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NWRI PESTICIDE RESEARCH SUMMARY FISCAL YEAR 2001-2002

J.K. Cooley and R. J. Maguire

NWRI Contribution No. 02-325

National Water Research Institute Pesticide Research Summary

Fiscal Year 2001-2002

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Abstract and Management Perspective

Unlike other toxic 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 risks to the environment posed by pesticides, to assess those risks, and to identify measures to minimize the risks. The results of these activities are communicated to PMRA for the purposes of risk reduction, registration re-assessment, and special reviews of pesticides.

This internal 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 2001-2002, and indicates resources expended for these studies. A summary is also given of pesticide analyses conducted by the National Laboratory for Environmental Testing of the National Water Research Institute.

Résumé et sommaire à l'intention de la Direction

Contrairement aux autres produits chimiques toxiques, les pesticides sont introduits délibérément dans l'environnement. L'utilisation de pesticides est habituellement basée sur un compromis entre les avantages du produit et ses risques pour l'environnement et la santé humaine. Les pesticides sont réglementés au Canada en application de la *Loi sur les produits antiparasitaires* et de son *Règlement*, qui sont administrés par l'Agence de réglementation de la lutte antiparasitaire de Santé Canada. Environnement Canada effectue des activités de recherche et de surveillance pour la détermination des risques pour l'environnement dus aux pesticides, l'évaluation de ces risques et la détermination de mesures permettant de les réduire au minimum. Les résultats de ces activités sont communiqués à l'ARLA, qui est responsable de la réduction des risques, des homologations et des réévaluations des pesticides, ainsi que des examens spéciaux pour ceux-ci.

Ce rapport décrit le cadre général de recherche sur les pesticides de l'Institut national de recherche sur les eaux, ainsi que les capacités de l'Institut dans certains domaines. De plus, il résume les recherches sur les pesticides effectuées à l'Institut au cours de l'année financière 2001-2002, en indiquant les ressources dépensées pour ces études. On y présente aussi un sommaire des analyses de pesticides effectuées par le Laboratoire national des essais environnementaux de l'Institut national de recherche sur les eaux.

Introduction

The National Water Research Institute (NWRI) in Burlington, Ontario and Saskatoon, Saskatchewan is Canada's largest freshwater research establishment. NWRI conducts a comprehensive 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. NWRI's mission is to generate scientific knowledge through ecosystem-based research to support the development of sound government policies and programs, public decision-making and early identification of environmental problems.

Research on pesticides at NWRI, like research on other toxic chemicals, is undertaken to assess their environmental risks by determining 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 Toxics Pollution Prevention Directorate, 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 2001/2002, and a list of NWRI publications and reports on pesticides.

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NWRI Pesticide Activities for FY 01/02

Title: Occurrence, fate and effects of nonylphenol ethoxylates and their metabolites.

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C. Marvin, NWRI, EC
P. Seto, NWRI, EC
G. Fox, CWS, EC
W. Fairchild, DFO, Maritime Region

Summary of Activities:

1) In collaboration with other researchers at Environment Canada and the Department of Fisheries and Oceans, studies continued for the determination of the effects of water-borne 4-nonylphenol (4-NP) and nonylphenoxyacetic acid (NP1EC) on the seawater adaptability, growth and survival of Atlantic salmon (*Salmo salar*) smolts. Experiments to determine whether 4-NP and NP1EC are acting as weak estrogens were performed this year at St. Andrews Biological Station where Atlantic salmon smolts' were exposed to environmentally relevant, pulse doses of water-borne 4-NP and NP1EC. 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 µg/L 4-NP, and to 50 and 200 µg/L NP1EC. DFO and EC collaborators also measured a number of other osmoregulatory, biochemical, and endocrine parameters on smolts throughout the experiment. Concentrations of 4-NP and NP1EC in harvested Atlantic salmon smolts are to be determined as well. 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. Chemical analyses on FY 2000 and 2001 field samples were completed. 4-NP was detectable at only 2 sites which were adjacent to effluent discharges in the Miramichi River. These concentrations were only minimally above the method detection limit of 0.060 µg/L. Nonylphenol ethoxylate and nonylphenol diethoxylate were also found in most 2001 estuarine samples and levels ranged from <0.025 µg/L to 0.066 µg/L. Analysis of pulp mill effluent and municipal wastewater effluents showed that these discharges are significant sources of NPEs to this river, however, levels are quickly dissipated in the river, probably due to dilution. Mean pulp mill effluent concentrations were 0.97 µg/L 4-NP, 0.22 µg/L NP1EO, 2.7 µg/L NP1EC, 3.8 µg/L NP2EC and 9.7 µg/L Σ-APE. The mean municipal effluent discharge concentrations were 0.14 µg/L 4-NP, 0.27 µg/L NP1EO, 7.7 µg/L NP1EC, 3.8 µg/L NP2EC and 14.8 µg/L Σ-APE. 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.

2) In collaboration with Dr. C. Marvin of NWRI, suspended sediment samples from the Detroit River were analyzed for alkylphenols, alkylphenoxyacetic acids and nonylphenol polyethoxylates. Total alkylphenolic levels in these samples ranged from 0.85 µg/g to 36 µg/g. The dominant compounds were 4-NP and NP1EO. This work will be added to the database of information for the Detroit River and St. Clair River Remedial Action Plan. This work was supported by the Great Lakes Basin 2020 Action Plan. Sampling and analysis for these parameters in this Canadian Area of Concern will be expanded to include the St. Clair River, Lake St. Clair and the Detroit River in FY 2002-2003. This study

falls under both the Clean Environment business line (result is the prevention or reduction of the environmental and human health effects posed by toxic substances or other substances of concern) and the Nature business line (result is priority ecosystems are conserved and restored).

