999.

Start date: April 1, 1999

End date: March 31, 2001

NWRI Pesticide Activities for FY 99/00

Title: Application of the probabilistic neural network methodology to predict toxicity to fish

Principal investigator: Klaus Kaiser (Klaus.Kaiser@CCIW.ca, TEL 905)336-4756, FAX 905-336-4989)

Summary of activities:

Application of the recently developed neural network methodology for the prediction of toxicity values to aquatic species continued with the computation of acute fish toxicity values for over 1,000 substances on the Canadian Domestic Substances List (DSL), as specified by the Commercial Chemicals Evaluation Branch (CCEB). There are over 20,000 substances on the DSL and most of them lack any measured ecotoxicity data. These substances include potential new pesticides, their precursors and metabolises. The ability of several prediction methods has recently been evaluated by an independent panel and the probabilistic neural network methodology (PNN) developed and applied here has been shown to have by far the best overall performance.

Resources:

1.1 PY in NWRI, 1 PY contractor
30K O&M
0K capital

Start date

April 1, 1999

End date

March 31, 2002

Publications, Reports, Conference/Workshop Presentations:

Kaiser, K.L.E. and S.P. Niculescu. 1999. Using probabilistic neural networks to model the toxicity of chemicals to the fathead minnow *(Pimephales promelas):* A study based on 865 compounds. Chemosphere, 38: 3237-3245.

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

Kaiser, K.L.E. and S.P. Niculescu. 1999. Probabilistic neural network (PNN) methodology for the prediction of acute toxicity of chemicals to fathead minnow based solely on chemical structure-derived input parameters National Water Research Institute Contribution, No. AEP-TN99-001, 39 p.

Kiihne, R., **K.L.E. Kaiser**, S.P. Niculescu, G. Schüürmann. Neural Network to Estimate Acute Toxicity of Chemicals to the Fathead Minnow and *Vibrio fischeri* Bacteria. SETAC 99 - Europe, Leipzig, May 1999, poster.

NWRI Pesticide Activities for FY 99/00

Title: Butyltin compounds in the Surf Scoter from the west coast of Canada

Principal investigator: Fan Yang

Collaborators: J. Elliott (CWS), R.J. Maguire (NWRI)

Summary of Activities:

Fifty-three Surf Scoter liver and feather samples from the west coast of Canada were collected by the Canadian Wildlife Service. An extraction method has been developed and reported for TBT analysis in feather samples.

The liver samples were extracted and analysed for the butyltin compounds. TBT was rarely detected, but DBT (0-183 ng as Sn/g) and MBT (0-129 ng as Sn/g) were found in most samples. The results indicated that butyltin compounds were bioaccumulated by duck and TBT was metabolized quickly in the liver.

Resources:

A-base PYs in NWRI 0.5
A-Base O&M in NWRI 15K
A-Base capital in NWRI 0K

External PYs (estimate)
External O&M (estimate)
External capital (estimate)

Start date April 1, 1999

End date March 31, 2001

Publications, Reports, Conference/Workshop Presentations:

F. Yang (1999). A mild extraction method for element speciation analysis from feather matrices. NWRI technical Note No. AEP-TN00-001.

NWRI Pesticide Activities for FY 99/00

Title: Occurrence and seasonal variation of tributyltin (TBT) in marinas on Lake Ontario

Principal investigator: Fan Yang

Collaborators: R.J. Maguire (NWRI)
Summary of Activities:

A survey of five marinas and one reference site on Lake Ontario, Canada was conducted to investigate the occurrence and variation of tributyltin (TBT) levels in water between April and December of 1998. The survey results revealed the presence as well as seasonal trends of TBT in these marinas. The TBT concentrations in water were found to coincide with boating activity. The level of TBT generally rose in summer when the boating activity was high, and the highest level of TBT found was 14 ng Sn/L. On average, 92% of the TBT was in the operationally-defined "dissolved phase" in the waters analyzed. The butyltin compounds were also found in surface sediment and paint chips from some non-aluminum hulled pleasure boats, with total concentrations of butyltin species (including dibutyltin and monobutyltin) ranging from 59 to 570 ng Sn/g dry weight, and from 0 to 146 μg Sn/g, respectively. The results clearly indicated that TBT in the marina waters primarily originated from antifouling paint on pleasure boats, even though the use of TBT as an antifouling agent was regulated in 1989.

