Pesticides Research and Monitoring Annual Reports 1989–1990 and 1990–1991

Environment Canada

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Preface

The Pesticides Program Management Committee (PPMC) has combined the fourth and fifth annual reports on activities carried out under Environment Canada's pesticides research and monitoring program. Contributors were asked to provide summaries of projects carried out under A-base as well as PESTFUND during 1989–90 and 1990–91 in their region, branch, institute, or service. The project reports submitted include final reports, progress reports on multiyear projects, and interim reports. In addition, projects carried out in past years but not previously reported are summarized.

Environment Canada's pesticide program has been very active with new and innovative research in these two years. The exchange of information among the different regions is increasing as is indicated by emerging collaborative efforts. The PPMC would like to take this opportunity to thank all who have contributed to pesticide research and monitoring at Environment Canada. This document is a compilation of all these efforts. It compiles the available information and targets a multidisciplinary pool of readers with pesticide interests. The main purpose of the document is to enhance contacts among researchers. Indices are provided by pesticide, keyword, and author. Also a list of abbreviations appears after the executive summary.

Avant-propos

Le Comité de gestion du programme des pesticides (CGPP) a combiné les quatrième et cinquième rapports annuels des activités réalisées dans le cadre du programme de recherche et de surveillance d'Environnement Canada relatif aux pesticides. Les auteurs ont été priés de fournir des résumés des projets réalisés au moyen des services votés et des subventions du PESTFUND en 1989-1990 et 1990-1991 dans leur région, leur direction, leur institut ou leur service. Les rapports soumis peuvent être des rapports finals, des rapports d'étape dans le cas de projets pluriannuels ou des rapports provisoires. On trouvera en outre des résumés des projets réalisés au cours des années précédentes dont on n'avait pas fait état dans le dernier rapport publié (1988-1989).

Le programme des pesticides d'Environnement Canada a fait preuve d'un grand dynamisme dans le domaine de la recherche au cours de ces deux dernières années. Les échanges d'informations entre les différentes régions se multiplient, comme l'attestent les nouvelles initiatives de collaboration. Le CGPP aimerait profiter de cette occasion pour remercier tous ceux qui ont contribué aux activités de recherche et de surveillance concernant les pesticides à Environnement Canada. Le présent document est une compilation de tous ces efforts. Il résume les informations disponibles et s'adresse à un bassin multidisciplinaire de lecteurs intéressés par les pesticides. Le principal objet du présent document est d'accroître les contacts entre les chercheurs. Le lecteur trouvera des index des pesticides, des mots clés et des auteurs. Une liste d'abréviations figure en outre à la suite du sommaire.

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Executive Summary

The projects are grouped into five regions and headquarters, based on where the work was actually conducted.

Atlantic Region. As large quantities of pesticides are used annually in the potato-growing industry of the Atlantic Region, studies investigating the presence of in-use pesticides in subsurface drainage are a major undertaking. The investigation into the quality of raw drinking water was in the final year of a four-year joint federal–provincial study. These and most other projects have in the past been conducted through a multiagency cooperative effort that is commendable.

Atmospheric transport and wet deposition of pesticides were investigated and were the principal mechanisms for the presence of lindane and *alpha*-BHC in isolated lakes of southern Labrador. Surprisingly, other pesticides (e.g., atrazine) are also following this route. Data are being analyzed both temporally and spatially.

Investigations determining the vulnerability of aquifers to pesticides are under way with analyses of data from lysimeters and piezometers. Data covering all aspects of environmental contamination are being compiled and modelled. The collaborative research provides additional information on regional pesticides of concern, their use, and their presence in the environment.

Research has associated a decline in diversity of bird species to pesticide use. These studies are reported here as well as studies to determine the potential relevance to migratory bird management of current lowbush blueberry cultivation practices.

Quebec Region. The Quebec region was involved in the development of phytotoxicity assays (mostly algal) that standardize and expedite the procurement of data. Microplate cultures of the green alga *Selenastrum capricornutum* or local species of algae were used in the laboratory to obtain pesticide toxicity data. The toxicological endpoint used reflected the mode of action of the pesticide under study thereby augmenting the sensitivity of the toxicity assay. EC_{50}s and LOECs were derived from these data.

Monitoring studies for pesticides in soil, surface water, tile-drain water, agricultural ditch water, rivers, and groundwaters were undertaken in areas of concern. There is increased emphasis on monitoring groundwaters as there is a dearth of information in this area. Models are used to assist in predicting potential local problems.

Monitoring for "cash crop" pesticides has grown in direct relation to interest in this agricultural sector. Work has begun to establish a site-specific water quality objective for atrazine in the Yamaska River.

Investigations in the region have dealt with the protection of wildlife through regulation, monitoring, and development of a warning system. The pesticide program in the region has outlined a reorientation described in an operational plan encompassing both long- and short-term planning.

Headquarters. A data base was created on post-spray pesticide residue levels in plants to evaluate fauna exposure. A pilot study was initiated to investigate the effects of sublethal dosing with fenitrothion, a cholinesterase inhibitor, on the reproductive

biology of the Tree Swallow and to evaluate the usefulness of the doubly labelled water technique to monitor disruptions in a breeding pair's time-energy budget. Fenitrothion was used in a behavioural toxicology study; the effects of sublethal organophosphate dosing on learning and memory in birds was examined. Interestingly, relatively high levels of the pesticide enhanced rather than impeded the future memory for food caches.

An R-memo for distribution by Agriculture Canada to pesticide registrants concerning nontarget plant guidelines was completed and is under peer review. Another study was undertaken to improve the methodology for testing toxicity of pesticides to algae and cyanobacteria. Good testing conditions with different species of algae and an identification of facilities where tests can be carried out effectively were initial priorities.

A comparison of the avifauna on farms using organic practices and those using chemical pesticides in different regions of Canada is being addressed. Studies are underway in the Maritimes, Quebec, Ontario, and Saskatchewan.

Nontarget plant toxicological assessments for MCPA and butylate using *Selenastrum capricornutum* and *Lemna minor* were made.

Water quality guidelines for several pesticides have been derived for protection of aquatic life, irrigation waters, and livestock waters. The guidelines for individual pesticides are based on an extensive literature survey and a toxicological data evaluation document. Throughout the regions exceedances have been reported and will be considered once the pesticides are reevaluated.

Ontario Region. Extraction, cleanup, and gas chromatographic analysis for 13 organophosphorus pesticides in water, sediment, and tissues have been developed by the National Water Quality Laboratory in support of a study by several agencies of Environment Canada concerning contamination in the Holland Marsh area of Ontario.

There was production of some unique reference materials in the form of sediment extracts in ampoules for trifluralin, triallate, atrazine, and other neutral herbicides of concern. Further, a method was developed to measure levels of acetylcholinesterase (AChE) in aquatic invertebrates exposed to low concentrations of organophosphate insecticides. Changes in AChE were evaluated as a potential biochemical indicator of sublethal toxicity. Other method development included herbicide effects on the photosynthetic activity of epilithic communities and a screening technique for the detection of trace contaminants in environmental samples utilizing immunoassays.

The antifoulant tributyltin has been under investigation. Its entry into the environment from sewage sludge, its LC_{50}, and its metabolic compartmentalization have been determined in both rainbow and lake trout. Studies have provided the acute toxicity of isomers of deltamethrin and its breakdown products to *Daphnia magna*. Deltamethrin and fenitrothion were the object of volatilization studies from surface and subsurface water microlayers. Another study related climatic variability with fungicide optimization.

An Expert System for Pesticide Regulatory Evaluation Simulation (EXPRES), a model to assay the potential for groundwater contamination by pesticides in the subsurface

environment, has been under development. A software package and Users Manual should be available in the near future.

Concentrations of herbicides in agricultural runoff have been compared in conservation versus conventional tillage practices. Conventional tillage contributed to increased leaching of herbicides. A separate study showed that azinphos-methyl (Guthion) and diazinon were present in surface waters of the fruit-growing region of the Niagara Peninsula. In wetland areas sampled in southern Ontario atrazine and metolachlor were detected at concentrations of up to 17 µg/L and 9 µg/L, respectively. Another study monitored the presence/absence of herbicides in both surface water and groundwater in the Big Creek watershed.

Western and Northern Region. Several studies were carried out in the Western and Northern Region assessing the physiological or behavioural effect of in-use pesticides on bird species. Many of the investigations are currently ongoing. An evaluation of the effectiveness of a data collection system to monitor effects of pesticides on Mountain Bluebirds and Tree Swallows was made. Also a study of the geographic distribution and the insecticides used on alfalfa grown for seed and forage in the prairies and an assessment of bird dependency on the crop were conducted.

The toxic threat of lindane originating from long-range aerial transport to freshwater life in western Canadian rivers was assessed. Results from the new, more sensitive, seven-day lethal and sublethal tests, using *Ceriodaphnia dubia* and *Pimephales promelas* led to the conclusion that aquatic resources in western Canadian rivers are not likely to be at risk from lindane.

A literature review provided evidence that dimethoate is very toxic to non-target insects, birds, and fish. The following data gaps were identified: the persistence and fate of dimethoate in Canadian water systems, soil degradation rates in Canadian soils, and the toxicity of dimethoate to soil organisms.

A literature search on the use of carbofuran in Canada was conducted. The region's long-term quality assurance program was redesigned following a review of the inhouse data on organic chemicals.

Rainbow trout exposed to triallate concentrations of approximately 0.14 µg/L established a bioconcentration factor of 789. Glyphosate applications to an enclosure in a prairie pond had no impact as measured by phytoplankton biomass and productivity.

Laboratory and field studies were performed to estimate the lethal and sublethal effects of exposure of representative nontarget organisms to bran-bait formulations using three insecticides. It was concluded that bran-bait formulations are an effective and environmentally sound means of controlling grasshoppers. A research partnership between Agriculture Canada and Environment Canada has "thus served to remove possible environmental constraints from an otherwise environmentally favourable pest management strategy".

The region has investigated the off-target movement of pesticides used under a zero-till regime, the accumulation of trifluralin and congeners in sediments and benthic fauna of prairie farm dugouts, and the fate and effects of the herbicides difenzoquat and sethoxydim in prairie wetland enclosures.

Pacific and Yukon Region. An extensive study was conducted to determine the concentration of organotins (mainly

tributyltin) in sediment, water, and biota from British Columbia marinas, shipyards, heavy boating traffic areas and control sites, and salmon farms. Data are currently being compiled and analyzed.

Monitoring of wood preservation chemicals in the Fraser River's sediments and flatfish population was completed and is currently undergoing analysis. The information obtained will be used during the re-evaluation of heavy-duty wood preservatives, to be announced by Agriculture Canada in 1992.

In British Columbia, tissues of wild and hatching salmon were monitored to determine if pesticides or chemical contaminants were affecting Pacific salmon stocks. Results are being processed.

Leaching studies were conducted on lumber in storage which had previously been treated with anti-sapstain products. The studies were to determine concentrations of active ingredients and their degradation products leached from the treated lumber exposed to rainfall events during storage. Concentrations found were compared to those allowed under the B.C. Provincial Anti-sapstain Chemical Waste Control Regulation.

Toxicity studies have shown that butoxyesters of 2,4-D and 2,4-DP, and Weedone CB and its carrier are highly toxic to juvenile salmonids of the Pacific northwest. The toxicity of dyes used as herbicide markers in forestry has been investigated and application rates given. Several studies with wood preservative pesticides used in wood utility poles and railway ties indicated that these are a potential constant source of pesticide and/or pesticide contaminants to the aquatic environment.

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List of Abbreviations

ACA	ammoniacal copper arsenate
ACh	acetylcholine
AChE	acetylcholinesterase
a.i.	active ingredient
AMPA	amino methyl phosphonic acid
ASTM	American Standard Test Methods
BB	Basacid Blue
BBE	butoxyethyl esters
BCNWA	Big Creek National Wildlife Area
BHC	benzene hexachloride
CAPCO	Canadian Association of Pesticide Control Officials
CCA	chromated copper arsenate
ChE	cholinesterase
CI	confidence interval
CP	chlorophenol
CPIC	Crop Protection Institute of Canada
CREAMS	Chemicals, Runoff, and Erosion from Agricultural Management Systems
DBCA	cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane carboxylic acid
DBT	dibutyltin
DDAC	didecyldimethyl ammonium chloride
DSI	disease severity index
EC_{50}	effective concentration 50 (50% effect)
EIA	Elisa immunoassay
ELS	early life stage
EXPRES	Expert System for Pesticide Regulatory Evaluation Simulations
GC/MS	gas chromatography/mass spectroscopy

GIS	geographic information systems
GLEAMS	Groundwater Loading Effects of Agricultural Management Systems
HCB	hexachlorobenzene
HCH	hexachlorocyclohexane
HPLC	high performance liquid chromatography
IA	immunoassay
IC_{50}	inhibition concentration 50 (50% inhibition)
IGATG	Inter-Governmental Aquatic Toxicity Group
IPBC	3-iodo-2-propynyl butyl carbamate
IWC	Interdepartmental Working Committee
K_{ow}	octanol/water partition coefficient
LC_{50}	lethal concentration 50 (50% death)
LEACHM	Leaching of Chemicals Model
LOEC	lowest observable effects concentration
MAPAQ	Ministère de l'agriculture des pêches et de l'alimentation du Québec
MAC	maximum acceptable concentration
MATC	maximum acceptable toxicant concentration
MBT	2-mercaptobenzothiazole
MBT	monobutyltin
MCPA	4-chloro-2-methylphenoxy acetic acid
MENVIQ	Ministère de l'environnement du Québec
MFO	multi-function oxydases
MOE	Ministry of the Environment
NAQUADAT	National Water Quality Data Base
ND	nondetectable
NWQL	National Water Quality Laboratory
NWRC	National Wildlife Research Centre
NWRI	National Water Research Institute

OC	organochlorine
OMNR	Ontario Ministry of Natural Resources
OP	organophosphate
PAH	polycyclic aromatic hydrocarbons
PBacid	3-phenoxybenzoic acid
PBalc	3-phenoxybenzylalcohol
PBald	3-phenoxybenzaldehyde
PCA	principal coordinate analysis
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo dioxin
PCP	pentachlorophenol
PCPA	*Pest Control Products Act*
PPMC	Pesticides Program Management Committee
PRZM	Pesticide Root Zone Model
PSII	Photosystem 2
QA/QC	quality assurance/quality control
R1TRF	α,α,α-trifluoro-N^4,N^4-dipropyltoluene-3,4-diamine
R2TRF	α,α,α-trifluoro-N^4,N^4-dipropyltoluene-3,4,5-triamine
RIA	radioimunoassay
R-memo	Memorandum to Registrants
RFU	relative fluorescence units
RUD	residue per unit dosage
SFR	sediment fixed residue
Sn	tin
SRC	Saskatchewan Research Council
SVR	sediment volatile residue
TBT	tributyltin
TCMTB	2-(thiocyanomethylthio)benzothiazole

UQUAM	Université du Québec à Montréal
UTRCA	Upper Thames River Conservation Authority
VOC	volatile organic compounds
VULPEST	Vulnerability to Pesticides

PESTICIDES PROGRAM IN THE ATLANTIC REGION
(Nova Scotia, New Brunswick, Prince Edward Island, Newfoundland)

dinoseb, metribuzin, atrazine

1. AGRICULTURE SUBSURFACE DRAINAGE PROJECT - (T.L. Pollock, H.J. O'Neill, D.A. Léger, P. Milburn, J.E. Richards, and C. Gartley, WQB*-Atlantic Region)

Keywords. tile drainage, potato, Atlantic, Prince Edward Island, New Brunswick

Introduction. Elevated nutrient levels in surface waters draining agricultural areas and chemical contamination due to pesticide use have been documented in several areas of North America. Pesticides may reach groundwater and surface water via surface runoff, erosion, leaching, spray drift, improper container disposal, and accidental spills. Large quantities of pesticides are used annually in the potato-growing industry of the Atlantic Region. In cooperation with Agriculture Canada and the New Brunswick Department of Agriculture, the Water Quality Branch, Atlantic Region, investigated the presence of in-use pesticides in subsurface drainage.