3) A small collaborative study with G. Fox of the CWS National Wildlife Research Centre resulted in some interesting data being generated on pooled herring gull liver homogenates from the Great Lakes Basin. Seven pooled samples were analyzed for 4-NP and nonylphenol ethoxylates. We did not expect to find any detectable levels but, instead found levels of 4-NP ranging from 0.19 mg/kg (wet weight) to 0.47 mg/kg (wet weight). As well, detectable levels of NP1EO, NP2EO, NP3EO, NP4EO, NP5EO and NP6EO were determined. A positive and almost linear relationship between concentrations of 4-NP and p.p'-DDE in the homogenates was also found. Work on these samples was funded by the Great Lakes Basin 2020 Action Plan and it falls under the Clean Environment business line (the result is the prevention or reduction of the environmental and human health effects posed by toxic substances or other substances of concern) and the Nature business line (result is priority ecosystems are conserved and restored) This work will be continued in FY 2002-2003.

Timeline

Start Date:
1May, 1998
2June, 2001
3June, 2001
End Date:
1) Ongoing
2) Ongoing
3) Ongoing

Resources:

A-base PYs in NWRI	2
A-Base O&M in NWRI	$5.0K
A-Base capital in NWRI	Nil
External PYs (estimate)	0
External O&M (estimate)	
GLB2020:	$15.0K
TSRI:	$10.3K;
Total External O&M (est.)	$25.3K
External capital (estimate)	$0K

Publications, Reports, Conference/Workshop Presentations:

Bennie DT and M Webber 2001. Persistence of alkylphenolics in anaerobically digested sewage sludge used as an amendment for agricultural soil. National Water Research Institute Contribution No. 01-031, Environment Canada, Burlington, Ontario L7R 4A6, 34+ pp.

Fairchild WL, Haya K, Burridge LE, Arsenault JT, Sherry J, Bennie D, Burnison K, MacLatchy D, Evans R, Eales JG and Brown SB. 2001. Effects of Endocrine Disruptors on Parr-Smolt Transformation in Atlantic Salmon (*Salmo salar*). Report to SALMODEL Workshop on Marine Mortality, August 10-12, Moncton, NB.

Servos M, Bennie D, Burnison K, Cureton P, Davidson N and Rawn T. 2001. Uncertainties associated with assessing the risk of and endocrine active substance in the Canadian environment. Water Qual. Res. J. Canada 36(2):319-330.

Brown SB, Arsenault JT, Haya K, Burridge LE, Eales JG, MacLatchy DL, Evans RE, Burnison BK, Sherry JP, Bennie DT, Fairchild WL. 2002. Effects of endocrine disruptors on growth and physiology of Atlantic salmon. 37th Central Canadian Symposium on Water Pollution Research, Burlington, ON, 4-5 February 2002.

Bennie DT, Servos MR, Burnison K and Seto P. 2001. Occurrence, fate and release of alkylphenol polyethoxylates in municipal effluents and industrial effluents in Canada. 22nd Annual Meeting of the Society of Environmental Toxicology and Chemistry, Baltimore, MD, 11-15 November, 2001.

Bennie D, Servos M, Burnison K, Seto P, Domey N, Tigner J, Karalis E, Atkinson AJ and Schnell A. 2001. Removal of toxic

substances and contaminants of concern by municipal wastewater treatment. 22nd Annual Meeting of the Society of Environmental Toxicology and Chemistry, Baltimore, MD, 11-15 November, 2001.

Arsenault JT, Fairchild WL, MacLatchy DL, Haya K, Burridge L, Bennie DT and Brown SB. 2001. Effects of 4-nonylphenol and estrogen on plasma IGF-1 of Atlantic salmon smolts. 22nd Annual Meeting of the Society of Environmental Toxicology and Chemistry, Baltimore, MD, 11-15 November, 2001.

Brown SB, Haya K, Burridge L, Swansburg E, Arsenault J, Eales J, MacLatchy D, Evans R, Burnison K, Sherry J, Bennie D and Fairchild W. 2001. Effects of Water-Borne 4-Nonylphenol on Atlantic Salmon (*Salmo salar*) Smolts. 2001 TSRI Regional Conference - EDCs, Hamilton, Ontario, 9-10 November 2001.

Arsenault J., Fairchild W, MacLatchy D, Haya K, Burridge L, Bennie D and Brown S. 2001. Effect of 4-nonylphenol and estrogen on plasma IGF-1 of Atlantic salmon smolts. 2001 TSRI Regional Conference - EDCs, Hamilton, Ontario, 9-10 November 2001.

Bennie D, Servos MR, Burnison BK, Seto P and Schnell A. 2001. Occurrence and fate of alkylphenol polyethoxylates in municipal effluents and industrial effluents in Canada. Aquatic Toxicity Workshop, Winnipeg, Manitoba, Sept. 30-Oct. 3, 2001.

Servos M, Maguire RJ, Lee H-B, Bennie D, Hay D, Seto P, Schnell A, Davidson N, Sutcliffe R, Cureton P and Rawn T. 2001. Environmental risk assessment of nonylphenol and its ethoxylates in Canada. Aquatic Toxicity Workshop, Winnipeg, Manitoba, Sept. 30-Oct. 3, 2001.

Dussault EB, Burnison BK, Lee H-B, McInnis R, Bennie D, McMaster M, Murphy EJ, Sherry J, Terry K, and Servos MR. 2001. Endocrine effects on nonylphenol, nonylphenol ethoxylates and nonylphenol ethoxycarboxylates on juvenile rainbow trout (*Oncorhynchus mykiss*). Aquatic Toxicity Workshop, Winnipeg, Manitoba, Sept. 30-Oct. 3, 2001.

Title: DDT and Dieldrin assessment and monitoring protocols for Point P elee National Park

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Summary of Activities:

Between 1948 and 1970, DDT applied at Point Pelee National Park (PPNP) for mosquito control in recreational areas and pest control in the orchards. Given the degradational properties of DDT, it would be expected that the DDT and its daughter products DDD and DDE would no longer exist at PPNP. However, several sampling programs undertaken during the past four years detected DDT and Dieldrin in the shallow soil at numerous locations within the Park, and at concentrations that often exceeded the Ontario Ministry of Environment (MOE) limits for DDT and Dieldrin for Recreational/Parkland landuse.