Resources:

A-base PYs in NWRI 0.5
A-Base O&M in NWRI 10K
A-Base capital in NWRI 0K

External PYs (estimate)
External O&M (estimate)
External capital (estimate)

Start date April, 1998

End date July, 1999

Publications, Reports, Conference/Workshop Presentations:

F. Yang and R.J. Maguire (2000). Occurrence and seasonal variation of tributyltin (TBT) in marinas on Lake Ontario. Water Qual. Res. J. Canada (in press).

A method for the analysis of butyltin chlorides in air by gas chromatography with atomic emission detection. L.M. Allan, D.K. Verma, F. Yang, Y.K. Chau and R.J. Maguire. American Industrial Hygiene Association Journal, in press.

NWRI Pesticide Activities for FY 99/00

Title: Third national survey for TBT in the Canadian environment

Principal investigator: R.J. Maguire

Collaborators: EC regional staff

Summary of Activities:

Sample collection from 300 locations, and analysis, continues.

Resources:

A-base PYs in NWRI 1.0 PY
A-Base O&M in NWRI 20K
A-Base capital in NWRI 0K

External PYs (estimate)
External O&M (estimate)
External capital (estimate)

Start date April 1, 1999

End date March 31, 2002

Publications, Reports, Conference/Workshop Presentations:

NWRI Pesticide Activities for FY 99/00

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

Principal investigators:

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

M. McMaster (mark.mcmaster@cciw.ca; TEL 905-319-6906; FAX 905-336-6430)

Collaborators:

G. Van Der Kraak (University of Guelph; gvanderk@uoguelph.ca; TEL 519-824-4120 xt 2593)

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. The objective of these studies is to determine if runoff is adversely affecting reproductive performance in resident species of forage fish. Regular fish collections using backpack electrofishing techniques were initiated in the summer of 1998 and are continuing. Small numbers of both sexes of Creek Chub (*semotilus atromaculatus*), Blacknose Dace (*rhynichthys atratulus*), and Johnny Darter (*etheostoma nigrum*) are collected and measurements of fork length, body weight, gonad weight and liver weight are recorded. Gonadal tissues are fixed and sectioned for histology which is conducted at the University of Guelph Veterinary College. Gonadal tissues are also incubated for production of sex steroids which are measured by radioimmunoassay. Since knowledge of the reproductive physiology of these species is not known, our secondary objective is to monitor the temporal profiles of gonadal development and steroid production over an entire year to establish normal seasonal development.

Resources:

A-base PYs in NWRI: 0.1 PYs between L. Luxon and N. Jones

A-Base O&M in NWRI: $3.1K
A-Base capital in NWRI: $9.4K for electroshocking unit

External PYs (estimate) 0.1
External O&M (estimate) $2.0K
External capital (estimate)

Start date
Study was initiated in summer 1998 and is ongoing until missing temporal aspects are completed.

End date: Estimate completion in summer 2001.

Publications, Reports, Conference/Workshop Presentations:

M. McMaster, M. Hewitt, J. Parrott, M. Servos, K. Munkittrick and W. Gibbons. The use of small fish species for environmental effects monitoring of point and non-point source inputs. Presented at Reproductive Physiology of Fish Conference, Bergen, Norway, July 1999.

NWRI Pesticide Activities for FY 99/00

Title: Fate of potato related agrochemicals in a calibrated watershed in New Brunswick.

Principal investigator:

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

Collaborators:

P. Milburn, Agriculture Canada, Fredericton NB (milburnp@em.agr.ca, TEL 506-452-3260; FAX 506-452-3316)

Denise Dewar, Crop Protection Institute of Canada, Etobicoke ON; TEL 416-622-9771; FAX 416-622-6764

S. Backus, NLET (sean.backus@cciw.ca, tel 905-336-4646)

K. Munkittrick, (krm@unb.ca, tel 506-452-6219)

Summary of Activities:

The objective of these studies is to systematically investigate agrochemical residues in surface and groundwater in a calibrated watershed utilized for intensive potato production.