The federal and provincial departments of agriculture were interested principally in the export of nutrients from the study sites.

Methods. In 1987 and 1988, the study was focused in northwestern New Brunswick on five tile-drained fields under active potato cultivation. Dinoseb and metribuzin were selected as the herbicides of interest for these sites. In 1989, a site in Cornhill, New Brunswick, was monitored for atrazine. The Cornhill site had a small field stream flowing parallel to the study fields. PESTFUND support was obtained in order to monitor the response of natural biota in the stream to tile-drain effluent. Preliminary work was also initiated on another tile-drained site on Prince Edward Island.

Results and Discussion. Both dinoseb and metribuzin were observed in tile effluent post-application and in the spring of the following year.

Results from the Cornhill sampling indicated a maximum atrazine concentration of 20 µg/L in the drainage tiles after the first post-application rain event. Stream monitoring indicated a maximum concentration of 13.9 µg/L. Results from the biological monitoring are undergoing interpretation.

The tile drainage work at Cornhill continued during 1990–91 with a focus on atrazine; the Prince Edward Island site was used to investigate chlorothalonil carryover from 1989.

Publication Medium. O'Neill, H.J. *et al.*, "Dinoseb Presence in Agricultural Subsurface Drainage from Potato Fields in Northwestern New Brunswick, Canada", *Bull. Environ. Contam. Toxicol., 43:* 935–940 (1989).

IWD Atlantic Region Report (IWD-AR-WQB-90-158).

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* The Water Quality Branch (Atlantic Region) is now known as the Monitoring and Evaluation Branch

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2. FEDERAL–PROVINCIAL DRINKING WATER SOURCES TOXIC CHEMICAL SURVEY - (WQB-Atlantic Region)

Keywords. Atlantic, surface water, groundwater, municipal water supply, water quality guidelines

Introduction. The fiscal year 1988–89 was the last of a four-year joint federal–provincial undertaking involving the Water Quality Branch, Health and Welfare Canada, the New Brunswick and Nova Scotia provincial departments of health, and the Prince Edward Island and Newfoundland departments of environment. This study involved the collection and analysis of raw surface water and groundwater sources serving various municipalities in each Atlantic province. Health and Welfare Canada investigated various volatile organic materials in raw and treated water, while the Water Quality Branch quantified major ions, metals, nutrients, environmental contaminants, and pesticides in raw water only.

Methods. In 1989, the project was downsized to focus on specific areas identified by the last four years' efforts. In Newfoundland, pentachlorophenol was the pesticide studied at 10 municipal supply sources, while in Nova Scotia, atrazine, aldicarb, chlorothalonil, and several OPs were quantified at four sources. Prince Edward Island had a full suite of variables quantified as this was its fourth year in the project. New Brunswick did not participate in 1989, but conducted its own investigation into VOCs in municipal supplies.

Results and Discussion. During 1989, a data summary report was prepared for each province for the period 1985 to 1988. The ubiquitous organochlorine alpha-BHC and the polyaromatic hydrocarbon fluoranthene have been observed in several sources. Any pesticide observations for which Canadian drinking water quality guidelines exist have been below the maximum acceptable concentration (MAC). Health and Welfare Canada has reported some volatile organic material in raw and treated sources. Perchloroethylene has been noted in two instances, indicating an emerging area of concern. These locations were resampled by the provincial departments responsible. The aesthetic guideline for colour has been exceeded by several municipalities that depend on surface water sources. Manganese and iron concentrations have also been reported in excess of the aesthetic guideline.

Publication Medium. An interpretative report has been prepared for the first four years of study and is available from the Water Quality Branch, Atlantic Region.

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3. ORGANIC CONTAMINANTS IN PRECIPITATION - (G.L. Brun and H.J. O'Neill, WQB-Atlantic Region)

Keywords. atmospheric transport, wet deposition, Labrador

Introduction. Atmospheric transport and subsequent deposition have been recognized as processes that put organic contaminants into the terrestrial environment. It was proposed that atmospheric input is the principle mechanism for lindane and alpha-BHC presence in isolated lakes of southern Labrador.

The Water Quality Branch, Atlantic Region, has been collecting monthly composite wet precipitation samples at three locations since 1980. Because of the sampling frequency and the length of this study, it is possible to describe seasonal and temporal patterns.

Methods. Data from three sites were assessed using box and whisker plots for monthly and yearly analysis. Ordinal ranks of monthly medians were used to assess seasonal patterns. All parameters quantitated were assessed where positive observations were reported. In 1989, the list of variables was expanded to include the triazine herbicides.

Results and Discussion. The presence of polycyclic aromatic hydrocarbons in wet precipitation has been shown to follow a seasonal pattern, with higher concentrations being observed during the cold months of the year. Concentrations at the three monitoring locations indicate local sources as the dominant mechanism.

Alpha-BHC and lindane observations at the three sites indicated temporal variability and were virtually identical. In 1983, they compared favourably with precipitation data from Lake Superior monitoring. The spatial similarities indicate that long-range transport is the dominant mechanism affecting the deposition of the hexachlorocyclohexane isomers.

atrazine was observed in precipitation from the Jackson, Nova Scotia, site and was confirmed using a mass selective detector in selected ion mode. Monitoring for atrazine is ongoing. Chlorothalonil was also added in 1990.

Publication Medium. None provided.

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4. AQUIFER VULNERABILITY PROJECT - (T. Hennigar, J. Gibb, F. Cruikshanks, T.L. Pollock, H.J. O'Neill, and D.A. Léger, WQB-Atlantic Region)

Keywords. lysimeters, piezometers, protocol, Atlantic, study plots

Introduction. Environment Canada, in cooperation with Agriculture Canada, is developing a proactive or anticipatory program to determine the environmental behaviour of pesticides and nitrates under climatic, physiographic, and soil conditions found in Atlantic Canada. This approach is intended to provide interested parties with the needed protocols for evaluating the chemistry and fate of agrichemicals, particularly as they relate to the new guidelines for the registration of pesticides in Canada. Another goal is to determine under what agricultural practices particular pesticides and fertilizers can be applied without causing unacceptable contamination of groundwaters. Certain pesticides suspected of being soluble and persistent enough to contaminate groundwaters will be subjected to controlled field applications.

To this end, a memorandum of understanding was signed with Agriculture Canada to conduct a five-year study at its Sheffield Farm Research Station in the Annapolis-Cornwallis Valley of Nova Scotia. The farm was chosen because it provides optimal study conditions. These include good project control (since it is a federal facility and a research station) and good logistics (e.g., close to IWD Atlantic Headquarters, available support facilities). It is representative of agricultural conditions in the Annapolis Valley; the well-drained sandy loams on the farm are typical of valley soils supporting a variety of crops including potatoes, berries, tobacco, and orchards.

Methods. The farm is located on the floor of the Annapolis-Cornwallis Valley and is bisected by a natural drainage channel. The soils of the farm have developed from glaciofluvial, fluviomarine, and till deposits. These overlie Triassic Wolfville bedrock, which consists mainly of poorly sorted and cross-stratified sandstones and conglomerates with intraformational claystone and siltstone.

A large part of the farm is covered with well-drained sandy loams of the Cornwallis and Somerset soil series. The aquifers beneath these permeable soils are vulnerable to contamination by pesticide and fertilizer residues. As such, the soils provide attractive sites in which to conduct experimental applications of pesticides and fertilizers to crops in order to assess the migration and fate of the residues with respect to groundwaters.

Results and Discussion. In 1989–90, water samples were collected from a series of piezometers on several potential study plots to ascertain background pesticide concentrations and to characterize the water quality. Bedrock and overburden piezometers were employed. Analytical results indicated that Site A was the most suitable to conduct field experiments on atrazine use. Several groundwater samples from other plots indicated triazine presence, which is a reflection of past practices in the area. Site A, however, indicated no triazine presence.

In 1989, lysimeters and additional piezometers were installed at Site A. In

1990, the site was cropped in corn and atrazine will be applied. The piezometers and lysimeters were sampled over the growing season to track atrazine migration to groundwater.

Publication Medium. None provided.

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5. RELATED PESTICIDE STUDIES - (WQB-Atlantic Region, federal departments, and provincial agencies)

Keywords. agrichemicals, inter-agency co-operation, Atlantic

Introduction. The presence of agrichemicals in the environment is a direct concern of Environment Canada, other government departments, and several provincial agencies. Frequently these agencies do not have the technical expertise or support to carry out specific aspects of their studies. The Inland Waters Directorate (IWD) attempts to provide technical input and, when possible, analytical support to specific projects.

Methods. Since 1988, Agriculture Canada has conducted a regional pesticide survey of farm wells in areas of intensive agriculture. Surveys have been done in areas where IWD has been conducting concurrent studies. In New Brunswick, dinoseb was the pesticide of interest, while in Nova Scotia, herbicides were targeted. Carbamate insecticides were the pesticides monitored in Prince Edward Island. Pesticide analysis is done by the Ottawa laboratory of Agriculture Canada, while major ion and nutrient data are produced by the Water Quality Branch (WQB) Regional Laboratory in Moncton. Approximately 60 samples are processed each year by the WQB. Data are exchanged in order to enhance IWD pesticide programming.

IWD (WQB) has also cooperated with the New Brunswick Department of Environment since 1989 in a phenoxyacid herbicide survey for MCPA in farm wells. Approximately 20 samples have been processed for MCPA, major ions, and nutrients. As with the Agriculture Canada samples, the New Brunswick provincial studies have been done in areas where IWD has been involved in pesticide studies.

Results and Discussion. Results from Agriculture Canada indicate that dinoseb was observed in some farm wells in New Brunswick, while atrazine, desethyl-atrazine, alachlor, and metolachlor were reported in wells in Nova Scotia. Those sites with positive observations are routinely followed up with a second sampling. Provincial officials responsible for health are kept apprised of all results.

MCPA results were forwarded to the New Brunswick Department of Environment, but these samples were blind so that any positive values might be attributed to quality control samples.

This interagency cooperation enhances the quality of data produced by IWD by providing additional information on regional pesticides of concern, their use, and their presence in the environment.

Publication Medium. None provided.

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6. THE APPLICATION OF GIS TECHNOLOGY TO TOXIC SUBSTANCES; RESOURCES-AT-RISK ASSESSMENTS - (H.J. O'Neill, WQB-Atlantic Region; and G.D. Howell, WPMB-Atlantic Region)

Keywords. GIS, land use, environmental monitoring, Atlantic

Introduction. Geographic information systems (GIS) are currently being applied to environmental monitoring and network design in at least two regions of Canada. A poster was prepared by IWD Atlantic Region to illustrate that existing GIS information could be improved with the inclusion of interpreted areal photographic data. The purpose was to show that GIS could be used on a project- and site-specific basis with direct applications to resources-at-risk assessments.

Methods. A map showing potential sources of pesticides was derived for the Tantramar Marsh at the head of the Bay of Fundy. This map was compared to one where agricultural and forestry data were further defined. The amount of agricultural pesticides employed, and the consequent environmental risk, in sod production, grain, and pasture vary. Areas of pesticide input associated with forestry applications, as well as those associated with vegetation control in rights-of-way and transportation corridors, were integrated and built into the refined analysis. A higher degree of data resolution using photographic data was obtained, thus presenting a more accurate description of the land use characteristics for the pilot site.

Results and Discussion. An areal analysis of the two maps indicated there were differences in the models. Because of the higher resolution and more accurate assignment of risk, there was a net shift in area to those of lower risk categories. Under the 1988 regional model, all potential and active agricultural land was classified as "high", while the refined 1990 model broke these down further so that, for example, sod production was high and pasture/grazing was low. The 1:250 000 regional data lacked the resolution to make a detailed analysis, with the result that the area was classed higher because of the generally better soil classes present in marshes. However, the 1:50 000 refined model shows more in detail in actual use and, therefore, is a more accurate representation of the actual pesticide input potential.

Publication Medium. None provided.

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azinphos-methyl

7. EFFECTS OF THE ORGANOPHOSPHATE PESTICIDE AZINPHOS-METHYL (GUTHION) ON THE BRAIN CHOLINESTERASE ACTIVITY OF TREE SWALLOWS, AND POPULATION STUDIES OF TREE SWALLOWS IN ANNAPOLIS VALLEY APPLE ORCHARDS, 1989 - (J. S. Boates, CWS-Atlantic Region)

Keywords. Tree Swallows, brain cholinesterase, apple orchards

Introduction. Scattered survey and anecdotal evidence indicates that bird diversity in Annapolis Valley orchards has decreased over the last several decades. Intensive use of chemical pesticides is characteristic of modern orchard growing; a broad array of chemicals is being sprayed throughout the bird nesting and rearing season. Theories possibly accounting for decreases in bird species diversity include direct and indirect effects of chemical pesticides, physical disturbance during spraying, and changes in the age structure of orchards. An initial, broadly based study indicated that overall there were no identifiable harmful effects of pesticide use on birds. However, the superficial nature of the investigation and the small sample sizes obtained would have precluded the finding of specific or localized effects of particular pesticides. The present study was aimed at determining the possible effects of azinphos-methyl, the most toxic pesticide used, on particular aspects of the biology of birds inhabiting the orchards.