This year's activities focused on using statistical analyses to identify regions of PPNP likely to have elevated concentrations of pesticide, and to define protocols for long-term soil monitoring of DDT and Dieldrin. Specific objectives include:

- Identify different regions of PPNP (based on soil and sediment types, organic carbon content, depth to water table, susceptibility to flooding by the marsh, former landuse activities), which have significant differences in pesticides types and concentrations;
- Determine the typical range of concentrations of Total DDT, compounds DDT-DDE-DDD, and Dieldrin to be expected within a specific region of the Park;
- Determine the variability in concentrations of Total DDT, compounds DDT-DDE-DDD, and Dieldrin among various regions of the Park;
- Recommend soil sampling protocols, including frequency of soil sampling with respect to former land-use areas, and schedule for sampling.

The statistical analyses of the distribution of Total DDT, DDT, DDE, DDD, and Dieldrin within PPNP are undertaken using existing data from the past studies, including 143 DDT analyses, 213 Dieldrin analyses and 114 organic carbon analyses, from soil and sediment.

Concentrations of DDT and Dieldrin are highly variable, ranging over several orders of magnitude. There is no correlation between the organic carbon content of the soil and concentrations of DDT and Dieldrin; pesticide concentrations are sufficiently low that all adsorption sites are not occupied. DDT is undergoing degradation in the soils at PPNP, with the principal transformation product of DDT being DDE everywhere at PPNP, except in the marshy soils and marsh sediments where there is a significant transformation to DDD.

With respect to the soils at PPNP, because of (a) the relatively slow rate of degradation, and (b) the extreme variability of concentrations within a given land-use zone, the focus must be placed on the number of samples obtained at a given time rather than the time interval between sampling. For example, concentrations of DDT and Dieldrin will not change much from year to year at a specific location, but concentrations may vary orders of magnitude at locations within metres of each other.

Based on our analysis of DDT and Dieldrin data, there appears to be five distinct regions within PPNP with respect to concentrations, degradation rates and variability, and this variability influences how frequently the soils should be sampled:

(a) Marshy Soils:
- very wide range of values, including values greater than MOE guidelines
- appears to be undergoing relatively fast degradation

- therefore monitor every 2-3 years

(b) Marsh Sediments:
- lowest concentrations, below MOE guidelines
- appears to be undergoing relative fast degradation
- exhibit proportionally more DDD and DDE than DDT
- do not need to monitor

(c) Orchards:
- relatively high concentrations and values greater than MOE guidelines
- appears to be undergoing relatively slow degradation
- therefore monitor every 5-6 years

(d) Former residential and natural areas:
- relatively low concentrations and most uniform concentrations, below MOE guidelines
- appears to be undergoing relatively slow degradation
- therefore do not need to monitor

(e) Camp Henry and Maintenance Compound:
- appears to have very variable degradation rates
- very wide range of values, including values greater than MOE guidelines
- therefore monitor every 3-4 years

Timeline	
Start Date:	***1998***
End Date:	***2003***

Resources (NWRI only):	
none	
A-base PYs in NWRI	0.4
External PYs (estimate)	0.5
A-Base O&M in NWRI	$5K
External O&M (estimate)	$5.9K
A-Base capital in NWRI	none
External capital (estimate)	none

Publications, Reports, Conference/Workshop Presentations:

Crowe, A.S., J.E. Smith, S. Spencer. 2001. DDT and Dieldrin Assessment and Monitoring Protocols for Point Pelee National Park. report submitted to Point Pelee National Park, March 2002. Environment Canada, National Water Research Institute, Burlington/Saskatoon, NWRI Contribution No. 02-007, 70pp.

Title: TBT in the Canadian environment

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Summary of Activities

Work this year focussed on the third national survey for TBT in water and sediment, selected analyses for the Canadian Wildlife Service, and an interlaboratory study on organotins.

National survey for TBT

Samples of water and sediment collected from about 200 locations are currently being analyzed. Laboratory preparation have been completed in quadruplicate for the 4 L water samples and are currently being analyzed by GC-FPD. This data and that previously collected for the sediment samples will be analyzed in the coming year.

Analyses for CWS

Analyses were completed for five composite liver samples (Barrows and Common Goldeneye ducks) for butyltins for CWS-Québec Region (L. Champoux). Tributyltin was not present in any of the samples. Monobutyltin and dibutyltin were found at very low levels in the 4 of the 5 samples. Analyses of other Surf Scoter blood, liver, and feather tissues for CWS-PYR (J.E. Elliott, L. Wilson) will continue in the next fiscal year.

Interlaboratory Study

Our laboratory participated in the Northern Contaminants Program Interlaboratory Study NCP II-6, The Analysis of Organotins in Biota and Sediments.

Timeline	
Start Date:	***Apr 1, 1999***
End Date:	***Mar 31, 2003***

Resources:	
A Base PY in NWRI	***1.0***
A Base O&M	***$25K***
A Base Capital	***$0K***

Title: Effects of Tributyltin (TBT) on Freshwater Invertebrates

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Summary of Activities:

Tissue samples collected from experiments to determine the kinetics of TBT uptake and depuration in *Hyalella azteca* were processed and the results analysed. Data analysis of the chronic effects of TBT on *Hyalella* based on survival, growth, and reproduction endpoints was completed. Both the kinetics data and the chronic effects data are being prepared for publication. Chemical analysis of samples collected from an experiment designed to determine the chronic effects of TBT on six species of freshwater invertebrates is in progress. This work is ongoing.

Kinetics Experiments

It is important to understand the behaviour of a contaminant in the organism in which it is being studied before designing toxicity bioassays. The purpose of this study was to address four issues of the kinetics of TBT in the freshwater amphipod, *Hyalella azteca*: depuration, effect of gut clearance on body concentration, time to steady state body concentration, and route of uptake from the environment. Tissue samples collected from experiments conducted last year were analysed for TBT. Body concentrations of TBT exhibit a biphasic decline, with a stronger decrease over the first 24 h that is attributed primarily to gut clearance. Gut contents contribute significantly to body concentrations of TBT at the start of depuration, accounting for 21-31% of the total body burden in water- and sediment-exposed amphipods, respectively. The more gradual decrease in TBT following 24 h is most likely due to excretion from the body. Half-lives of TBT in *Hyalella* were calculated from the depuration rate constants to be 6 d and 12 d for amphipods exposed to spiked water and spiked sediment, respectively. *Hyalella* accumulate TBT rapidly, reaching steady state within 14 d. BCFs are in the range of $2\text{-}3\times10^4$. Equilibrium body concentrations are similar between amphipods exposed to spiked water and those exposed to spiked sediment, indicating that the primary route of uptake is via dissolved TBT. However, the rate of uptake is significantly higher in sediment-exposed amphipods, a phenomenon that cannot be explained by kinetics alone. The results of this study have significant implications in the experimental design of studies involving the effects of TBT in *Hyalella*. As gut contents contribute significantly to body concentrations of TBT, gut clearance of 24 h is necessary for an accurate determination of exposure. Bioassays of less than 14 d in duration will underestimate toxic effects as well as the bioconcentration factor. And finally, since dissolved TBT is the bioavailable fraction, it is a more relevant measure of toxicity than TBT in the sediment, a fact that is important when measuring environmental concentrations as part of a risk assessment.