Background:

The Black Brook Watershed, located north of Grand Falls, New Brunswick, covers approximately 1450 ha and represents the most intensely farmed watershed in the Maritimes. The upper and central part of the watershed has mostly undulating to gently rolling topography with slopes of 1-6% in the upper and 4-9% in the central parts, and few hummocks. In the lower portion, topography becomes more rolling with slopes of 5-16%. The soils in the Black Brook Watershed are typical of those underlying most of the New Brunswick potato producing areas. Land use in the watershed is dominated by agriculture. Agricultural land constitutes approximately 925 ha or approximately 65% of the land base, the rest being either forested or urban/residential. This pattern has changed only slightly over the past 40 years. The major crop is potatoes in rotation with grain, peas and hay for forage. Some of the land is kept under pasture. Detailed information on farming systems and management practices has been collected through farmer interviews and field surveys.

Based on topographic features, soil conditions, and most importantly cropping and management practices, eight (8) sub-watersheds were identified and instrumented with permanent gauging stations for measuring discharges and collecting water samples for chemical and sediment analyses. Stations are winterized for continuous year-round

monitoring. A groundwater monitoring network has been installed and is comprised of six (6) multilevel piezometers to 40 m depth. One piezometer was installed in the upper forested region of the Black Brook Watershed and is used as a control for water quality parameters. The remaining five are in a single sub-basin of the Black Brook Watershed that is intensely cropped to potatoes and associated rotation crops. These five are configured to provide a typical cross-section and longitudinal section of the basin. Water table depths vary from 2 m from the soil surface in the basin floor to 14 m from the soil surface at the top of slopes.

While a knowledge base for chlorides, nitrates and soil fluxes has been generated for the system, comparatively little is known about pesticide behaviour. Leaching is aggressive in Black Brook (more than in PEI) which will address some hypotheses about leaching behaviour predicted for some chemicals. We are interested in establishing a connection between surface baseline levels and groundwater levels. Groundwater represents an integration of temporal and spatial residues in the system and the delay from surface applications to observable levels in groundwater is in the order of months to years. It has only been in the last decade that leaching of supposedly "unleachable" chemicals was identified as a problem. This was shown with dinoseb (fungicide) in tile drainage which would not have been predicted (Milburn *et al.* 1991). These results demonstrated that non point sources can affect groundwater quality over the long term, *i.e.*, in groundwater, residues can be detected that have not been used in the watershed for years.

Study Design

Agrochemical Residues

To avoid degradation and problems associated with preservative forms for multiple residues, samples will be extracted within 24 h in Fredericton. A multiple residue analysis has been developed for potato pesticides using graphitized carbon solid phase extraction (SPE) (Hewitt *et al.*, 2001). Water samples (1L surface water; 4L groundwater) are filtered (1μm; filters kept for analysis) and subjected to SPE. Filters and SPE cartridges are then frozen and shipped to Burlington, thereby avoiding sample degradation and reducing shipping expenses. Filters and SPE cartridges are thawed, eluted and analyzed by gas chromatography-mass spectrometry for agrochemical residues. This method also allows for the detection and confirmation of multiple target residues as well as profiling for degradation products. Sampling will be initiated in July 2000. We will conduct a coordinated groundwater and surface water sampling regime throughout the growing season for the major agrochemicals used in potato production (see list below). Groundwater will be monitored monthly at 3 depths for each of the 6 stations in the network. Surface water baseflow (source: groundwater) will also be monitored monthly at one station near the exit of the basin. Additional surface water samples will be collected during a small number of selected rain events. Existing gauging stations will provide surface flow information for event sampling. All samples will be collected by Agriculture and Agri-Food Canada (AAFC) staff in New Brunswick.

The temporal and spatial characteristics of residues in surface and groundwater will be compared to each other and to population responses of slimy sculpin in the system.

Agrochemicals analyzed for in surface and ground water in Black Brook

Insecticides
imidacloprid
carbaryl
endosulfan I and II

Herbicides
metribuzin
linuron
metobromuron

Fungicides
chlorothalonil
promocarb
chlorothalonil

For additional funding, an application has been made to the Matching Investment Initiative (MII) of Agriculture and Agri-food Canada through the AAFC Research Centre at Fredericton. Under this Initiative, a Crop Protection Institute grant provided to Munkittrick and Hewitt (1999) may be matched by AAFC to procure further funds for research on residue fluxes in the Black Brook system.

References

Agriculture and Agri-Food Canada (AAFC). 1997. Agriculture in Harmony with Nature, Strategy for Environmentally Sustainable Agriculture and Agri-Food Development in Canada. Catalogue No. A22-166/1-1997E. Available from Publications Section, AAFC, Ottawa. 72 pp.