Objectives. The objectives of the study were to determine: 1) the effect of azinphos-methyl spraying on the brain cholinesterase (ChE) activity of nestling Tree Swallows; and 2) the potential implications for other birds inhabiting the orchards.

Methods. After determining a dose-response curve in the laboratory, nestlings of various ages were orally dosed with Guthion to determine if age and ChE inhibition due to the dosage were related. Field experiments with oral dosing included the effect on weight gain of nestlings and the ability of adults to feed young. Different swallow nestlings were placed on the ground and in a nest box before an aerial application of Guthion to determine exposure of young to spray droplets and ChE inhibition. Information related to nidiology, including nesting success, was also recorded.

Results and Discussion. Oral dosing of nestlings to determine possible age-related differences in ChE inhibition revealed no significant difference between dosed and control nestlings at three days old. However, results indicated that nine- and 16-day-old nestlings showed depressed ChE levels three hours after dosing.

Oral dosing of one- to two-day-old nestlings with Guthion, sufficient to produce a 50% ChE inhibition level, showed no significant difference in weight gain over the 16-day nestling period between dosed and control nestlings.

Routine spraying had no significant effect on the ChE levels of ground versus nest box birds. The three-hour period before brain samples were taken may not have been long enough to detect a response. Data analysis of sprayed versus unsprayed plots for nestling ChE inhibition has yet to be completed.

The results from these studies show no significant effects on the bird species studied. More focused studies on ChE inhibition and the intensity of exposure to spray droplets may yield more significant results in the future. The high number of applications per season and the large volumes of pesticides used warrant further investigation into any possible wildlife impact.

Publication Medium. None provided.

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triforine, hexazinone, azinphos-methyl, dimethoate, captan

8. BIRD USE OF LOWBUSH BLUEBERRY FIELDS IN NEW BRUNSWICK AND NOVA SCOTIA - (C. Ellingwood and P.A. Pearce, CWS-Atlantic Region)

Keywords. lowbush blueberry, birds, foraging, New Brunswick, Nova Scotia

Introduction. The lowbush blueberry has been developed over recent years into one of the most important horticultural crops in Nova Scotia and to a lesser, but significant, extent in New Brunswick. Growth of the industry has resulted from more fields being cultivated and managed and from the increased use of pesticides and fertilizers to improve yields. The lowbush blueberry is, however, a native plant in eastern Canada to which many bird species are attracted as a source of food and as nesting habitat. One species, the Vesper Sparrow, is found almost exclusively in and around blueberry fields in the Maritimes.

Little is known about the use of blueberry fields by birds and their exposure to toxic chemicals being applied to the fields. Therefore, the Canadian Wildlife Service conducted a study to determine the potential relevance of current lowbush blueberry cultivation practices to migratory bird management.

Objectives. The objectives of this study were to 1) assess the bird use (foraging) of the blueberry fields by species nesting on or adjacent to the blueberry fields, 2) monitor the application of pesticides throughout the growing season and the effect on the resident bird population, and 3) determine the extent of pesticide use across Canada and the timing of applications.

Methods. Blueberry fields in Westmorland County, New Brunswick, and Cumberland County, Nova Scotia, were monitored over the entire growing season until harvest. Weekly surveys were conducted at each field to determine visitation rates (number of birds per hour of observation) and the species foraging and/or nesting on or by the fields. Extra effort was made during post-spray surveys to look for behavioural sublethal effects and to search for casualties. Information on the types of pesticides used, application rates, and timing of sprays was obtained from the growers.

Results and Discussion. Twenty-three species of birds were observed on the blueberry fields over the course of the study. Ten of these were found to be actually nesting on the fields or on the very edge of the fields. Savannah Sparrows were particularly common, and the locally uncommon Vesper Sparrow was found on four fields. American Robins accounted for 67.7% of the 1192 visits recorded, for an overall visitation rate of 10.6 visits per hour. Other common visitants included the Song Sparrow, Cedar Waxwing, Starling, and Dark-eyed Junco.

The initial fungicide sprays in May and June, using Funginex (triforine) and captan, occur when birds are beginning to nest, although both are believed to be nontoxic to birds. Cygon (dimethoate) and Guthion (azinphos-methyl) are applied in mid- to late July to combat the blueberry maggot. Adult birds are feeding young at this time or fledglings are foraging on their own. Birds fed readily on the ripening berries, even immediately post-spray, but no evidence of

sublethal effects was observed and no casualties were found. More intensive studies may be necessary in the future.

Publication Medium. None provided.

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9. SPATIAL AND TEMPORAL PATTERNS OF ORGANIC CONTAMINANTS IN WET PRECIPITATION IN ATLANTIC CANADA - (G.L. Brun, H.J. O'Neill, and G.D. Howell, IWD-Atlantic Region)

Keywords. atmospheric transport, Maritimes, wet deposition

Introduction. Atmospheric transport and deposition are well-recognized mechanisms that put organic contaminants into terrestrial ecosystems. For ten years, IWD, Water Quality Branch, has been collecting monthly composite wet precipitation samples at three locations in maritime Canada.

Methods. Samples are quantified for past-use pesticides, in-use pesticides, and other environmental contaminants such as PCBs, chlorinated phenols, and chlorinated benzenes. Data have been analyzed both spatially and temporally.

Results and Discussion. Pesticide detections have been infrequent, with the exception of lindane and alpha-BHC. The presence of PAHs has been shown to follow a seasonal deposition pattern, with higher concentrations during the colder months. Concentrations of PAHs are postulated to be coming from local sources, while lindane and alpha-BHC are attributed to long-range (international) mechanisms. Early in 1990, chlorothalonil was added to the parameter suite.

Publication Medium. Brun, G.L., H.J. O'Neill, and G.D. Howell, "Spatial and Temporal Patterns of Organic Contaminants in Wet Precipitation in Atlantic Canada", *Environ. Sci. Technol., 25(7):* 1249–1261 (1991).

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10. FEDERAL–PROVINCIAL DRINKING WATER SOURCES TOXIC CHEMICAL SURVEY - (WQB-Atlantic Region and provincial government personnel)

Keywords. Atlantic, raw municipal water

Introduction. This project has been an ongoing effort between the governments of Newfoundland, Nova Scotia, and Prince Edward Island and Environment Canada to monitor the quality of raw water serving Atlantic Canadian municipalities. The 1990 program is somewhat smaller than in the past, with a narrow focus on priorities identified in the first four years of the study (1985–88) and on provincial concerns.

Methods. Samples were collected from municipal supply sources in Newfoundland, Nova Scotia, and Prince Edward Island, and quantified for major ions, metals, nutrients, and in-use pesticides.

Results and Discussion. Two supplies have reported concentrations of atrazine and desethylatrazine of <1 µg/L, while all other pesticide parameters have been undetected. Nitrate concentrations generally reflect the extent of agriculture in the nearby area.

Publication Medium. An interpretive report for 1985–88 is available and an SOE Factsheet was released in 1991.

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chlorothalonil

11. CHLOROTHALONIL RESIDUES IN SURFACE AND SUBSURFACE WATERS CLOSE TO AREAS OF INTENSIVE AGRICULTURE - (H.J. O'Neill, P. Milburn, D.A. Léger, J. MacLeod, and J. Richards, WQB-Atlantic Region)

Keywords. fungicide, surface water, potato, tile drainage, Prince Edward Island, New Brunswick

Introduction. Fungicides account for 60% of agricultural pest control product use in the Atlantic Region, and chlorothalonil is one of the major fungicides used in the potato production industry. This project was a cooperative effort between Environment Canada and Agriculture Canada to monitor chlorothalonil in various hydrologic compartments.

Methods. Surface water, tile-drainage water, aquifer, and precipitation sampling were carried out during 1990. Surface water sites were in Prince Edward Island in an area of intensive potato production. Tile-drainage sites were at two Agriculture Canada research sites and at one commercial grower. A survey of private wells was carried out in St. André parish of northwestern New Brunswick where potato production accounts for 25–30% of land use. Chlorothalonil was added to the parameter suite for the precipitation monitoring project with samples being quantified monthly. All other sampling was on a grab sample basis, except one tile site where intensive sampling was carried out.

Results and Discussion. Four out of 66 tile-drainage samples collected from replicated plots indicated chlorothalonil residues at concentrations of 0.005–0.008 µg/L in the spring of 1990, seven months post-application. No chlorothalonil was reported in any of the duplicate samples collected from the 19 private wells surveyed. Chlorothalonil was detected at 2 of 11 surface water stations at concentrations ranging from 0.006 to 0.011 µg/L. Concentrations in precipitation from the two monitoring sites ranged from not detected to 0.034 µg/L, with maxima occurring in April and August. The April maximum is postulated to be a result of silvicultural use of chlorothalonil, while the August maximum is consistent with regional agricultural use.

Publication Medium. Interim results were distributed internally and a journal submission made to the *Canadian Water Resources Journal* in June 1991.

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atrazine, chlorothalonil

12. AQUIFER VULNERABILITY PROJECT - (T.L. Pollock, D.A. Léger, and H.J. O'Neill, WQB-Atlantic Region)

Keywords. aquifer, Nova Scotia, piezometer, lysimeters

Introduction. This project is being led by the Water Planning and Management Branch (WPMB) to develop a proactive approach to pesticide use. The pesticide atrazine is the target chemical for 1990 because of its known leaching characteristics. Chlorothalonil was added to the parameter list for 1991.

Methods. Late in 1989, a site at Sheffield Mills, Nova Scotia, on Agriculture Canada property was instrumented with piezometers that enter both bedrock and overburden aquifers. Background sampling was carried out in 1989 by the Water Quality Branch. In 1990, suction lysimeters were installed on two study fields, where atrazine would be applied on one field and background sampling for 1991 work would be done on the other.

Results and Discussion. Results from 1989 indicated that one of the selected sites was suitable for atrazine application. Results from in-season post-application sampling have indicated concentrations to a maximum of 18 µg/L for atrazine in one set of suction lysimeters. Results are more sporadic late in the summer because of dry soil conditions and lack of samples from some lysimeters. This project has a three-year time horizon and results are being forwarded to WPMB.

Publication Medium. Yearly project summaries have been prepared by WPMB.

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atrazine, metribuzine, chlorothalonil, dinoseb

13. SUBSURFACE DRAINAGE PROJECTS - (T.L. Pollock, H.J. O'Neill, and D.A. Léger, WQB-Atlantic Region)

Keywords. surface water, groundwater, Atlantic, root zone, Prince Edward Island, New Brunswick

Introduction. Elevated nutrient concentrations in surface water and groundwater and chemical contamination due to pesticide use are well documented in North America. The use of tile-drainage effluent to monitor the quality of water leaving the root zone and entering the saturated zone is increasing because of the field-scale nature of study sites. High amounts of precipitation and high pesticide use in Atlantic Canada, combined with the typically thin overburden, make this region susceptible to leaching. At the invitation of Agriculture Canada, Environment Canada is collaborating on studies to monitor in-use pesticides leaving the root zone (unsaturated zone).

Methods. Agriculture Canada operates several research stations in the region where tile-drainage is actively monitored for nutrients. Environment Canada cooperates by monitoring in-use pesticides at these same sites. Detailed site histories and crop rotations are known, as are tile flow and pesticide applications. In 1987–88, dinoseb and metribuzin were monitored at sites in northwestern New Brunswick. In 1989–91, atrazine was monitored at four tile plots in Cornhill, New Brunswick, while in 1990 chlorothalonil was monitored at a site in Prince Edward Island as part of a 1990 PESTFUND project.

Results and Discussion. The results for the 1987–88 work have been published (see below), while the results for 1989–91 are undergoing interpretation. atrazine concentrations in tile-drainage have been observed to a maximum of 20 µg/L, three days post-application. Sampling continued at the Cornhill site until mid-1991.

Publication Medium. O'Neill, H.J. *et al.*, "Dinoseb Presence in Agricultural Subsurface Drainage from Potato Fields in Northwestern New Brunswick, Canada", *Bull. Environ. Contam. Toxicol., 43:* 935–940 (1989).

Milburn, P. *et al.*, Leaching of Dinoseb and Metribuzin from Potato Fields in New Brunswick, *Can. J. Agric. Eng.* (forthcoming).

An interpretive data report on the 1987–88 tile study is currently available.

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general

14. RELATED PESTICIDE STUDIES - (WQB-Atlantic Region, federal departments, and provincial agencies)

Keywords. organochlorine, pentachlorophenol, CAPCO, multi-jurisdiction

Introduction. The presence of pest control products in the environment is a multi-jurisdictional issue of interest to several agencies other than Environment Canada. The Water Quality Branch (WQB) attempts to provide technical input and, when possible, analytical support to specific projects.

Methods. Agriculture Canada conducts a regional pesticide survey of farm wells for in-use products. WQB has assisted by analyzing concurrent samples for major ions and nutrients. It has also provided limited analytical support to the New Brunswick Department of Municipal Affairs and Environment in a screening survey of farm wells.

Organochlorine insecticides and pentachlorophenol are parameters included in the Federal–Provincial Water Quality Agreements. These parameters were included in the recurrent survey conducted in Newfoundland. Though analyses were performed at the National Water Quality Laboratory (NWQL) in Burlington, Ontario, regional WQB staff conducted sampling and data interpretation.

It should also be noted that the WQB Regional Laboratory participates in national round-robin quality control programs, such as the Canadian Association of Pesticide Control Officers (CAPCO) check program and National Water Research Institute (NWRI) round-robin studies.

Publication Medium. None provided.

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15. PRINCE EDWARD ISLAND ALDICARB STUDY — COMPUTER SIMULATIONS -

(A.S. Crowe, M.W. Priddle, J.P. Mutch, and R.E. Jackson, NWRI)

Keywords. numerical simulation, field sampling, Prince Edward Island, groundwater contamination

Introduction. From 1985 to 1988, groundwater monitoring beneath three potato fields to which the pesticide aldicarb had been applied showed that residues of the two toxic transformation products had persisted in the groundwater.