Chronic Toxicity Experiment

The chronic toxicity of TBT on the survival, growth, and reproduction of *Hyalella* was investigated over two generations, using body burdens as a measure of exposure. A mortality rate model was fitted to the survival data to calculate LC25s and LC50s, while nonlinear regression models were used to calculate IC25s

for growth and reproduction. Growth is a less sensitive measure of toxicity than survival, and while reproduction appears to be a more sensitive endpoint than survival, the data are highly variable (Table 1). Multi-generational studies are not necessary as there are no detectable differences between generations. TBT levels in the Canadian environment are high enough to induce chronic effects in *Hyalella*. Further research is necessary to determine effects on other, more sensitive freshwater invertebrates.

Table 1. Toxicity of TBT to *Hyalella azteca* in comparison to environmental concentrations in Canada.

Endpoint		Sediment (95% CI)[a]	Water[b]	Tissue[c]
Survival	4-wk LC50	1512 (1159-1972)	153	4170
	10-wk LC50	786 (473-1306)	61	2368
	10-wk LC25	365 (154-865)	30	1223
Growth	10-wk IC25	900 (662-1225)	73	2758
Reproduction	10-wk IC25	111 (25-486)	17	472
Environmental Concentrations[d]		4-975	3-18	

a. Units are ng Sn/g dry weight sediment.
b. Units are ng Sn/L; values computed from water-sediment relationship.
c. Units are ng Sn/g dry weight tissue; values computed from tissue-sediment relationship.
d. Reference: Chau, Y.K., R.J. Maguire, M. Brown, F. Yang and S.P. Batchelor. 1997. Occurrence of organotin compounds in the Canadian aquatic environment five years after the regulation of antifouling uses of tributyltin. Wat. Qual. Res. J. Can. 32(3):453-521.

Multi-Species Experiment

Last year, a chronic, spiked sediment experiment was carried out involving the simultaneous exposure of six freshwater invertebrate species to TBT to determine their relative sensitivities. Survival, growth, and reproduction were measured. This year, chemical analysis of water and tissue samples was completed. Analysis of sediment samples is ongoing, as is the data analysis.

Timeline

Start Date:	April 1, 1999
End Date:	September 30, 2003

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

Publications, Reports, Conference/Workshop Presentations:

Bartlett, A.J., D.G. Dixon, R.J. Maguire, S.P. Batchelor and U. Borgmann. 2001. Accumulation of tributyltin in *Hyalella azteca* as an indicator of chronic toxicity: Survival, growth, and reproduction. In: McKernan, J.M., B. Wilkes, K. Mathers and A.J. Niimi. Proceedings of the 28th Annual Aquatic Toxicity Workshop: September 30-October 3, 2001, Winnipeg, Manitoba. Can. Tech. Rep. Fish. Aquat. Sci. 2379:68-69 (abstract of poster presentation).

Bartlett, A.J., D.G. Dixon, R.J. Maguire, S.P. Batchelor and U. Borgmann. 2001. Accumulation of tributyltin in *Hyalella azteca* as an indicator of chronic toxicity: Survival, growth, and reproduction. 22nd Annual Society of Environmental Toxicology and Chemistry Meeting: November 11-15, 2001, Baltimore, Maryland. PM051 (abstract of poster presentation).

Bartlett, A.J., D.G. Dixon, R.J. Maguire, S.P. Batchelor and U. Borgmann. 2001. Kinetics of tributyltin uptake and depuration in *Hyalella azteca*: Implications for experimental design. In: McKernan, J.M., B. Wilkes, K. Mathers and A.J. Niimi. Proceedings of the 28th Annual Aquatic Toxicity Workshop: September 30-October 3, 2001, Winnipeg, Manitoba. Can. Tech. Rep. Fish. Aquat. Sci. 2379:7-8 (abstract of platform presentation).

NWRI Pesticide Activities for FY 01/02

Title: Persistent Organic Pollutants in the Great Lakes and associated Areas of Concern

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Collaborators:
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Dr. G. Stern, DFO,
Dr. S. Painter, Ontario Region;
Mr. M. Charlton, AEMRB, NWRI

Summary of Activities:

NWRI together with its collaborating agencies continued lake-wide surficial sediment surveys in FY 01/02 as part of the Great Lakes Sediment Assessment Program. The goal of this program is to assess spatial and temporal trends in persistent organic pollutants (POPs), including a variety of pesticides, in the Great Lakes. Sediment core data and comparison of contemporary surficial sediment levels with historical values have indicated a general decline in pesticide contamination in sediments of both Lakes Erie and Ontario over the past thirty years. Sediment pesticide concentrations in most areas have declined to levels below guideline values established for the protection of aquatic biota. Lakes St. Clair and Superior were sampled in FY 01/02; data from these surveys will be compared with previous Environment Canada surveys to assess the degree of improvement in environmental quality since the advent of initiatives to reduce pesticide loadings to the Great Lakes.

Timeline	
Start Date:	1997
End Date:	Ongoing

Resources (NWRI only):	
A-Base PYs in NWRI	1.5
A-Base O&M in NWRI	$45K

Publications, Reports, Conference/Workshop Presentations:

Painter, S., Marvin, C.H., Rosa, F., Reynoldson, T.B., Charlton, M.N., Fox, M.E., Thiessen, P.A. and Estenik, J.F. 2001. Sediment contamination in Lake Erie: A 25-year retrospective analysis. Journal of Great Lakes Research, 27:434-448.