Hewitt, M. and S. Backus. 2001. A multiresidue method for the extraction and analysis of potato agrochemicals in surface and groundwater. Manuscript in preparation.

Milburn, P., O'Neil, H.J., Gartley, C., Pollock, T., Richards, J.E. and Bailey, H. 1991. Leaching of dinoseb and metribuzin from potato fields in New Brunswick. Can. Agric. Eng. 33(2): 197-204.

Resources:

A-base PYs in NWRI: 0.2 PY

A-Base O&M in NWRI: $15.0K

A-Base capital in NWRI: $150K for GC-MS system

External PYs (estimate) 0.1
External O&M (estimate) $10.0K
External capital (estimate)

Start date
Pesticide method development initiated in spring 2000.

End date: Complete sample collections in Fall 2001.

Publications, Reports, Conference/Workshop Presentations:

Gray, M. **M. Hewitt**, K. Munkittrick. Population responses of slimy sculpin in agricultural regions of the upper Saint John River. Presented by M. Hewitt to the Crop Protection Institute of Canada. Guelph ON. January 7 2000.

NWRI Pesticide Activities for FY 99/00

Title: Agricultural runoff of pesticides with potential endocrine disrupting activity.

Principal investigator: Mark Servos mark.servos@cciw.ca 905-336-4778

Collaborators: Jim Sherry, NWRI, M. Hewitt, NWRI, Bill Ernst, EC Atlantic Region Bill.Ernst@ec.gc.ca

Summary of Activities:

Participating as one of many partners in a TSRI funded project (086) on the effects of agricultural runoff on the endocrine responses in fish in streams in PEI. The work is part of a larger study of intensive agriculture and endocrine disrupting substances, including animal wastes, pesticides and municipal sludges. The study uses caged fish, SPMD and water samples to identify endocrine active compounds and predict the potential risk to aquatic ecosystems.

Resources:

A-base PYs in NWRI 10K
A-Base O&M in NWRI 5K
A-Base capital in NWRI

External PYs (estimate)
External O&M (estimate) 10K TSRI
External capital (estimate)

Start date March 1999

End date March 2002

NWRI Pesticide Activities for FY 99/00

Title: Fate and persistence 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 1999/00 period were focused primarily on finalizing the preparation of three reports and conducting reviews on pesticide research. Research was conducted with collaborators Dena McMartin (PhD. Student) and Professors G. Hill and J. Gillies, University of Saskatchewan. A paper on pesticides in the Prairies was published in the Canadian Water Resources Journal and a second manuscript was submitted to the Journal of Biotechnical Bioengineering, describing the bioremediation characteristics of binary mixtures of 4-chloro-phenol, phenol and glucose by *Pseudomonas putida*. In support of possible collaborative studies with Céline Boutin (CWS), discussions were held with Bill Lee and Allan Cessna on application of LC/MS for the determination of sulphonylurea herbicides in water and plants. As a result of this exchange, contacts were established with Ed Furlong, US Geological Survey, for technology transfer on electrospray ionization LC/MS methods. In support of TSRI Project # 176, Headley also cooperated with Dr. Tony Newton and Beverley Wood, UWI, on the application of GC/MS and LC/MS for the determination of pesticide EDS in biofilm and groundwater.

1. 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.

Biodegradation of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) by a strain of *Pseudomonas* bacteria in surface water was monitored by high pressure liquid chromatography (HPLC). Two biodegradation experiments were completed using South Saskatchewan River water collected in the spring and summer of 1999 and amended with one of four initial 2,4-D concentrations. Each set of samples was also assessed under three different pH levels and dissolved organic carbon (DOC) contents to determine the effects of these parameters on the rate of substrate biodegradation.

First-order kinetics was observed in all successful biodegradation cases. Nutrient concentrations (including nitrate, ammonium, phosphate, and silicate), total organic carbon (TOC), colour, and other physical water quality parameters were evaluated at the start and end of each biodegradation experiment. DOC, pH, and heterotrophic and *Pseudomonas cepacia* populations were monitored more frequently. On average, an acclimation period of eighteen days was required before the onset of rapid 2,4-D biodegradation (half-life values consistently between 30 and 40 hours). Autoclaved controls displayed insignificant losses indicating that all 2,4-D depreciation from the

amended samples was due solely to biotic factors.