Objectives. The objectives of this study are to 1) undertake computer simulations of the transport and transformation of the pesticide in order to predict the fate of the pesticide in the subsurface; and 2) obtain a better understanding of the processes controlling the fate of aldicarb on Prince Edward Island.

Results and Discussion. Three existing models were evaluated (LEACHM, PRZM, VULPEST). LEACHM was chosen for the study because it has the most accurate representation of water flow and it allows for the simulation of the fate of daughter products (aldicarb sulfoxide and aldicarb sulfone). Attempts to calibrate the model to four years of field data (1985–88) were unsuccessful. Although the field data indicated persistent and relatively high concentrations with little short-term variation, the model predicted large slugs of pesticide moving through the unsaturated zone followed by a return to very low concentrations. The most likely cause for the difference is the dual porosity nature of the sandstone matrix. Diffusion into the matrix (high concentrations) and subsequent slow release of pesticide (in times of low concentrations) results in the damped observed response. The results of modelling also indicate that slow infiltration through the overlying till, low pH, and low subsurface temperatures act in combination to inhibit the transport and degradation of aldicarb. Results of the LEACHM simulations indicate that an application at plant emergence rather than at planting would significantly reduce pesticide concentrations reaching the water table.

Publication Medium. Priddle, M.W., R.E. Jackson, and J.P. Mutch, "Contamination of the Sandstone Aquifer of Prince Edward Island by Aldicarb and Nitrogen Residues", *Ground Water Monit. Rev., 9:* 134–140 (1989).

Jackson, R.E., J.P. Mutch, and M.W. Priddle, "Persistence of Aldicarb Residues in the Sandstone Aquifer of Prince Edward Island, Canada", *J. Contam. Hydrol., 6(1):* 21–36 (1990).

Mutch, J.P., Fate and Migration of Aldicarb in an Unsaturated/Saturated Flow System on Prince Edward Island, M.Sc.E. thesis, Department of Civil Engineering, University of New Brunswick, Fredericton, New Brunswick, 230 pp. (1989).

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aldicarb

16. PRINCE EDWARD ISLAND ALDICARB STUDY — FIELD SAMPLING - (M.W. Priddle, J.P. Mutch, and R.E. Jackson, NWRI)

Keywords. nitrates, field sampling, Prince Edward Island, groundwater contamination

Introduction. From 1985 to 1988, groundwater monitoring beneath three potato fields to which the pesticide aldicarb had been applied showed that residues of the two toxic transformation products had persisted in the groundwater.

Objectives. The objectives of this study are to determine 1) if high concentrations of aldicarb still persist in the groundwater of Prince Edward Island, and 2) what the present concentrations and areal extent of contamination are.

Results and Discussion. During the first week of July 1989, 26 groundwater samples were collected from monitoring wells at two of the National Water Research Institute's (NWRI) research sites on Prince Edward Island. Water levels and several field parameters were also measured at this time. aldicarb analysis was conducted in the Groundwater Chemistry Laboratory at NWRI. In general, aldicarb and nitrate concentrations were lower than those measured during the previous four years. However, aldicarb has not been applied at either of these sites during the past three years. The maximum total aldicarb concentration was 6.6 µg/L, which is lower than the drinking water guideline of 9 µg/L.

Publication Medium. Priddle, M.W. and R.E. Jackson, Agricultural Impacts on Groundwater — Research on Prince Edward Island, submitted to *Canadian Water Resources Journal.*

Jackson, R.E., J.P. Mutch and M.W. Priddle, "Persistence of aldicarb Residues in the Sandstone Aquifer of Prince Edward Island, Canada", *J. Contam. Hydrol., 6(1):* 21–36 (1990).

Mutch, J.P., Fate and Migration of aldicarb in an Unsaturated/Saturated Flow System on Prince Edward Island, M.Sc.E. thesis, Department of Civil Engineering, University of New Brunswick, Fredericton, New Brunswick, 230 pp. (1989).

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17. AQUIFER VULNERABILITY STUDY SITE — ANNAPOLIS VALLEY, NOVA SCOTIA - (M.W. Priddle and R.E. Jackson, NWRI)

Keywords. groundwater contamination, Nova Scotia

Introduction. As part of a continuing program to assist the Water Planning and Management Branch (IWD/Atlantic Region), a field sampling and analysis of groundwaters for pesticides at the Sheffield Farm site in the Annapolis Valley, Nova Scotia, was conducted by staff from the National Water Research Institute (NWRI).

Objectives. The objectives of the study were to 1) explain the proper field procedures for pesticide sampling to staff of the Water Planning and Management Branch, 2) obtain groundwater samples for chemical analysis, and 3) provide general assistance with this project as required.

Results and Discussion. Two trips were made to the Sheffield Farm site, during which procedures were discussed and groundwater samples collected. A total of 19 monitoring wells were sampled for three classes of pesticides, metals, major ions, and nutrients. Analyses were conducted by the Water Quality Branch in Moncton, New Brunswick.

Publication Medium. None provided.

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aldicarb

18. THE FATE OF ALDICARB IN THE SUBSURFACE OF PRINCE EDWARD ISLAND - (A.S. Crowe and M.W. Priddle, NWRI)

Keywords. field sampling, Prince Edward Island, groundwater contamination

Introduction. Although aldicarb is designed to degrade quickly within the subsurface, high concentrations of dissolved total aldicarb were found in routine analyses of groundwater samples obtained from domestic wells on Prince Edward Island during the last several years.

Objectives. The objectives of this research are to 1) study the causes of the persistence of the pesticide aldicarb on Prince Edward Island, and 2) through continued sampling of the groundwater, to determine if aldicarb still persists in the groundwater and the areal extent of contamination.

Results and Discussion. During May 1990, field sampling and analysis for the pesticide aldicarb was conducted at two National Water Research Institute (NWRI) field sites on Prince Edward Island. All wells at the two sites were sampled, for a total of 37 groundwater samples. Water level measurements were also taken at this time. Of the 37 samples, 46% contained total aldicarb residues greater than 1 µg/L (the approximate limit of detectability), with the maximum value being 7.7 µg/L. It is important to note that Temik (active ingredient - aldicarb) had not been applied to either of these fields since May 1986.

Publication Medium. Jackson, R.E., J.P. Mutch, and M.W. Priddle, "Persistence of aldicarb Residues in the Sandstone Aquifer of Prince Edward Island, Canada", *J. Contam. Hydrol., 6(1):* 21–36 (1990).

Mutch, J.P., R.E. Jackson, D.I. Bray, and M.W. Priddle, "The Fate of aldicarb in an Unsaturated/Saturated Flow System on Prince Edward Island, Canada", in: *Proceedings of the Tenth Annual Hydrology Days Conference*, Fort Collins, Colorado, April 10–12, 1990, pp. 123–138 (1990).

Mutch, J.P., R.E. Jackson, M.W. Priddle, and D.I. Bray, "The Fate and Simulation of aldicarb in the Soil and Groundwater of Prince Edward Island", National Water Research Institute Contribution #90-165 (1991). Submitted as an IWD Scientific Series Report, 175 pp.

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diflubenzuron

19. THE ACUTE AND CHRONIC EFFECTS OF DIMILIN (DIFLUBENZURON) ON FRESHWATER AND MARINE AQUATIC INVERTEBRATES - (K. Doe, M. Nicol, and W. Ernst, EP-Atlantic Region)

Keywords. acute chronic, effects; Dimilin; invertebrates; *Daphnia magna*; lobster larvae

Introduction. Dimilin (active ingredient - diflubenzuron or 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl) urea) is an insect growth regulator. Its mode of action is to block chitin synthesis. It is being considered for use in Canada in controlling forest insect defoliators, as well as for controlling sea lice infestations on fish. The product is not yet registered in Canada for these uses.

Objective. Since many aquatic invertebrates are dependent on chitin synthesis for survival, a series of bioassays were undertaken to determine the effects of Dimilin on freshwater and marine nontarget invertebrates.

Methods. First- and second-stage lobster larvae (*Homarus americanus*) were exposed to Dimilin formulations in filtered Halifax Harbour seawater. These animals were exposed to Dimilin formulations for eight days followed by four days in clean seawater. Animals were fed freshly hatched brine shrimp (*Artemia* sp.) daily, and test solutions were renewed every two to three days. Daily observations were made on moulting and survival.

Daphnia magna neonates (≤24 hours old) were exposed to Dimilin formulations in moderately hard, reconstituted fresh water (EPA formulation, hardness 80–100 mg/L as $CaCO_3$) for one or two days. Animals were then transferred to clean water and held to day 21 and monitored for survival, growth, and reproduction. Animals were fed living cells of *Chlorella vulgaris* and a suspension of fish food (Tetramin) throughout the exposure and post-exposure period.

Results and Discussion. Dimilin was found to be highly toxic to first- and second-stage lobster larvae. Four- and eight-day LC_{50} values were 1.5 and 1.2 µg/L for first-stage lobsters, and 2.8 and 2.0 µg/L for second-stage lobsters, respectively. Effects on moulting were evident at about the same exposure concentrations as for effects on survival.

For *Daphnia magna* in fresh water, the 24-hour LC_{50} was >100 µg/L a.i. By day 4 of the tests, the LC_{50} value was between 0.1 and 0.32 µg/L for both exposure durations. Animals that survived the short-term exposures grew and reproduced normally.

These results show that Dimilin can be very toxic to nontarget organisms, even in exposures as short as 24 hours. These results, together with the use patterns, bioavailability, and degradation rate of this pesticide, should be considered before it is registered for use in aquaculture and forestry.

Publication Medium. Journal (not selected).

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pentachlorophenol, creosote, chromated copper arsenate

20. TOXIC CONTAMINANTS IN SOILS AND SEDIMENTS AT FOUR WOOD PRESERVATION FACILITIES IN ATLANTIC CANADA - (J.J. Bamwoya, EP-Atlantic Region)

Keywords. soil, sediments, PAH, wood preservation

Introduction. In 1991, there were five vacuum/pressure impregnation facilities in Atlantic Canada: one in New Brunswick, three in Nova Scotia, and one in Newfoundland. The four plants studied occupied an estimated total area of 20 hectares and used the following types and amounts of inorganic and organic wood treatment chemicals.

An estimated total of 550 000 kg a.i. of waterborne chromated copper arsenate (CCA) preservative were consumed annually at three plants. The most commonly used commercial wood preservative formulation was Koppers Wolmanac 50%; Timber Specialities K-33 (C-50) preservative was used at one plant. Each of these preservative formulations contains approximately 23.75% chromic acid, 17.00% arsenic pentoxide, and 9.25% copper oxide.

Approximately 1 000 000 L of 100% coal tar creosote solution and about 15 000 kg a.i. of Penta were used annually at one of the plants. Carbochem and Vulcan Glazd Penta (86% pentachlorophenol and 10% other chlorophenols and related compounds) were the major organic wood preservative formulations in use.

In addition, waterborne ammoniacal copper arsenate (ACA) was being used for wood preservation at one plant during the course of this study. Chemonite Wood preservative (3.8% cupric oxide and 2.9% arsenic pentoxide) was the preferred ACA commercial formulation. This practice was discontinued in 1990 in favour of Koppers CCA.

Methods. Soil and sediment samples were collected from the vicinity of Atlantic Canada's active wood preservation facilities. All samples were to 5 cm depth and were homogenized before analysis for their respective contaminants.

Results and Discussion. Notwithstanding the sparse sampling density (total of 29 samples), the data suggest heavy soil contaminants accumulation of arsenic, copper, polycyclic aromatic hydrocarbons, and chlorophenols, especially in drying and storage areas for treated lumber. The most highly contaminated soils contained heavy metal concentrations as high as 10.9 mg/g arsenic and 61.9 mg/g copper, along with polycyclic aromatic hydrocarbons in excess of 7.0 mg/g and pentachlorophenols as high as 0.3 mg/g. The contaminants appear to decrease progressively with increasing distance from the wood treatment plants.

High concentrations of arsenic and the low-molecular-weight polycyclic aromatic hydrocarbons were measured in low-lying drainage areas near the wood treatment facilities. However, copper and the high-molecular-weight polycyclic aromatic hydrocarbons appear to be relatively immobile and had less tendency to leach from soils at wood treatment sites. The major chlorophenol contaminant was pentachlorophenol, along with occasional low concentrations of tetrachlorophenol and

trichlorophenol. All the contaminants measured in this study were in higher concentrations than the CCME assessment interim criteria levels and most exceeded the interim remediation criteria levels for commercial/industrial soils. The elevated levels of contamination observed at the four wood preservation sites studied may be potentially harmful to nearby aquatic ecosystems and groundwater resources. More detailed studies are needed to document the extent of operational environmental releases of preservation chemicals at wood treatment sites in Atlantic Canada, and to recommend contamination control and remediation measures.

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sodium hypochlorite, calcium hypochlorite

21. SURVEY OF BIOCIDE USE IN DOMESTIC WATER AND WASTEWATER TREATMENT IN THE ATLANTIC REGION - (C.A. Garron, EP-Atlantic Region)

Keywords. disinfectants, water treatment, wastewater, chlorine

Introduction. The addition of chlorine compounds is one of the most widely used means of disinfecting potable water and wastewater. In recent years, there has been increasing concern about the addition of chemical disinfectants to water because of the detrimental effects such treatments can have on receiving environment aquatic organisms as well as on the human population. The exposure of receiving environments and human consumers to disinfectant chemicals in water is a function of the type and amounts of chemicals used and the amount of time between treatment and consumption or release.

Objective. The purpose of this survey was to determine the use pattern of water and wastewater biocides in the Atlantic Region, including types of facilities, types and quantities of biocide used, and quality of the effluent.

Methods. Data collection was by means of a questionnaire sent to water and wastewater treatment facilities. This was followed up with telephone interviews and personal visits to clarify responses to the questionnaires. It was also determined, by means of a telephone subsample, whether the use pattern for those who did not respond was proportional to that reported in returned questionnaires.

Results and Discussion. Questionnaire responses indicated that a large number of treatment facilities use some form of chlorine as a disinfectant. Two facilities indicated that they use ultraviolet light, and all others indicated only primary or secondary treatment, with no disinfection process.