Marvin, C.H., Painter, S., Charlton, M.N., Rosa, F., Myers, D. and Button, D. 2001. Spatial and temporal trends in sediment contamination in Lake Erie. *Abstracts from the 44th Conference on Great Lakes Research*, June 10th-14th, Green Bay, Wisconsin.

Marvin, C.H., Painter, S., Charlton, M., Rosa, F., Thiessen, P.A. and Estenik, J.F. Sediment contamination in Lake Erie: A spatial and temporal overview of banned, current-use and emerging-issue compounds. *Program and Notes of the Lake Erie in the Millennium Binational Conference*, March 28th-29th, Windsor, Ontario.

NWRI Pesticide Activities for FY 01/02

Title: The impact of agricultural management practices on pesticide transport to surface waters, ground water and a ir.

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Collaborators

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T. Wolf, RB, AAFC
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Summary of Activities:

1) In collaboration with Elliott, NWRI, Saskatoon and Tollefson, PFRA, Outlook continued study of nitrate and pesticide leaching/preferential flow of potato on a tile drained site on the Canada-Saskatchewan Irrigation Diversification Centre, Outlook.. Potato is grown in a 3-year rotation with canola and wheat. In years when potato is grown, ground water samples are collected weekly during the growing season and monthly during winter. When other crops are grown, samples are collected every t 2 weeks during the growing season and monthly during the winter.

2) In collaboration with Wolf, AAFC, Saskatoon and Hilliard, PFRA, Saskatoon, continued the study to determine the effectiveness of various vegetation types in intercepting pesticide application drift to prevent deposition into prairie wetlands and other sensitive areas.. Field trials were conducted using low, medium and high vegetation types. Analyses to determine deposition of pesticide and fluorescent dye on petri dishes were completed.

3) In collaboration with Elliottt, NWRI and Hilliard, PFRA, Saskatoon, continued study on the effect of tillage system on surface water runoff by using field data to compare two models: the Agriculture Non-Point Source (AGNPS) model and the Cold Region Hydrologic Model (CRHM). The CRHM handles snow melt better and we are continuing to further develop that model.

Timeline

Start Date:

1) April, 2000
2) April, 2000
3) April, 1995
   1998

End Date:

1) Ongoing
2) Ongoing
3) Ongoing

Resources (NWRI only):

A-base PYs in NWRI	0
A-Base O&M in NWRI	$6.0K
A-Base capital in NWRI	Nil
External Pys	0
External O&M	AFIF: $30.0K;
Total External O&M	$30K
External capital	$0K

Publications, Reports, Conference/Workshop Presentations:

Cessna, A.J., Elliott, J.A., Tollefson, L. and Nicholaichuk, W. 2001. Herbicide and nutrient transport from an irrigation district into the South Saskatchewan River J. Environ. Qual. 30:1796-1807.

Elliott, J.A., Cessna, A.J. and Hilliard, C.R. 2001. Influence of tillage system on water quality and quantity in prairie pothole wetlands. Can. Water Resources J. 26:165-181.

Cessna, A.J., Elliott, J.A. 22001. Seasonal variation of concentrations of herbicides and

inorganic ions in prairie farm dugouts. Final report to the Sustainable Water Management Committee and the Water Quality Technical Committee, 95 pp.

Cessna, A.J. and Elliott, J.A. 2001. Seasonal variation of herbicide and nutrient concentrations in prairie farm dugouts. 22nd Annual Meeting of the Society of Environmental Toxicology and Chemistry, Baltimore, MD, 11-15 November, 2001.

Cessna, A.J. and Elliott, J.A. 2001. Seasonal variation of herbicide and nutrient concentrations in prairie farm dugouts. 2001 National Meeting of the Expert Committee on Weeds, 25-28 November, 2001, Quebec City, QB.

Cessna, A.J. 2001. Strategy for coordination among research projects and other national initiatives. Agriculture and water quality workshop, Agriculture and Agri-Food Canada, Strategic Policy Branch, 29-30 November, 2001,Ottawa, ON.

Cessna, A.J., Chambers, P., Zoski, E., Mills, P. and O'Donovan, J. 2001. Herbicide concentrations in the Wapiti River and two of its tributaries. Western Canada Trace Residue Analysts' Workshop. 27-29 May, 2001, Winnipeg, MB.

NWRI Pesticide Activities for FY 01/02

Title: Pesticides in Black Brook, NB.

Principal investigators:

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Summary of activities

Regular samples of groundwater and surface water were taken throughout the entire year to determine pesticide fluxes in the potato belt of New Brunswick. Analytical protocol for the extraction of 8 pesticides had been previously developed. A new LC-MS instrument-method, for these compounds was developed. The method was designed to investigate the phenomenon of matrix effects, which often complicate pesticide analysis. A manuscript on the method is in preparation. An additional study was initiated to investigate the impact of pesticide residues as potential causative agents in brook trout early life stage mortality, in the Black Brook incubators. To determine if active compounds are present in sediments accumulated in egg incubators deployed in agricultural areas, large scale sediment extractions were performed and extracts for were used for testing with medaka. Pesticide fluxes in real-world situations provide information on leachability, movement and fate which is used by Agriculture Canada, PMRA and EC to study the fate and effects of modern pesticides.

Timeline	
Start Date:	***2001***
End Date:	***on-going***

Resources	
A-base PYs in NWRI:	***0.4***
A-Base O&M in NWRI:	***4K***
A-Base capital in NWRI:	***none***
External PYs (estimate) :	***0.2***
External O&M (estimate:	***10K***
External capital (estimate):	***none***

Publications, Reports, Conference/Workshop Presentations:

Hewitt, M., J. Toito, S. Backus, P. Milburn. 2001. A multi-residue method for surface and groundwater analysis of agrochemicals associated with potato production in Atlantic Canada. Presented at multi-stakeholder meeting in St. Andre, New Brunswick, July 19, 2001.