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

The contribution of gross riverine OCP (organochlorine pesticide) transport to estuaries of Russian seas and Lake Baykal was determined to help understand OCP transboundary transfer and to provide a basis for estimating Russia's contribution to global pollution by these pesticides. The official OGSNK/GSN data ranks sea/ocean/lake basins in the following order based upon the amounts of total OCPs received from agricultural use: Eastern Arctic>Western Arctic>Pacific>Baltic>Caspian>Azov/Black>Baykal. A similar ranking was obtained using an independent set of data: Eastern Arctic>Pacific>Caspian>Western Arctic>Baltic>Azov/Black. In terms of riverine flow-associated discharge of HCH isomers (i.e., sum of ?-, ?- and ?-HCH) estuaries of the Kara, Okhotsk and Beloye (White)/Barents seas received more pesticides than other seas. No HCH was discharged to estuaries of the Eastern Siberian and Bering seas. For DDT and its derivative (DDE), estuaries of the Kara, Caspian, Okhotsk and Baltic seas received the greatest amounts. During our study period (1986 to 1996), HCH transport was more prevalent in the majority of rivers reflecting both the official ban on the use of DDT in the former Soviet Union and the greater popularity of HCH as a pesticide. In general, it appears that Russian rivers play a significant role in OCP contamination of some estuaries of regional seas, especially those of the eastern Arctic basin, such as the Kara Sea.

3. Review of methods and reports on pesticides

Dr. Headley served as External Reviewer on behalf of: (a) Jenny Cossham, Managing Editor, John Wiley & Sons, Ltd., for a proposal for a reference work in residue analytical methods for agrochemicals, and (b) the Editor, Journal of Agriculture and food Chemistry, for two manuscripts on the kinetics of degradation of agrochemicals in aquatic environments. On behalf of the department, he also provided internal review for the reports/manuscripts (c) "Review of Canadian Environmental Quality Guidelines (water, sediment, and tissue) for dioxins and furans", (d) "Diffuse geographic distribution of herbicides in northern prairie wetlands" by D.B. Donald, N. Gurprasad and L Quinnett-Abbott.; and (e)"Residues of Glyphosate and its metabolite AMPA in conola seed following preharvest applications" by A.J. Cessna, A.L. Darwent, L.Townley-Smith, K.N. Harker and K.J. Kirkland.

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

Publications, Reports, Conference/Workshop Presentations:

McMartin, D., J.V. Headley, J. D. Gillies and H. G. Peterson. 2000. Biodegradation kinetics of 2,4-dichlorophenoxyacetic acid (2,4-D) in South Saskatchewan River Water. Canadian Water Research Journal 25(1): 81-92

Zhulidov, A.V., J.V. Headley, D.F. Pavlov, R.D. Robarts, L.G. Korotova, Y.Y. Vinnikov

and O.V. Zhulidova. Riverine fluxes of the persistent organochlorine pesticides hexachlorocyclohexane and DDT in the Russian Federation. 2000. Chemosphere 41: 829 - 841

NWRI Pesticide Activities for FY 99/00

Summary of analyses on pesticides conducted by the National Laboratory for Environmental testing in 99/00