Chlorine gas was found to be the most commonly used disinfectant. This study indicated that approximately 607 000 kg of chlorine gas are used in the treatment of wastewater and 531 600 kg are used in the disinfection of potable water each year in the Atlantic Region. Of the four Atlantic provinces, Nova Scotia was found to be the greatest user of water treatment biocides, followed by Newfoundland, New Brunswick, and Prince Edward Island.

Sodium hypochlorite and calcium hypochlorite products were used to a lesser extent than chlorine gas with a total of 5 600 kg calcium hypochlorite per year and 34 000 L sodium hypochlorite per year, compared with 1 138 600 kg chlorine gas per year. All sodium and calcium hypochlorite products reported are registered pest control products, as defined by Agriculture Canada's *Pest Control Products Act*. Chlorine gas, however, is not registered by Agriculture Canada.

The use of chlorine biocides for water and wastewater treatment represents a larger use than the combined amounts of pesticides used for agricultural and forestry purposes in the region.

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pentachlorophenol, borax

22. SOIL CONTAMINATION AT ELEVEN WOOD PROTECTION FACILITIES IN THE ATLANTIC REGION IN 1989 - (L.A. Rutherford, P.A. Hennigar, and W.H. Horne, EP-Atlantic Region)

Keywords. anti-sapstains, soil contamination

Introduction. Green lumber is susceptible to surface attack by sapstain and mould fungi. The pigments of these fungi stain the wood, reducing its marketability. The most frequently used method of control is the application of fungicides or anti-sapstain chemicals, a process that is commonly referred to as "wood protection".

In Atlantic Canada, the most commonly used anti-sapstain products in 1989 were Permatox-10 (pentachlorophenol) and Ecobrite (borax). In 1989, 11 sawmills were known to be using anti-sapstain chemicals in Atlantic Canada. Six of those mills were located in New Brunswick and five in Nova Scotia. All of those mills were known to have few or no measures in place to prevent the adjacent environmental contamination by wood protection chemicals.

Objective. The purpose of the study was to assess the extent and magnitude of soil contamination at all regional wood protection facilities.

Methods. Soil samples (top 5 cm) were collected at various locations according to topography, soil types, and operational procedures from each of the 11 sites. Samples were obtained at various distances from the dip tank, in treated lumber storage areas, and adjacent to stored shavings from treated wood. Soils were analyzed for chlorophenates (di-, tri-, tetra-, and pentachlorophenol as well as tetrachlorocatechol and tetrachloroguaiacol) and boron.

Results and Discussion. Results indicated that surface soils were heavily contaminated by chlorophenols and contaminated by boron, particularly within 10 m of treatment areas. Mean PCP concentrations were 322 µg/g within 1 m of dip tanks, 227 µg/g 1 to 10 m from dip tanks, and 0.51 µg/g in treated lumber storage areas. Boron concentrations averaged 187 µg/g within 10 m of treatment areas and 44 µg/g in lumber storage areas where borax-based wood protection chemicals had been used. The widespread contamination observed at those facilities may be attributed to operational procedures that lacked sufficient environmental protection measures (e.g., lack of drip pads near treatment areas, inadequate amount of time in drip areas). The highest concentrations of chlorophenols and boron in the surface soils at those sites exceed current Canadian assessment and remediation criteria for contaminated sites. In addition, the high concentrations of chlorophenols could pose a serious threat to the aquatic environment and groundwater supplies near those operations.

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malathion, atrazine, dimethoate

23. EVALUATION OF A LINED PIT FOR THE TREATMENT OF DILUTE PESTICIDE WASTE AT AGRICULTURE CANADA'S HERVE J. MICHAUD EXPERIMENTAL FARM - (M. Dober, EP-Atlantic Region)

Keywords. pesticide degradation, lined pit

Introduction. A joint project was undertaken by Agriculture Canada and Environment Canada to evaluate a technology to collect and treat wastewater contaminated with low concentrations of pesticides. This procedure involves the use of lined concrete pits partially filled with soil and gravel into which the dilute pesticides wastes are fed. Water evaporates from the pit surface while the pesticide residues are biologically and photochemically degraded. The successful demonstration of this dilute pesticide waste treatment technology in the United States prompted Environment Canada to promote the installation of a pilot system to evaluate the effectiveness of this technology in Atlantic Canada.

Methods. The design and construction of a pesticide degradation pit at the Herve J. Michaud Experimental Farm in Buctouche, New Brunswick, was based on calculations of evaporation rates, expected feed volumes and required volume. The pit was operational in time for the 1990 farm season. Operational data on selected pesticides were obtained during the season and evaluated to determine the effectiveness of this method of treatment for dilute pesticide wastewater.

The operational data included the following information: the quantity of product used in the spray formulation, the dilution factor, the amount of residue remaining in the spray tank, and the quantity of rinse water used to clean the spray tank. In addition, samples of the rinse water, pit sediments, and groundwater were collected and analyzed to provide additional information on which to evaluate pit effectiveness.

Results and Discussion. The data obtained from this study indicated a general effectiveness of the pesticide degradation pit. Three of the four pesticides evaluated were found to degrade. Malathion, atrazine, and dimethoate were degraded to 89%, 71%, and 94%, respectively, within 120 days. (These values are based on the assumption that the pesticide residue remained in the top level of sediment.) The results for the fourth pesticide indicate some inconsistencies in the operational data. Therefore, no definitive conclusions can be drawn regarding the effectiveness of this technology on that compound.

Agriculture Canada has constructed similar pits at two other research stations in the Atlantic Region, while a third is in the design stage.

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2,4-D, dicamba, picloram

24. RESIDUES OF 2,4-D, DICAMBA AND PICLORAM IN BLUEBERRIES (*Vaccinium angustifolium*) ON TRANSMISSION LINE RIGHTS-OF-WAY FOLLOWING AN OPERATIONAL SPRAY PROGRAM

- (R.C. Martin, Newfoundland Department of Environment and Lands; W.L. Pierce, EP-Atlantic Region; and D.A. Barry, Newfoundland Power Co.)

Keywords. Newfoundland, herbicides, blueberries, residues

Introduction. The single most important use pattern for herbicides in Newfoundland is for brush control along transmission line rights-of-way. Public concern for this practice and the public's penchant for picking berries along these rights-of-way prompted the initiation of this study.

Objective. The objective of this study was to assess the length of time herbicide residues persist in berries of interest to the public following treatment of transmission line rights-of-way.

Methods. Sampling took place on two transmission lines, one treated with Tordon 101 and one treated with Dycleer/2,4-DP. Operational spraying took place between June 20 and July 10, 1989, while berry and foliage samples were collected on August 24 and October 12, 1989. Duplicate samples were collected at the same sites the following year on September 5, 1990.

Results and Discussion. Residues were found to vary widely, probably because of the inherent variability in the initial spray application. Despite the variation, residues declined after two months following the spray. Residues resulting from the two different formulations were significantly different, with the Dycleer/2,4-DP producing higher residues. Residues detected in August and September 1989, immediately following the spray, exceeded Health and Welfare Canada's maximum residue limits for human food. Observed levels of active ingredient ranged from 67.8 ppm (2,4-D) to less than 0.02 ppm (picloram) in August, while in October, dicamba ranged from 33.9 ppm to less than 0.01 ppm. Sampling of berries and leaves in September 1990 failed to detect any level of residue in the treated areas.

It is noteworthy that berries collected in August and October 1989, following the spray, were so badly withered and of such poor quality that the general public probably would not have picked them.

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PESTICIDES PROGRAM IN THE QUEBEC REGION

general

1. A NEW PHYTOASSAY PROCEDURE USING FLUORESCENCE INDUCTION -

(P.-Y. Caux, C. Blaise, P. Leblanc, and M. Taché, St. Lawrence Centre)

Keywords. *Selenastrum capricornutum*, microplate, bioassay, fluorescence induction, triazines, PSII inhibitors

Introduction. The fluorescent induction curve of photosynthesis can be modified by any factors affecting one or more transients. For example, S-triazine herbicides associate with a 32-kDa protein in complex B of photosystem II, which has the effect of blocking and inhibiting the transfer of electrons between quinone acceptors (Shulz *et al.*, 1990). This inhibition results in a strong increase of the fluorescence emission (Kautsky effect) and can only be detected efficiently by the use of a fluorometer. The use of fluorescence-generated EC_{50}s for chemicals inhibiting the biological energy transfer mechanism in photosynthesis is regarded to be a more sensitive toxic parameter than growth-generated EC_{50}s (Caux *et al.*, 1988). To our knowledge there are no reported studies investigating factors affecting the variability of the fluorescence response in the microplate algal assay. Thus, these investigations were aimed at establishing a standard protocol for toxicity testing coupling the microplate technique and the fluorescence Kautsky effect.

Objective. The purpose of this study was to determine the principal physical factors affecting the photosynthetic fluorescence induction response (Kautsky effect) of algae grown in microplates.

Methods. Microplates were inoculated with a culture of *Selenastrum capricornutum* and the effect of evaporation processes, cell concentration, algal culture volume, probe distance, adjacent well proximity, plate well shape, and plate opaqueness were investigated.

Results and Discussion. It was found that levels of relative fluorescence units (RFU) varied heterogeneously in a microplate whose 96 wells were inoculated with algae at constant inoculum conditions for four days. In order to account for this, the above parameters were analyzed. It was found that intraplate variation of RFU levels occurred as a result of media evaporation from peripheral wells. RFU levels were directly proportional to the culture cell concentration and to the culture cell volume, but indirectly proportional to the culture distance from the light-harvesting probe. RFU from black microplates gave a lesser response, but with less variation than from translucent microplates.

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atrazine, butylate, dinoseb, MCPA, metolachlor, aldicarb, methamidophos, phorate, benomyl

2. OCCURRENCE AND TRENDS OF PESTICIDES IN GROUNDWATER IN THE MONTREAL REGION IN SOILS VULNERABLE TO PESTICIDE LEACHING -

(P.-Y. Caux and M. Taché, St. Lawrence Centre)

Keywords. groundwater, leaching

Introduction. The drafting of a groundwater action plan under the St. Lawrence Action Plan led to the preparation of a preliminary report (Pelletier, 1989) and to feasibility studies. On the basis of these studies, areas in the Montreal region vulnerable to pesticide leaching were located. The studies were based largely on field work conducted by Bernard Rondeau and on the work of McRae (1988), Cohen *et al.* (1984), and McCormack (1985). Wells and piezometers (a total of 29) vulnerable to contamination were identified. According to the report by SAGE (1988) on the relative density of the use of priority herbicides, insecticides, and fungicides in Quebec watersheds, nine pesticides met the criteria of our project: they are used extensively in the regions under study, they have a high potential for leaching, and they are found in the areas vulnerable to leaching. The nine pesticides are atrazine, butylate, dinoseb, MCPA, metolachlor, aldicarb, methamidophos, phorate, and benomyl.

The purpose of this project was to determine the level of contamination of groundwater by these pesticides in regions for which statistics show potential contamination.

Methods. Fifteen wells were selected on the basis of the vulnerability of the surrounding soil, their proximity to farmland, and the ease of access to them. They were divided geographically into three groups: six stations on Île Perrot, east of Montreal; five stations on the north shore of the St. Lawrence, 50 km east of Montreal, in the municipalities of Lavaltrie and Lanoraie; and four wells on the south shore of the St. Lawrence, 50 km east of Montreal, in the municipalities of Contrecoeur and Verchères.

All of the wells were sampled using Kemerer samplers on June 26, July 9, August 9, August 22, and September 10, 1990. Immediately after sampling, the temperature, pH, conductivity, and oxygen content were measured and the samples were sent for pesticide analysis.

Results and Discussion. Concentrations of atrazine ranging from 0.02 to 5.1 µg/L were measured in three wells. In one well on Île Perrot, 3.9 µg/L of atrazine was detected in June, 2.3 µg/L in August, and 5.1 µg/L in September. This well was located in sandy soil near a cornfield. In Contrecoeur, 0.06 µg/L of atrazine was measured in a buckwheat field in August. In a well at a dairy farm, 0.47 µg/L of atrazine was measured in August and 0.20 µg/L was measured in September. These concentrations were unexpected because the soil on this farm was relatively rich in organic matter. In addition, 0.24 µg/L of phorate was detected in August in a well in Verchères close to forage crops. No other pesticides were detected.

This very limited study indicates that certain agricultural pesticides are leaching into the groundwater in Quebec. It also reveals that the establishment of a groundwater sampling network and data base on water quality in Quebec is needed.

Publication Medium. None at present.

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atrazine, metolachlor

3. FIELD VERIFICATION OF THE GLEAMS MODEL IN EASTERN CANADA -

(P.-Y. Caux, St. Lawrence Centre, L. Masse and S. Prasher, McGill University, and A. Bernier, C&P, Quebec Region)

Keywords. groundwater, GLEAMS (model), Saint-Amable, leaching

Introduction. A field study was carried out in 1988–89 to determine the fate and transport of two commonly used herbicides, atrazine and metolachlor, in soil and groundwater in two corn fields in Quebec, one on sandy soil in the St. Amable region and the other on clayey soil in the St. Lawrence lowlands. The data collected were compiled using the recently developed GLEAMS simulation model (Groundwater Loading Effects of Agricultural Management Systems).

The purpose of the study was to test the accuracy of the GLEAMS model in predicting pesticide leaching in cultivated areas.

Methods. The two corn fields were sprayed with atrazine and metolachlor at dosages of 2.35 and 2.4 kg/ha, respectively. Runoff water and soil water samples were collected several times.

A first- and second-order analysis of uncertainty was used to determine the impact of soil type and the chemical properties of the pesticides on the predicted pesticide levels.

Results and Discussion. Model predictions were close to field measurements in the 0- to 20-cm sampling zone. The half-life values for the herbicide had to be reduced from 40 days in 1988 to 20 days in 1989 to obtain better predictions by the model. Warmer conditions in 1989 resulted in a faster rate of degradation of the herbicides in the second year. However, the model did not predict leaching of atrazine beyond the 0- to 20-cm sampling zone, which is contrary to what was observed in both fields in 1988.

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aldicarb, metribuzin, fenvalerate

4. MONITORING OF THE OCCURRENCE AND MOVEMENT OF PESTICIDES USED IN POTATO CROPS IN THE NICOLET RIVER BASIN - (C. Bastien and P.-Y. Caux, St. Lawrence Centre, and C. Madramootoo, McGill University)

Keywords. potatoes, Nicolet River, commercial crop, surface runoff, tile drainage

Introduction. The Quebec Department of Agriculture, Fisheries and Food and McGill University have focused considerable efforts on research on water and soil conservation in agricultural basins. The purpose of their work is to minimize soil and chemical losses, particularly through better drainage systems, specifically soil losses in fields planted in potatoes due to surface runoff caused by precipitation. A project was developed to evaluate the movement and fate of pesticides used in commercial potato production. The project is also aimed at advising producers on the changes to be made in the use of pesticides and, perhaps, on better crop management practices.