Marlatt, V., G. Van Der Kraak M. Hewitt. 2001. A Comparison of Three *In Vitro* Assays to Evaluate the Estrogenicity of Compounds in Rainbow Trout (*Oncorhynchus mykiss*). Presented at Society of Environmental Toxicology and Chemistry, 22nd Annual Meeting, Baltimore, Maryland, USA, November 11-15, 2001.

Hewitt, M. J. Toito, C. MacEachen, S. Backus and P. Milburn. 2002. Development of a multi-residue method for determination of agrochemicals associated with potato production in Atlantic Canada. Presented at TSRI Saint John River Symposium, University of New Brunswick, Saint John NB, January 25, 2002.

NWRI Pesticide Activities for FY 01/02

Title: Assessing the ability of pesticides in PEI potato fields to cause anti-estrogenic and estrogenic effects in fish.

Principal Investigator:

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Rita Mroz (Atlantic Region).
Ken Doe (EC, Atlantic Region) 506 851 3486, ken.doe@ec.gc.ca

Summary of Activities:

This study provides knowledge on the ability of run-off from potato fields in PEI to cause estrogenic effects in fish. The results of the study will be useful to EC and the Agricultural sector. Vg was measured in the plasma of several hundred fish previously exposed to PEI streams in 2001. Data analysis is in progress; however, no vitellogenin (Vg) induction was observed at any of the agricultural sites. Fish were exposed to pulses and continuous doses of estradiol and pesticides in a laboratory test at EC's Moncton laboratory. The pesticides (Endosulfan, Atrazine and Linuron) were selected based on heavy use in PEI potato fields and suspected endocrine activity. The Vg levels in the plasma samples from the experiments are currently under analysis.

Timeline	
Start Date:	***1999***
End Date:	***2002***

Resources (NWRI only):	
A-base PYs in NWRI	0.1
A-Base O&M in NWRI	
A-Base capital in NWRI	
External PYs (estimate)	0.5
External O&M (estimate)	$5.9K
External capital (estimate)	none

Publications, Reports, Conference/Workshop Presentations:

Mroz, R., Ernst, W., Rutherford, L., Kennedy, K., Sherry, J. and E. Bentley 2002. Potential endocrine disruption in freshwater systems near agricultural areas on Prince Edward Island. Presented at ATW, Winnipeg. Sept. 30 - Oct 3, PL 088.

Hoekstra, P.F. (University of Guelph), Dayeh, V. (University of Waterloo), Sherry, J., Solomon, K.R. (University of Guelph), Bols, N. (University of Waterloo), and Muir, D.C.G. Enantiomer- specific toxicity of o,p'-DDT to rainbow trout hepatocytes. Presented at SETAC Annual Meeting 2002.

Title: Tests of biological activity of herbicides, insecticides, fungicides and their effects on the immune system of fish

Principal Investigator:
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Collaborator:

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Summary of Activities:

This study investigates the biological activity of several herbicides, insecticides, fungicides and their effects on immune system of fish. The pesticides selected for this study are member of a class of chemicals that share the characteristic ability to alter, or disrupt, the body's hormone or endocrine system. These chemicals have also been listed for in depth review for environmental toxicity and environmental concentration by Environment Canada (Ecosystem Health Division - Ontario Region). All the pesticides standards were analyzed by GC-MS for their purity check up. Two sets of stock solutions in concentrations ranging from 1000ppm to 10000ppm were prepared in ethanol and dimethyl sulfoxide.Goldfish macrophages were exposed *in vitro to* atrazine, endosulfan, metolachlor, cyanazine and metribuzin to determine whether these compounds could modulate antimicrobial responses of fish macrophages. The data suggest that exposure of fish to these pesticides may alter the innate killing mechanisms of macrophages, rendering the host more susceptible to infectious disease. The data is particularly relevant for gill macrophages that may be directly exposed to these chemicals. The findings from this study are novel, and to date little is known about the modulating effects of these pesticides on the immune system of fish. This information will be essential for assessing environmental impacts of these pesticides on fish populations, and help support regulatory decisions to either justify or limit their usage. A manuscript of this work is in preparation. Recent evidence suggests that many commonly used pesticides modulate physiological activities in non-target organisms. Sixteen different pesticides were originally proposed to be tested for their ability to modulate the immune response of goldfish and murine macrophages *in vitro*. Some of these pesticides have been used in Ontario in quantities greater than 25,000 kg/year for crop protection, and all pesticides have been listed by the US-EPA as potential endocrine disrupting chemicals. This work supports departmental needs to assess environmental hazards and risks associated with the use of these compounds. Immunomodulating activity was assessed for the following compounds in both fish and mammals: atrazine, cynanzine, endosulfan, metolachlor, and metribuzin. Immunomodulatory activity of glyphosate and 2,4-D was also assessed in mammalian macrophages. Atrazine, cynanzine, endosulfan, and metolachlor suppressed macrophage antimicrobial activity (nitric oxide and respiratory burst activity) in fish, but had little effect on mammalian macrophages, except for metolachor which also drastically suppressed mammalian macrophage activity. Metribuzin displayed the least suppressive effect on macrophage antimicrobial activity. 2,4-D and glyphosate did not affect mammalian macrophage antimicrobial responses

Timeline
Start Date:
End Date:

Resources (NWRI only):	
A-base PYs in NWRI	0.4
A-Base O&M in NWRI	$5K
A-Base capital in NWRI	none
External PYs (estimate)	0.5
External O&M (estimate)	$5.9K

External capital (estimate) none

Publications, Reports, Conference/Workshop Presentations:

Mohan Kohli & Norm F. Neumann. A poster entitled "Immunomodulatory effects of pesticides on Fish macrophages function". 28th Annual Aquatic Toxicity Workshop. Held in Winnipeg, Manitoba on September 30, 2001.

NWRI Pesticide Activities for FY 01/02

Title: Application of the probabilistic neural network methodology to predict toxic effects of chemicals to biota.