Director: N.D. Warry: (905)336-4563 Dave.Warry@CCIW.ca

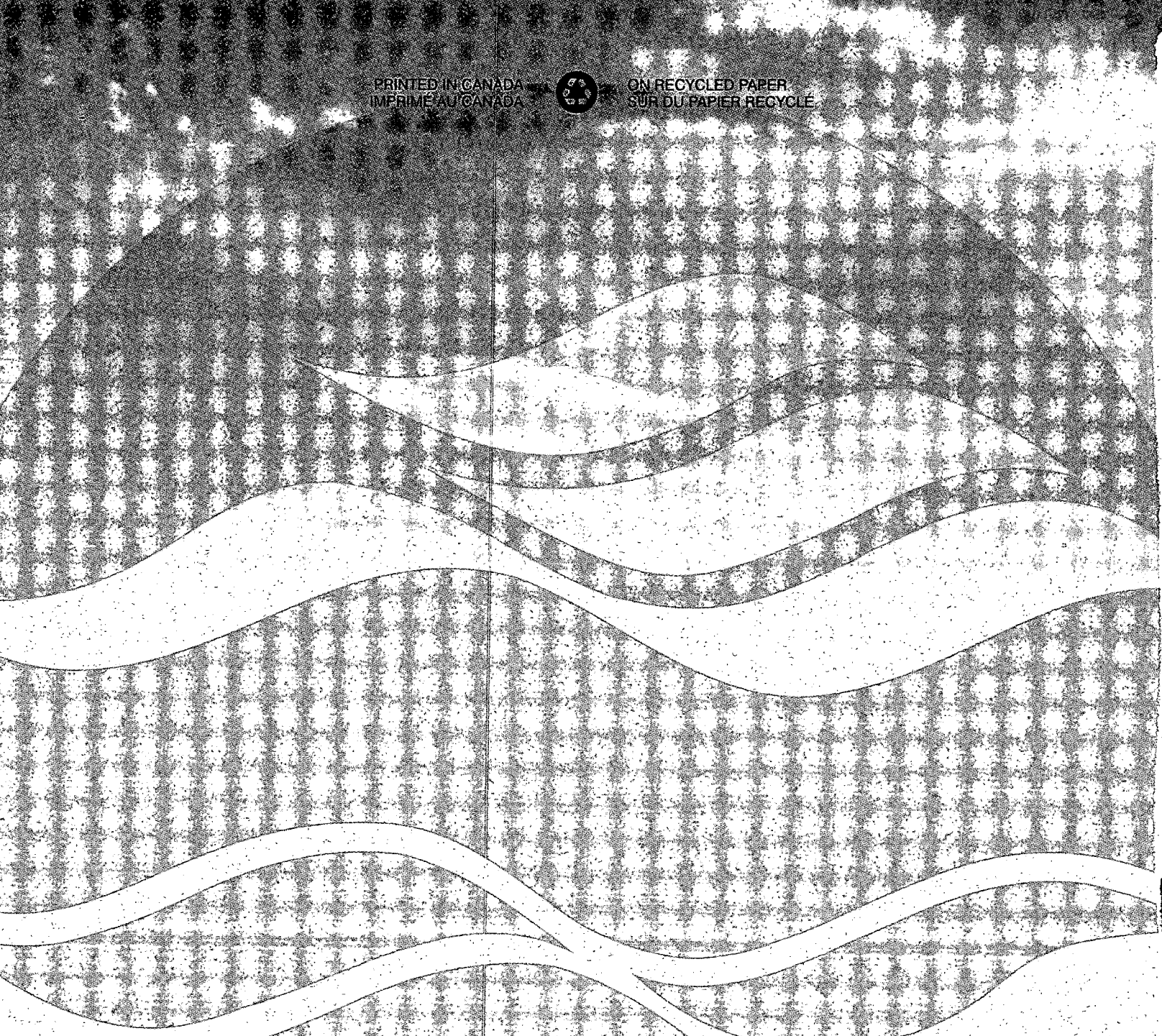
Number of Analytical Results Generated for Pesticides at NLET

Substrate	Analysis	Number of Results	%
Water	chlorobenzenes	1,400	0.92%
	organochlorine pesticides and polychlorinated biphenyls	34,160	22.44%
	organophosphate pesticides	3,302	2.17%
	toxaphene	609	0.40%
		39,471	25.92%
Sediment	chlorobenzenes	1,552	1.02%
	organochlorine pesticides and polychlorinated biphenyls	51,717	33.97%
	toxaphene	9,000	5.91%
		62,269	40.90%
Biota	organochlorine pesticides and polychlorinated biphenyls	74,983	49.25%
	toxaphene	14,400	9.46%
		89,383	58.70%
TOTAL		152,261	100.00 %

Number of Projects by Region

Region	Number of Projects
Ontario	7
Quebec	2
PNR	7
P&Y	2
NWRI	5
Northern	3

PRINTED IN CANADA
IMPRIMÉ AU CANADA
ON RECYCLED PAPER
SUR DU PAPIER RECYCLÉ



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

National Hydrology Research Centre
11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

Institut national de recherche sur les eaux
Environnement Canada
Centre canadien des eaux intérieures
Case postale 5050
867, chemin Lakeshore
Burlington, Ontario
L7R 4A6 Canada

Centre national de recherche en hydrologie
11, boul. Innovation
Saskatoon, Saskatchewan
S7N 3H5 Canada

NATIONAL WATER RESEARCH INSTITUTE
INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX

Environment Canada Environnement Canada

Canada