The principle is simple. It consists in keeping the agricultural chemicals in the fields in order to increase the productivity and cost-effectiveness of commercial cultivation and to protect the environment (especially aquatic systems) from seasonal aggression by contaminants. To this end, appropriate agricultural management tools and criteria are required. The CREAMS model (Chemicals, Runoff, and Erosion from Agricultural Management Systems) and the more recent GLEAMS model (Groundwater Loading Effects of Agricultural Management Systems) are the most complex models available for predicting soil erosion and the fate of chemicals in agricultural fields. These models, developed by Knisel (1980), are used in the United States as both planning and conservation tools. These models and others, such as the VULPEST model (Vulnerability to Pesticides), have not yet been tested for conditions in Quebec in terms of the fate of pesticides in the environment. However, little data is available on pesticides in Quebec.

Objectives. Our study provides information on the quality, quantity, and rate of runoff of metribuzin, aldicarb, and fenvalerate in the Nicolet River watershed from fields planted in commercial potato crops. The specific objectives are 1) to measure pesticide losses in surface runoff during application periods; 2) to estimate temporal and spatial contamination levels (on a small scale) and pesticide loadings into the Nicolet River; 3) to examine the breakdown of pesticides in soil and water; 4) to measure the physicochemical and hydrological properties of the runoff in order to document the dynamics of pesticide movement and persistence in a small tributary of the Nicolet River; 5) to verify the relevance of the above models to conditions in Quebec; 6) to advise management organizations of the levels of pesticide contamination in two adjacent fields that are believed to have different soil characteristics; and 7) to obtain information on the use and application of pesticides by farmers in the Nicolet River area (by means of a questionnaire).

Methods. The study was conducted near two potato fields of roughly 7 ha in the Nicolet River basin on the farm of André Boudreau in Saint-Léonard-d'Aston, Quebec. The herbicide metribuzin and the

insecticides aldicarb and fenvalerate were used in both fields. The runoff and drainage waters were collected in a V-notch weir. They were sampled when there was surface runoff or in the agricultural drain, or in other words after each rainfall event.

Soil samples were collected to analyze the residual pesticide concentrations before planting, midway through the growing season, and at the time of harvesting.

Rainfall data were recorded by means of a rain gauge, and runoff water and drainage water in the weir were measured.

The water samples were analyzed to determine their physicochemical properties and the samples of water and soil were analyzed for pesticides. A mineralogical analysis of the soil was conducted using X-ray crystallography.

To obtain the best possible picture of the annual loading of pesticides in a small tributary of the Nicolet River, a questionnaire was distributed to 20 to 30 farmers in the region (Mauricie-Bois-Francs) on the use of pesticides used in agriculture. The same questionnaire had been used in the Brandon, Ontario, region for Kintore Creek. It was translated and adapted to the Nicolet River region. With the cooperation of Rosaire Blier, an agrologist with the Quebec Department of Agriculture, Fisheries and Food, a good response rate was obtained from the farmers.

Results and Discussion. aldicarb was not detected in any of the samples. Because of technical difficulties, sampling could not be carried out immediately after application of aldicarb. This pesticide is known to be very mobile, and its leaching potential in groundwater is increased by the presence of an unsaturated permeable zone and by the absence of organic matter (Soren and Stelz, 1985). The octanol/water partition coefficient (K_{ow}) of aldicarb is very low, and it has a solubility in water of 6 g/L (Priddle *et al.*, 1987). Studies have shown that the persistence of aldicarb and its metabolites varies considerably depending on the soil type, presence of vegetation, field conditions, humidity, and pH. In the present study, the unsaturated zone may have been very permeable to aldicarb. It will be possible to confirm this once the soil analysis data are available.

High concentrations (34 to 70 µg/L) of metribuzin were measured in some samples. The concentrations were higher in samples of runoff water than in samples of drainage water.

The guideline for metribuzin for the protection of aquatic life is 1.0 µg/L. The above figures represent the concentrations measured in the surface and runoff waters from fields and do not necessarily correspond to the concentrations in nearby rivers and streams. These concentrations are representative of those observed by other researchers in similar conditions (Pauli *et al.*, 1990), but are also somewhat higher.

Metribuzin has a very low K_{ow}, and it is highly soluble in water (1200 mg/L) (Jensen *et al.*, 1989). According to Glotfelty *et al.* (1984), losses of this compound are dominated by movement in the water phase, as opposed to movement on eroded soil sediment. Losses occur approximately two weeks after application (Pauli *et al.*, 1990), and roughly 3% is lost (Baker, 1985; Brown *et al.*, 1985; Glotfelty *et al.*, 1984; Johnson and Baker, 1982 and 1984). In this study, losses of less than 1% were observed, unlike those observed in the above studies. It must be noted that the samples were collected one

month after application of the pesticide and that there was no significant rainfall during that period. Several researchers (Hatzios and Penner, 1988; Roberts *et al.*, 1979) have suggested that the movement of metribuzin does not occur by means of runoff in the subsoil. Our study reveals that the movement of metribuzin occurs when the soil is saturated with water and during heavy precipitation.

Residual concentrations (average of 0.028 μg/g) in soil samples collected in September 1989 reveal that metribuzin is persistent. Other studies (Pauli *et al.*, 1990) cite metribuzin concentrations ranging from 0.11 to 0.026 mg/kg, depending on the depth of the sampling zone.

According to the questionnaire completed by the farmers from the Saint-Léonard-d'Aston region, commercial potato production accounts for 30% of the production in this region. The farmers use metribuzin to control weeds in their potato fields.

Fenvalerate was detected in very small concentrations in the surface water samples (from 0.04 to 0.08 μg/L). Fenvalerate was persistent in the soil, since several samples contained residual concentrations. When the results on the soil properties are available, it will be possible to explain or predict the persistence of this pesticide using the K_{ow} value. Very few studies exist on fenvalerate. An attempt should be made to obtain more data on this insecticide.

atrazine was detected in a number of soil and water samples. However, Mr. Boudreau had not used this pesticide for five years in field A and had never used it in field B. The presence of atrazine can be explained by one of three possible factors: 1) an error in the laboratory methodology; 2) the persistence of atrazine in the soil; or 3) wind transport. Laboratory error can be ruled out because the laboratory has an excellent quality control system. Although not impossible, the persistence of atrazine in the environment after five years is unlikely. The transport of pesticides by wind during spraying appears to be the most likely explanation, particularly since the questionnaire reveals that 60% of the farmers use atrazine. This region, which is located in the St. Lawrence lowlands, is highly exposed to winds.

One of the principal objectives of this project was to study pesticide movement in the fields. As previously stated, the experimental data must be compared with the predictions of a computer transport model (CREAMS). On the basis of the results of the soil analyses done by the University of Quebec at Montreal, a correlation can be established between pesticide movement and soil properties. The mineralogic characteristics and organic content may provide an indication of the leaching potential of the pesticides.

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metribuzin, phorate, fenvalerate, aldicarb

5. PESTICIDE LEVELS IN AGRICULTURAL DRAINAGE SYSTEMS IN QUEBEC - (C. Bastien and P.-Y. Caux, St. Lawrence Centre)

Keywords. Nicolet River, tile drainage, runoff, groundwater

Introduction. Few data are available on the transport of pesticides in surface water and groundwater in Quebec. As a result, surface runoff and subsurface drainage water were sampled in two potato fields in Saint-Léonard-d'Aston, Quebec, in 1989–90 and 1990–91. Soil samples were also collected at the two sites at the surface (0–5 cm) and at a depth of 25 cm.

Methods. The soil and water samples were analyzed in 1989–90 for the pesticides metribuzin, fenvalerate, and aldicarb, and in 1990–91 for metribuzin and phorate. Precipitation, surface runoff, and subsurface drainage flow were recorded during the two growing seasons.

Results and Discussion. Metribuzin was detected in concentrations of up to 3.47 µg/L in the tile drainage water and in concentrations of up to 47.086 µg/L in surface runoff. Fenvalerate was detected in concentrations of up to 0.05 µg/L in surface runoff. Although phorate was not detected in any of the water samples, it was detected in concentrations of up to 0.020 µg/g in the soil samples. Metribuzin was detected in concentrations of up to 0.23 µg/g in the soil, and fenvalerate was detected in concentrations of up to 0.013 µg/g at the surface (0–5 cm). The pesticide concentrations were higher in samples collected at the surface than in the 25-cm sampling zone. aldicarb was not detected in any of the water or soil samples.

The CREAMS computer model (Chemicals, Runoff, Erosion from Agricultural Management Systems) was used to simulate pesticide movement in the potato fields. Predicted and measured values were compared. The model tended to overestimate pesticide losses in runoff and did not take pesticide losses due to percolation into account.

Publication Medium. M.Sc. thesis, McGill University. American Society of Agricultural Engineers (forthcoming).

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atrazine, 2,4-DP, lindane, endosulfan, diazinon, p, p'-DDE, p, p'-DDT, chlordane, alpha-*BHC*

6. PESTICIDES IN TRIBUTARIES OF THE ST. LAWRENCE RIVER (1989–1990) -

(P.-Y. Caux and S. Forrest, St. Lawrence Centre)

Keywords. St. Lawrence tributaries, water quality guidelines, monitoring

Introduction. Six St. Lawrence tributaries draining basins of intense agricultural activity were monitored during the 1987 and 1988 growing seasons in order to determine the concentrations and spatial and temporal variations of pesticides in the water. A program report was published (Forrest and Caux, 1990). The rivers under study were the Yamaska, St. François, Assomption, St. Régis, St. Jacques, and Tortue. Each aquatic system was divided into four compartments: surface waters, suspended solids, bottom sediments, and fish. A total of 40 pesticides were studied. In surface waters, the measured concentrations of seven pesticides exceeded their respective water quality guideline for the protection of aquatic life. They consisted of two herbicides-atrazine and 2,4-DP-and five insecticides-lindane, endosulfan, diazinon, p, p'-DDE, and p, p'DDT. In the 1987–88 sampling season, 62 samples exceeded the water quality guideline: atrazine, 21; 2,4-DP, 1; lindane, 7; endosulfan, 4; diazinon, 23; p'-DDE, 3; and p'-DDT, 3.

The measured concentrations of atrazine, diazinon, and lindane exceeded their respective guidelines (2.0, 0.08, and 0.01 µg/L, respectively) in three or more of the rivers sampled. The maximum measured concentrations of atrazine and diazinon were 20.7 and 28.3 µg/L, respectively, and both were measured in the St. Régis River. The maximum measured concentration of lindane was 0.0958 µg/L and was recorded in the Assomption River.

Pesticide loading into the St. Lawrence River was calculated for two rivers: the Yamaska and the Assomption. The maximum measured loading of atrazine residues from the Yamaska River into the St. Lawrence was 0.29 g/s or 25 kg/d, while maximum measured loadings of lindane from the Assomption were 0.029 g/s or 2.5 k/d. Generally speaking, pesticides were not found in other compartments of the aquatic systems at the concentration ranges observed in surface water, although some were detected. The pesticides most commonly found in the sediments and fish were the more persistent organochlorines, such as alpha-BHC, cis- and trans-chlordane, and p,'-DDT.

Several physicochemical parameters of the river systems were monitored concurrently with the pesticides to establish correlations. The correlations are analyzed in the report to explain the method of dispersion of the pesticides.

The purpose of this study is to monitor pesticides used in agriculture in Quebec in the short term and to establish a long-term operational plan for current, ongoing monitoring.

Methods. On the basis of the above activities, the study plan for 1989–90 and the next few years was established. During the 1989–90 sampling season, the seven pesticides found in 1987–1988 at concentrations exceeding the water quality guidelines for the protection of aquatic life were studied in the rivers where they had been detected. This made it possible to

conduct a much more stringent quality control program and to submit the data for statistical analysis.

Results and Discussion. The results of the analyses of the 1989–90 sampling will be the subject of a report to be published soon. However, we wish to note that an operational plan has been developed. Among other things, the short- and long-term pesticides monitoring program can be summarized as follows:

1) A report similar to that prepared by SAGE Ltd. will be published soon and then every five years. It will regularly assess the situation of pesticides in Quebec and will contain a list of critical pesticides in specific watersheds. The prototype developed by SAGE was just a beginning, since it was based largely on pesticide sales. A number of improvements are suggested, such as the incorporation of agricultural land use studies (telemetry), agricultural statistics by census area, studies of soils and their leaching potential, and models. Close cooperation with various interested groups is anticipated, including the Department of the Environment and the Quebec Department of Agriculture, Fisheries and Food.

2) The year in which the report is produced (or the following year), complete sampling of critical pesticides will be carried out to determine which ones are found in high concentrations in our aquatic systems.

3) On the basis of this preliminary screening, efforts over the next three to four years will be focused on a few specific pesticides in order to use the available funds in the best possible way.

Publication Medium. Forrest, S. and P.-Y. Caux, *Pesticides in Tributaries of the St. Lawrence River. 1987–1988 Program Report.* St. Lawrence Centre, Montreal, 144 pp. (1990).

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atrazine

7. DERIVATION OF A SITE-SPECIFIC WATER QUALITY OBJECTIVE FOR atrazine IN THE YAMASKA RIVER - (R.A. Kent, IWD-HQ; P.-Y. Caux, St. Lawrence Centre; M. Wong, IWD-HQ; and M. Taché, St. Lawrence Centre)

Keywords. Yamaska River, fluorometry, *Selenastrum capricornutum*

Introduction. The purpose of this study is to establish a site-specific objective for atrazine for the protection of aquatic life in the Yamaska River.

Certain environmental variables are known to alter the toxicity of some chemicals (for instance, pH and temperature can affect the toxicity of ammonia, and water hardness can affect the toxicity of cadmium, copper, lead, and nickel). However, few data are available on the quality of the water of rivers and the effect that it may have on the fate or toxicity of pesticides. It may be that the physicochemical and biological composition of different watercourses may alter the potential toxicity of a pesticide. The study is designed to verify whether the toxicity of a given concentration of pesticide is the same when the physicochemical composition varies. By comparing the toxicological data with the physicochemical parameters of samples from different sources, it may be possible to predict the behaviour of pesticides in a given hydrologic basin.