Principal investigator

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Summary of Activities:

Building on earlier work on modeling toxicity to aquatic species, i.e., fathead minnow (*Pimephales promelas*), the crustacean *Daphnia magna*, the ciliate *Tetrahymena pyriformis* and bacterium *Vibrio fischeri*, research continued on the development and application of the Probabilistic Neural Network (PNN). Significant progress was achieved by application of the methodology to the interaction of compounds with steroid receptor complexes. Two different endpoints were used, (i) binding to the progesterone receptor and comparison with other models using the identical data sets for model training and testing, and (ii) the relative binding affinity (RBA) of over 1100 chemicals to the estrogen receptor. For the latter, significant sub-models could be derived for compounds containing specific chemical functional groups, including chlorine containing compounds, and carboxylic acids. These models have been developed on the basis of several hundreds of training compounds and have been cross-validated with independent test chemicals. Fig. 1 shows the measured versus predicted log(RBA) for the compounds in the training set.

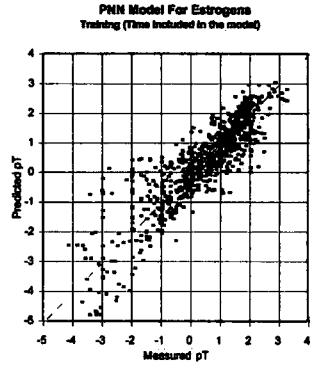

Figure 1. Measured versus predicted estrogen receptor binding affinities (training set) for 1100 chemicals; values given are log(RBA), where RBA is the relative binding affinity to the estrogen receptor with the reference compound estradiol arbitrarily set to 100% (log RBA = 2.00).

Timeline	
Start Date:	***1997***
End Date:	***on-going***

Resources (NWRI only):	
A-Base PYs in NWRI	***0.1***
A-Base O&M in NWRI	***$2.5K***
A-Base capital in NWRI	***none***

Publications, Reports, Conference/Workshop Presentations:

Kaiser KLE, Niculescu SP. 2001. Modeling acute toxicity of chemicals to *Daphnia magna*: a probabilistic neural network approach. Environ. Toxicol. Chem. 20:420-431.

Niculescu SP, Kaiser KLE. 2001. Modeling the relative binding affinity of steroids to the progesterone receptor with probabilistic neural networks. Quant. Struct.-Act. Relat., 20:223-226.

Kaiser KLE, Niculescu SP, Schultz TW. Probabilistic neural network modeling of the toxicity of chemicals to Tetrahymena pyriformis with molecular fragment descriptors. Proc. 9th Intl. Workshop on QSAR in Environmental Sciences, in press.

Kaiser KLE, Niculescu SP. 2001. On the PNN modeling of estrogen receptor binding data for carboxylic acid esters and organochlorine compounds. Water Qual. Res. J. Canada, 36: 619-630.

NLET Support to Pesticide Activities for FY 2001-02

The National Laboratory for Environmental Testing (NLET) provides analytical support and advice with regard to pesticides to program managers involved in monitoring and research at the National Water Research Institute and at all regional offices of Environment Canada. A summary of NLET involvement in pesticide activities for FY 2001-02 is provided below.

National Water Research Institute

Summary of Activities:

NLET provides the chemical analysis to determine organochlorine pesticide, congener polychlorinated biphenyls (PCB) and toxaphene contaminant concentrations in animals and fish of the Greenland food chain. The study is in Phase 3 of an international collaboration under the Arctic Monitoring and Assessment Programme (AMAP), which was funded by the Department of Arctic Environment, National Environmental Research Institute, Copenhagen, Denmark.

NLET manages the analytical aspects of the study and is also responsible for the supervision of work contributed by NWRI technical staff. The program requires mandatory bi-annual performance evaluation for organochlorine pesticides, PCB congeners and toxaphene in biota through samples provided by Quasimeme, the European quality assurance agency.

NLET is a major contributor of pesticide data to the Northern Contaminant Programs (NCP), National Science Foundation (NSF) and National Environmental Inventory (NEI) for samples from Alberta, Alaska, Labrador and Resolute. Samples are mainly biota and sediment from locations within the Arctic Circle. NLET participates in the annual external quality performance testing programs (NIST, NCP, DOE, CFIA) on congener polychlorinated biphenyls, brominated diphenyl ethers, toxaphene, organochlorine pesticides, methyl mercury and organotins.

NLET supplies quality assured organochlorine pesticide, congener PCB and polynuclear aromatic hydrocarbon data to support a five year study on sediment types in areas of concern in the lower Great Lakes of Canada. Each year 150 samples are anticipated with collections in catchments from riverine, harbour and open lake areas. The study was initiated in fiscal year 2000-01 to facilitate assessment of contaminant burdens and effectiveness of remedial activities.

NLET is a principal data provider for organochlorine residues in studies funded under the Toxic Substances Research Initiatives (TSRI) program. Samples are mainly sediment from remote global locations.

Substrate	Analysis	Number of Results
Water	organochlorine pesticides and polychlorinated biphenyls	500
	toxaphene	120
Sediment	organochlorine pesticides and polychlorinated biphenyls	23,500
	toxaphene	3,024
	polynuclear aromatic hydrocarbons	2,070
	methyl mercury	50
	brominated diphenyl ethers	1500
Biota	organochlorine pesticides and polychlorinated biphenyls	75,400
	methyl mercury	150
	toxaphene	10,400

Ontario Region

Summary of Activities:

NLET manages the Ontario Region Chemistry Services Unit that generates trace organic pesticide data for the Niagara River Monitoring Program. Ontario Region is the main data provider for the Niagara River Toxics Management Plan through the Declaration of Intent signed by Environment Canada, the U.S. Environmental Protection Agency, New York State Department of Environmental Conservation, and the Ontario Ministry of the Environment.

NLET is the principal data provider for Ontario Region's International Atmospheric Deposition Network (IADN) commitment. Work products require NLET to participate in IADN and CAEAL proficiency testing programs, and third party audits by USEPA, IADN and CAEAL to assess quality control practices. NLET also is responsible for the provision of trace organic pesticide data for Great Lake assessment programs on transboundary pollution and tributary inputs, to fulfill obligations under the Canada-U.S. Great Lakes Water Quality Agreement.

Substrate	Analysis	Number of Results
Water	chlorobenzenes	3024
	organochlorine pesticides and polychlorinated biphenyls	47,600
	toxaphene	390
	herbicides	1050
	organophosphate pesticides	480
	polynuclear aromatic hydrocarbons	8,700
	Brominated diphenyl ethers	375
Sediment	organochlorine pesticides and polychlorinated biphenyls	12,180
	polynuclear aromatic hydrocarbons	2415
	chlorobenzenes	840

Quebec Region

Summary of Activities:

NLET provided analytical services to St. Lawrence Centre scientists involved in the integrated St. Lawrence River Management Program.

Substrate	Analysis	Number of Results
Water	neutral herbicides	299

Prairie and Northern Region

Summary of Activities:

To enable the preparation of reports to the Prairie Provinces Water Board and the International Red River Pollution Board, NLET provides quality-assured trace organic pesticide data for aquatic assessment of water systems and early identification of unusual water quality conditions. Data are also provided to support National Park agreements, and federal/provincial and international water quality agreements for water quality monitoring. NLET contributes trace organic contaminant data to studies on biodiversity in aquatic environments, which support the Canadian Biodiversity Strategy and the United Nations Convention on Biological Diversity.

In the North, trace organic pesticide data furnished by NLET are used for the Nahanni National Park Reserve Monitoring Program. Nahanni National Park Reserve is an Ecological Monitoring and Assessment Network (EMAN)

site located in the Northwest Territories. Data are also provided to support numerous aquatic quality monitoring programs such as the NWT-Nunavut Aquatic Quality Network and the NWT-Alberta Transboundary Rivers Aquatic Quality Program.

Substrate	Analysis	Number of Results
Water	organochlorine pesticides	1702
	organophosphate pesticides	78
	polynuclear aromatic hydrocarbons	1288
	neutral herbicides	975
	acid herbicides	804
Sediment		
	organochlorine pesticides and polychlorinated biphenyls	207
Biota		
	organochlorine pesticides and polychlorinated biphenyls	2280

Pacific and Yukon Region

Summary of Activities:

Environment Canada staff in Pacific and Yukon Region rely on NLET for the provision of quality assured trace organic pesticide data to support the B.C. Water Quality Monitoring Network and to facilitate water resource planning and environmental assessments in the region.

Substrate	Analysis	Number of Results
Biota	organochlorine pesticides and polychlorinated biphenyls	9956

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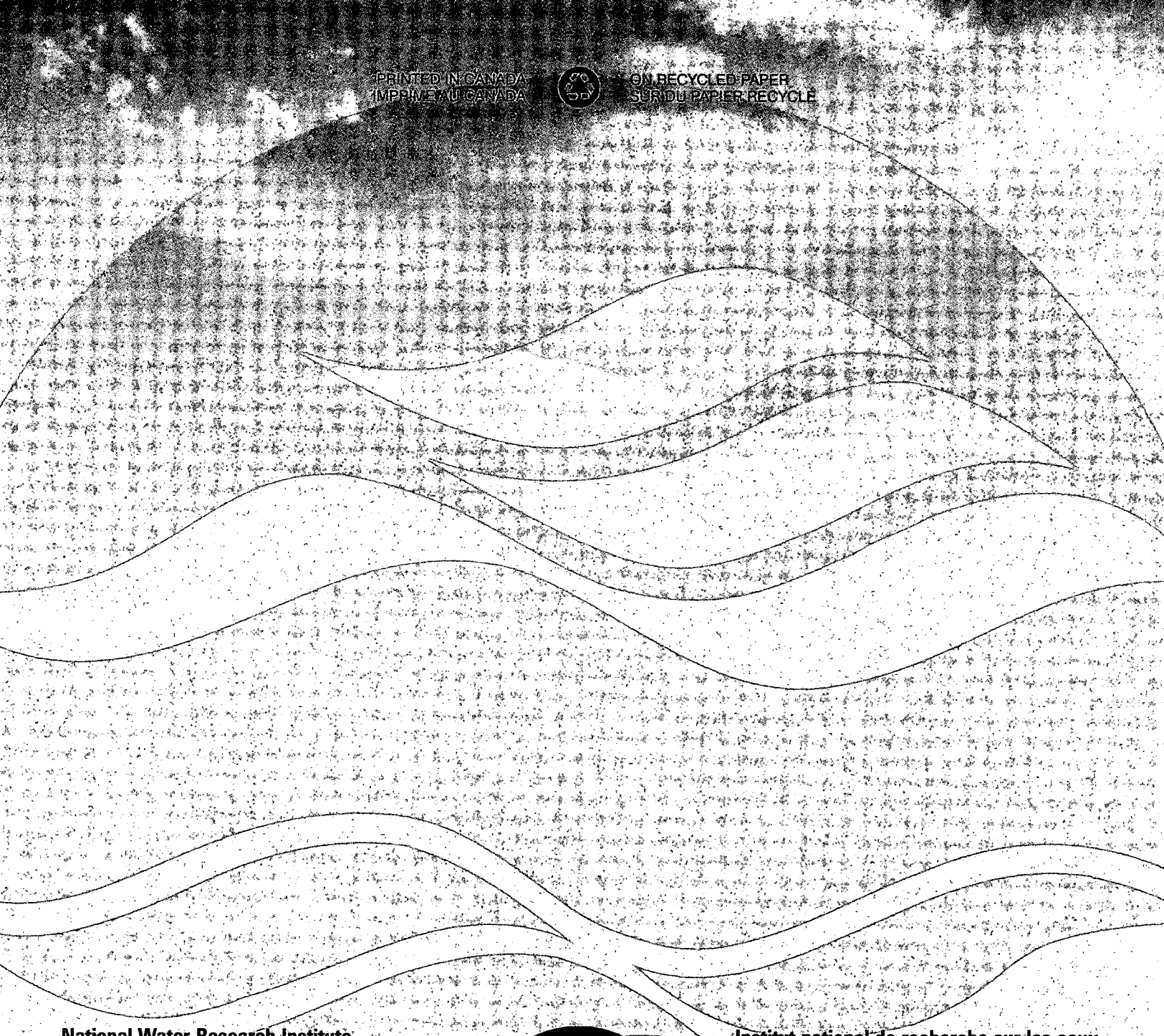

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