Methods. In this study, the toxic potential of atrazine was determined on the basis of the photosynthetic activity of the green alga *Selenastrum capricornutum* and algae from the environment (Yamaska River). The activity was measured by means of fluorescence emitted by the plant matter using the microplate technique and fluorometry. In addition, the physicochemical composition of the environment was analyzed, and a diversity study was conducted in order to predict the behaviour of the pesticides. The results of microplate assays with *Selenastrum capricornutum* and the diversity study are presented below.

Results and Discussion. The results of the phytotoxicity tests using microplates for the samples collected in April differed from those of the samples collected in August. Because the samples were filtered, the biological components were not the cause of this difference. It would seem that the physicochemical properties of the water were the determining factor, since all other factors were constant. The data on the physicochemical properties of the water are being compiled and interpreted. All parameters will be analyzed in order to assess the variable or variables that play a determining role.

The diversity study data were the subject of principal component analyses, in order to determine the axes corresponding to the maximum variance in a multidimensional space. Two analyses were conducted. The first analysis, which dealt with each site individually, provided for five periods of monthly sampling. It was observed that at most of the sites, with the exception perhaps of the control site, the phytoplankton diversity differed greatly in time. The second analysis, which compared the different sites, showed that the diversity differed from one site to the next. It covered the various groups of species in the phytoplanktonic populations of the Yamaska

River basin. It was observed that some of these groups of species peak in space and time. Thus, among the ciliates, the largest populations occurred in July at the mouth of the river.

The analyses also indicated the distribution of these groups of species at each site. The existing populations are naturally regulated by the nutrient regime of the environment in which they occur and by natural ecological succession. A depleted environment, such as the Lac Brome site, cannot support the diversity found in a richer environment, such as that of the river mouth. Generally speaking, Bacillariophyceae were predominant in May and June. Later, when the water warmed up and the light conditions became favourable, Chlorophyceae became predominant. Then, when nitrogen became the limiting factor, Cyanophyceae became predominant, since they can bind atmospheric nitrogen. At the Lac Brome site, Chlorophyceae were still predominant even in September, which indicates that the levels of nitrogen were still relatively high. However, these observations will have to be compared with the physicochemical analyses of the environments to give them a more concrete basis.

The study of the phytoplankton clearly shows that each site of the Yamaska River is spatially and temporally distinct, which confirms the hypothesis of the variability of the biological component of the environment. It remains to be determined whether variations can be attributed to toxicological effects. Phytotoxicity studies using microplates with algae from the study sites may be able to provide an answer to this question.

Since ambient water conditions vary according to geographic region, Canadian water quality guidelines are sometimes modified in the derivation of a site-specific objective. Canadian water quality objectives are set by the Canadian Council of Ministers of the Environment in the form of numerical limits established to protect the use of the water at a particular site. The establishment of objectives complements the guideline development process by using toxicological studies that reflect local environmental conditions and the sensitivity and influence of local species.

Publication Medium. *Canadian Journal of Botany* (considered).

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atrazine, metribuzin, endosulfan, azinphos-methyl, phorate

8. EVALUATION OF THE CONTAMINATION OF SURFACE WATERS BY PESTICIDES USED FOR COMMERCIAL CROPS IN THE NICOLET RIVER BASIN - (P.-Y. Caux, M. Taché, and C. Bastien, St. Lawrence Centre)

Keywords. commercial crop, Nicolet River, questionnaire, monitoring

Introduction. In an initial internal study, extremely high concentrations of metribuzin were measured in surface and drainage waters from potato fields. The concentrations were almost 100 times higher than the recommended guidelines for the protection of aquatic life.

By means of a questionnaire distributed to farmers in the region, information was collected on the pesticides employed, their use, and method of application. It was revealed that many farmers were engaged in commercial farming. According to the regional agrologist, the entire region is devoted, by plots, to commercial crops, which is a recent trend, and has not yet been reported or studied.

The level of contamination of the watercourses in this region by the pesticides most commonly used for commercial cropping was determined by sampling the watercourses and the subbasins of the region up to their mouth or point of discharge into the Nicolet River. According to the SAGE report (1988), a large number of priority pesticides are used in the Nicolet River basin. However, there are virtually no studies on pesticide contamination in this sector.

Methods. The study was conducted at Saint-Léonard-d'Aston in the Mauricie-Bois-Francs region, where the Nicolet River basin is located. A concurrent study on the quality, quantity, and rate of runoff of pesticides from the potato fields was conducted.

Three streams (sub-basins) were sampled during the period in which the pesticides were applied, from April to September 1990 (samples were collected eight times at three sites during the six-month period, for a total of 72 samples). The following pesticides were analyzed: atrazine, metribuzin, endosulfan, azinphos-methyl, and phorate.

Results and Discussion. Two of the pesticides under study were found: atrazine and metribuzin. Measured concentrations of atrazine were 0.04 to 0.88 µg/L in the month of July. atrazine persisted until the month of September (from 0.15 to 0.43 µg/L). The questionnaire comfirmed that atrazine is the most widely used pesticide in the region. Measured concentrations of metribuzin were 0.22 to 0.41 µg/L for the month of June.

This study shows that although pesticides were present in the streams that drain fields of commercial crops, their concentration was substantially reduced (100 times) by the phenomenon of dilution. It should be noted that all concentrations measured were lower than the Canadian water quality guidelines for the protection of aquatic life.

Publication Medium. Internal report.

Reference

SAGE. *Recueil des principaux pesticides en usage au Québec*, D. Cossette, I. Giroux and R. Poulin (eds.), 3 vol., SAGE Ltée, Quebec (1988).

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2,4-D, bromoxynil, cyanazine, diquat dibromide, glyphosate, hexazinone, imazamethabenz methyl, metolachlor, picloram

9. COMPARATIVE ASSESSMENT OF HERBICIDE PHYTOTOXICITY TO *Selenastrum capricornutum* USING MICROPLATE AND FLASK BIOASSAY PROCEDURES

- (D. St-Laurent and C. Blaise, St. Lawrence Centre; P. MacQuarrie, CCB-HQ; R. Scroggins, IPB-HQ; and B. Trottier, UQUAM)

Keywords. algal growth inhibition assay, bioassay, copper sulphate, environmental monitoring, herbicide, microplate, registration, phenol, phytotoxicity, potassium dichromate, *Selenastrum capricornutum*, zinc chloride

Introduction. Test requirements for nontarget plants for registration of pesticides in Canada are presently being considered. The phytotoxicity information generated as a result of these tests will be of value for individual pesticide registration assessment as well as for environmental monitoring following registration. An algal toxicity microtest, performed in 96-well microplates, has been proposed as a valid alternative to flask tests to assess nontarget plant toxicity. This microplate assay has been developed with *Selenastrum capricornutum*, a green alga commonly employed in North America for diverse environmental applications and one of several green algae recommended as a test species for aquatic plant toxicity testing. A recent intercalibration exercise conducted with the microplate assay has further indicated its usefulness and reliability, and has contributed to protocol optimization. However, before this microtest can be considered as an appropriate option to a flask procedure, a validation study with pesticides was deemed essential.

Objective. The major objective of this study was to assess the performance of the algal microplate test in comparison to a classical flask assay in reporting herbicide toxicity.

Methods. Algal growth inhibition EC_{50}, resulting from 96-h exposures to four reference chemicals (phenol, copper sulfate, potassium dichromate, and zinc chloride) and to nine herbicides reflecting different chemical classes, modes of action, and uses (2,4-D, bromoxynil, cyanazine, diquat dibromide, glyphosate, hexazinone, imazamethabenz methyl, metolachlor, and picloram), were determined by both procedures and compared.

Results and Discussion. Ninety-six hour EC_{50} determined with *Selenastrum capricornutum* as the indicator species essentially demonstrated good intermethodological data concordance for all chemicals, with the exception of diquat dibromide, whose phytotoxicity in the microplate assay (EC_{50} = 4.9 µg/L) was nearly seven times that of the flask assay (EC_{50} = 34.2 µg/L). Comparisons with other data in the scientific literature relating to similar herbicides with the same or different green algal indicator species appeared to corroborate the overall data obtained in our study. More than four orders of magnitude separated the most toxic (cyanazine, flask and microplate EC_{50} of 17.6 and 16.9 µg/L, respectively) and the least toxic (imazamethabenz, flask and microplate EC_{50} of 89.1 and 91.1 mg/L, respectively) herbicide. The biprocedural phytotoxicity comparison described in this work suggests that the simpler algal microplate assay can be an appropriate alternative to the flask

technique to evaluate the algal growth inhibition effects of herbicides.

Publication Medium. St-Laurent, D., C. Blaise, P. MacQuarrie, R. Scroggins, and B. Trottier, "Comparative Assessment of Herbicide Phytotoxicity to *Selenastrum capricornutum* Using Microplate and Flask Bioassay Procedures", *Environ. Toxicol. Water Qual., 7:* 1–14 (1991).

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atrazine, cyanazine

10. DETERMINATION OF THE IC_{50} AND LC_{50} OF TWO TRIAZINE HERBICIDES (atrazine AND CYANAZINE) USING THE ALGA *Selenastrum capricornutum* -

(L. Ménard, M. Taché, and C. Blaise, St. Lawrence Centre)

Keywords. bioassays, *Selenastrum capricornutum*, flow cytometry, fluorescein diacetate, toxicity tests

Introduction. The widespread use of pesticides in agriculture poses a risk of contaminating the aquatic environment. As a result, it would appear important to determine the risks posed by pesticides to phytoplankton. Triazine herbicides are among the most widely used herbicides in agriculture (SAGE, 1988). Two triazine herbicides were selected for this study: atrazine and cyanazine.

The microplate algal assay procedure developed by Blaise *et al.* (1986) is a sensitive and reliable technique for quantifying the IC_{50} (median inhibitory concentration), which can be used to determine the toxic potential for phytoplankton. This technique and flow cytometry were used to quantify the IC_{50} and LC_{50} (median lethal concentration).

Methods. The determination of the IC_{50} consists in carrying out several dilutions of the pesticide to be tested and adding algae and nutrients to it. After incubation for 96 hours at 24°C under continuous lighting, the density of the algae was determined using a particle counter (Coulter®, ZM model). The concentration that inhibits 50% of the cell growth was estimated by inverse prediction.

The determination of the LC_{50} was obtained by flow cytometry (FACScan model, Becton Dickinson). Esterase activity, shown by the fluorescein diacetate, and fluorescence emitted by chlorophyll were used to estimate cell viability. The LC_{50} was also determined by inverse prediction.

Results and Discussion. The IC_{50} values for atrazine and cyanazine were 25.97 µg/L (95% confidence interval (CI): 19.13 to 32.40 µg/L) and 59.35 µg/L (CI 95%: 47.15 to 71.65 µg/L), respectively. The LC_{50} was 25.57 µg/L (CI 95%: 22.95 to 27.03 µg/L) for atrazine and between 180 and 200 µg/L for cyanazine. atrazine is therefore more toxic to green alga. With a view to risk management, these two parameters will be used to more effectively assess the toxic potential of the pesticides for aquatic life.

Publication Medium. None provided.

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chlorpyrifos, general

11. EFFECTS OF THE TREATMENT OF LAWNS WITH PESTICIDES AND FERTILIZERS ON THE AMERICAN ROBIN AND ON AN IMPORTANT COMPONENT OF ITS DIET, THE EARTHWORM - (C. Lépine, R. Décarie, R. Brunet, and D. Coderre, GREBE Inc.; J-L. DesGranges, CWS, Quebec Region)

Keywords. songbirds, lawns

Introduction. The purpose of the study is to determine whether the use of the insecticide chlorpyrifos–either immediate or repeated over several years–has an effect on the use of lawns by the American Robin (*Turdus migratorius*) and the European Starling (*Sturnus vulgaris*) in residential areas. It is also designed to assess the effect of the repeated use of chlorpyrifos on lawns on the number of earthworms and, consequently, on the nesting success of the American Robin. One component of the study was aimed at assessing the impact of chlorpyrifos on robins in captivity.

Methods. Four companies provided information concerning lawn care since 1986 in a neighbourhood of Duvernay, in Laval. Residents who had not used the services of these companies provided information concerning their lawns. The abundance and frequency of occurrence of American Robins and European Starlings on lawns in this neighbourhood were recorded 17 times between July 4 and August 11, 1989.

The effect of chlorpyrifos on birds in captivity was measured by the degree of inhibition of blood and brain acetylcholinesterase (AChE) activity as a function of the duration of exposure and the dosage used. The experiments consisted in spraying a lawn with a pre-established dosage of chlorpyrifos and placing 9 to 12 caged robins on it. Blood and brain samples were then collected to measure the effects of the treatment on the degree of AChE inhibition.

Results and Discussion. The repeated use of chlorpyrifos does not appear to affect the use of lawns by robins and starlings. However, it did result in a decline in the biomass and abundance of earthworms. At this time of the year, their activity is reduced and they are less abundant on all lawns. Concurrently, the robin's diet shifts to fruit, making it less dependent on earthworms.

The effect of chlorpyrifos on American Robins in captivity was more significant than anticipated, even at a so-called normal dosage. Extreme temperatures appear to affect the speed of contamination of robins in captivity. The dominance and, as a result, rate of activity of robins in large groups in captivity also seem to have an effect on the individual response to treatment. Further experiments are required concerning the effect of individual behaviour on the speed of contamination, the capacity of robins to choose between contaminated and noncontaminated sites, the effect of temperature on the degree of contamination, the effect of contamination on the rate of activity of the bird, and the duration of recovery following treatment.

Publication Medium. Décarie, R. and J.-L. DesGranges (eds.), *Effets physiologiques et comportementaux du traitement des pelouses au chlorpyrifos sur le Merle d'Amérique (Turdus migratorius)*, technical report produced by GREBE Inc.

for Environment Canada and Dow Chemical Co., Canadian Wildlife Service, Quebec Region, 82 pp. and appendices (1990).

Coderre, D., *Effets de l'insecticide chlorpyrifos sur l'abondance, la biomasse et la diversité de la communauté lombricienne en milieu urbain*, technical report produced by GREBE Inc. for Environment Canada and Dow Chemical Co., Canadian Wildlife Service, Quebec Region, 30 pp. (1990).

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azinphos-methyl

12. EFFECTS OF THE TREATMENT OF POTATO FIELDS WITH AZINPHOS-METHYL ON BREEDING BIRDS IN QUEBEC - (D. Graham, SAGE Ltd.; J-L. DesGranges, CWS, Quebec Region)

Keywords. birds, feeding behaviour

Introduction. The study deals with the feeding behaviour of birds in cultivated areas exposed to pesticides. It is also designed to assess the effects of azinphos-methyl on birds in potato fields.

Methods. Two study sites were selected: a control site located on a farm in Portneuf-Station where organic farming is carried out, and an experimental site in Pont-Rouge which practices conventional farming. The main field activities consisted in observing for approximately 70 hours the feeding behaviour of breeding specimens, some of which were captured (84) and marked (15), mapping the areas in order to detect movements after spraying, and collecting blood and brain samples to study cholinesterase activity.

Results and Discussion. The effects of azinphos-methyl were studied by measuring the degree of inhibition of cholinesterase in the blood and mapping the areas before and after spraying. The effect of the azinphos-methyl could not be determined on the basis of a preliminary review of the data. No change was observed in the occupation of the areas, either in terms of the identity of the marked specimens or of the spatial distribution of the birds in the areas. The analyses of the inhibition of cholinesterase activity were also negative, although the small sample size made interpretation difficult.

The results of the study of feeding behaviour were more interesting. They appear to support the hypothesis that in agricultural environments in Quebec, the feeding behaviour of birds plays a critical role with respect to their exposure to pesticides. Through close to 70 hours of field observation, we observed that the actual potato fields were very seldom, if ever, frequented by any species of bird. The only exception was the Vesper Sparrow, which was regularly observed in the fields. However, the nature of the activities of this bird could not be determined owing to problems associated with field observations.

Publication Medium. Graham, D.J. and J.-L. DesGranges, *Effets de l'azinphos-méthyl (Guthion™) sur les oiseaux fréquentant les champs de pomme de terre et l'influence des facteurs comportementaux*, technical report by SAGE Ltd. for Environment Canada, Canadian Wildlife Service, Quebec Region, 46 pp. and appendices (1990).

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dimethoate, diazinon

13. EFFECTS ON BIRDS OF THE TREATMENT OF CHRISTMAS TREE PLANTATIONS WITH DIMETHOATE, DIAZINON, AND INSECTICIDAL SOAP - (G. Rondeau, Foresterie intégrée du Québec Inc.; and J.-L. DesGranges, CWS-Quebec Region)

Keywords. songbirds, Christmas tree plantations

Introduction. The cultivation of Christmas trees in plantations requires the use of many pesticides, including organophosphorus insecticides, such as diazinon and dimethoate. A biological insecticide-insecticidal soap-is also used. The purpose of this study was to determine the effects of the three products on breeding bird populations in that type of agroforest habitat.

Methods. The research was carried out in the spring of 1989 and 1990 in balsam fir (*Abies balsamea*) plantations in southeastern Quebec. The breeding behaviour of the American Robin (*Turdus migratorius*) and Song Sparrow (*Melospiza melodia*) was monitored. The study variables included adult mortality following insecticide application, the behaviour of breeding birds, nestling mortality, and exposure of the birds to organophosphorus insecticides. Seven Christmas tree plantations were studied, and a total of 87 American Robin nests and 41 Song Sparrow nests were visited every three days on average.

Results and Discussion. Through analyses of blood cholinesterase (ChE) activity prior to and from 24 to 48 hours after application, we showed that American Robins, Song Sparrows, and Chipping Sparrows (*Spizella passerina*) breeding in the treated plantations were exposed to diazinon and dimethoate ($p < .05$). Despite sharp reductions in ChE (and, in some cases, marked inhibition), no cases of adult mortality were recorded following the treatments. Cases of complete or partial mortality were recorded in American Robin and Song Sparrow nestlings. Abandonment of nests and egg infertility were ruled out as the principal causes of mortality. Rather, it would appear that American Robin eggs are particularly sensitive to diazinon (and, to some extent, dimethoate), particularly when spraying is carried out early in the incubation stage. In the case of the Song Sparrow, it was primarily the nestlings that succumbed after diazinon was sprayed on the nestlings themselves or when the eggs were contaminated with dimethoate. The ingestion of food contaminated by these organophosphorus insecticides appears to be the main cause of mortality among Song Sparrow nestlings, a species that usually feeds in the plantations (robins go off the plantations to feed). Twice as many cases of total mortality were recorded among the American Robin and Song Sparrow nestlings exposed to diazinon (31% and 38%, respectively) than among the control nests. The cases of total mortality observed in American Robin and Song Sparrow broods exposed to dimethoate were similar to those recorded for control nests (18% and 25% compared to 14% and 21%, respectively). No mortality was recorded for nestlings exposed to insecticidal soap.

Publication Medium. A technical report of the Canadian Wildlife Service (Quebec Region) was published in January 1992 and a scientific article was submitted to *Applied Ecology*.

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Bacillus thuringiensis

14. EFFECTS OF SEVERE DEFOLIATION CAUSED BY SPRUCE BUDWORM ON THE STRUCTURE OF BIRD COMMUNITIES IN WHITE BIRCH–BALSAM FIR STANDS - (G. Rondeau, Foresterie intégrée du Québec Inc.; and J.-L. DesGranges, CWS, Quebec Region)

Keywords. biological insecticides, songbirds, conifer forest, spruce budworm

Introduction. This study was carried out in the Laurentian forest reserve, north of Quebec City. It was designed to compare the bird communities of two adjacent white birch–balsam fir stands following a spruce budworm infestation. One of the stands was protected against the infestation by aerial spraying of the biological insecticide *Bacillus thuringiensis*; the other was left untreated and was ravaged by the insect.

Methods. We described the structure and composition of the two stands and the level of defoliation of the conifers in the stands. We then examined them from the perspective of the bird communities in order to determine whether the changes in the vegetation as a result of the infestation affected the breeding species of the ravaged stand.

Results and Discussion. Following the spruce budworm infestation, the trees in the unprotected stand lost most of their needles, which promoted the growth of light-demanding species, particularly raspberry plants, in the shrub strata. The changes in the structure of the fir stand forced the avifauna to adapt to new conditions.

Contrary to what would have been expected, the diversity and total density of the bird species in the healthy fir stand did not differ significantly from that of the ravaged fir stand. However, half of the 20 species selected for the study were more abundant in one stand or the other. It was only in the species in the shrub strata that there was a significant difference between the two study sites, being more numerous in the protected fir stand (for example, the Blackpoll Warbler and the Tennessee Warbler). These results seem to indicate that the reduction in the number of young healthy conifers and their gradual replacement by raspberry plants due to a spruce budworm infestation results in a slight decline in the abundance of bird species that feed in the lower parts of trees and in the regeneration of firs. On the whole; however, the results further indicate that the structure of the bird communities remains relatively unchanged despite major disruptions in the stand.

Publication Medium. Scientific article submitted to the *Canadian Journal of Zoology*.

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general

15. PESTICIDES IN QUEBEC - (G.J. Douglas, SAGE Ltd.; F. Perron and J.-L. DesGranges, Conservation and Protection, Quebec Region)

Keywords. Quebec, context, warning system, pesticide survey

Introduction. The issue of pesticide use in Quebec involves many groups and individuals and is producing positive and negative effects against a highly complex socioeconomic and environmental backdrop. This report provides an overview of the key aspects of this issue, including the players, risks, problems, and solutions. It also examines the advisability of establishing a warning system in Quebec regarding the mortality of small wildlife due to pesticides.

Results and Discussion. A three-part report was prepared as part of this project. The first volume concerns the context and problem. It reviews the current status of pesticides regulation, the use of pesticides in Quebec, the monitoring of their deleterious effects, problems regarding their use, and the solutions that may be proposed. The second volume comprises a summary of the views of the key players contacted and a directory of some 300 Quebec groups and individuals involved in this field. The third volume supports the proposed warning system respecting wildlife affected and presents many recommendations regarding the implementation of such a system.

Publication Medium. SAGE Ltd., *Les pesticides au Québec*, report prepared by SAGE Ltd. for Conservation and Protection, Environment Canada, Quebec Region, 3 vol. (1991).

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general

16. HABITAT PREFERENCE AND RECENT FLUCTUATIONS IN BIRD POPULATIONS IN AGRICULTURAL AREAS IN QUEBEC - (G. Falardeau and J.-L. DesGranges, CWS, Quebec Region)

Keywords. birds, demographic trends, breeding habitat

Introduction. The changes that have occurred in agricultural practices may well have had negative effects on certain species of birds that breed in rural areas. The decline in the area of farmland, the mechanization of cropping practices, and the increasingly extensive use of pesticides to protect crops pose serious risks to the reproduction and maintenance of bird populations in cultivated areas. The purpose of this study is to attempt to evaluate the scope of these risks.

Methods. We used Breeding Bird Survey (BBS) data to determine the habitat preferences (evaluated in 1981 and 1982) of birds in cultivated areas and to determine the fluctuations in these bird populations in Quebec. The trends detected were then analyzed, taking into account the ecological and behavioural characteristics of the species and the changes in agricultural practices that have occurred during this period in Quebec.

Results and Discussion. Little new information on breeding habitats was obtained from the Breeding Bird Survey, which is a collective study designed primarily to monitor bird populations. However, the analysis of demographic trends revealed that 10 of the 28 species studied increased significantly in number between 1970 and 1986. Three of the species, the Ring-billed Gull, Mourning Dove, and Upland Sandpiper, have expanded their range considerably toward the northeast, particularly in Quebec, over the past 20 years. The other species whose numbers are on the rise are (in descending order of significance) the Eastern Kingbird, Rock Dove, Yellow Warbler, Northern Oriole, American Crow, American Robin, and Chipping Sparrow. Six species have experienced significant decreases in population, with the Brown-headed Cowbird, which has shown a marked decline since 1979, and the Vesper Sparrow, whose numbers dropped sharply between 1970 and 1974, being the hardest hit. The other species with declining populations are the European Starling, Common Grackle, Barn Swallow, and Savannah Sparrow. Five of these six species are omnivorous and feed on the ground in fields, a fact that should make them more vulnerable to harm from changes in agricultural practices (pesticides and tillage implements). However, species that nest on the ground in fields do not seem to be particularly affected, although their exposure to harmful agricultural techniques should be as great as for the preceding group. Three of the declining species (European Starling, Common Grackle, Brown-headed Cowbird) may have suffered adverse consequences attributable to programs aimed at reducing the populations of "blackbirds" that winter in the United States.

Publication Medium. *Canadian Field-Naturalist* (forthcoming).

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PESTICIDES PROGRAM AT HEADQUARTERS

general

1. ANALYSIS OF A DATA BASE ON PESTICIDE RESIDUES ON PLANTS -

(A. Baril, B. Collins, C. Rogers, and B. Conilh de Beyssac, CWS, -HQ)

Keywords. residues, wildlife exposure

Introduction. There are several ways in which wildlife can be exposed to pesticides, one of which is ingestion of freshly treated vegetation. There are often few data on the residues present after application of a given pesticide. As a result, it is necessary to rely on data obtained on other pesticides applied under similar conditions on the same crops. The purpose of our project was to update the data base. The last summary, carried out by Hoerger and Kenaga, dated back to 1972.

Methods. The project consisted of conducting an extensive bibliographic search and compiling as much information as possible on the analyses of pesticide residues found on plants immediately following treatment. This information can be used to assess the exposure of wildlife to these toxic products.

In order to be able to compare the data compiled with the data presented by Hoerger and Kenaga (1972), we computerized the latter. Each sample analyzed was classified, in accordance with the principles presented by Hoerger and Kenaga, into one of the following eight categories: berries and small fruits, forage crops, fruits, grasses, range grasses, seeds, leaves and leafy crops, and pods containing seeds.

On the basis of the dosage applied and the concentration of the residues, the concentration of residues per unit dosage (RUD) were calculated. An upper limit and typical limit of the RUD were also calculated for each of the above categories.

The general breakdown of the RUD values was analyzed statistically using the SAS program (SAS, 1987) by means of a normality test programmed by D'Agostino and Bélanger (1990). Variance analyses were performed using a program in Microsoft FORTRAN written by B. Collins, a biostatistician with the Canadian Wildlife Service.

Results and Discussion. A comparison of the average RUD values of the various categories reveals that berries and small fruits and forage crops have a higher typical limit. Consequently, these RUD values will have an effect on the estimation or prediction of the rate of exposure of the wildlife associated with these crops.

The categories fall into one of two distinct groups: 1) grasses and forage crops and 2) berries and small fruits, pods containing seeds, and fruits. The category of leaves and leafy crops was not significantly different from either of these two groups, although its average RUD value was closer to that of the first group than to that of the second.

By means of a second variance analysis based on data broken down according to the class of product used, a significant distinction was made between the RUD values obtained during treatments with herbicides and those obtained during treatments with fungicides and insecticides. The following four new groups were formed:

- Group 1: forage crops, grasses, and leaves and leafy crops treated with fungicides or insecticides.

- Group 2: forage crops, grasses, and leaves and leafy crops treated with herbicides.

- Group 3: berries and small fruits, fruits, and pods containing seeds treated with fungicides or insecticides.

- Group 4: berries and small fruits, fruits, and pods containing seeds treated with herbicides.

The fourth group, which contained only four data, could not be integrated into a new variance analysis, which confirmed the significant difference among the first three groups ($p = .05$).

For the predictions for these three groups, we propose that rather than using the maximum RUD values, we use their confidence limits at 95%, which have the advantage of integrating a safety factor. On the basis of our study, we were able to confirm the relative validity and utility of RUD values (concentrations of residues per unit dosage), with a few limitations and precautions.

Publication Medium. Scientific article.

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fenitrothion

2. ENERGETIC AND REPRODUCTIVE CONSEQUENCES OF CHOLINESTERASE-INHIBITING PESTICIDES IN BIRDS - (P. Mineau and C. Ellingwood, CWS-HQ)

Keywords. anticholinesterase, bird reproduction, bird physiology

Introduction. There have been surprisingly few attempts to assess the consequences of sublethal exposure to anticholinesterase insecticides (organophosphates or carbamates) under controlled conditions in breeding birds. The only work to date has been carried out in a single species: the European Starling. Because of that species' apparent lack of sensitivity to organophosphates, it is desirable to replicate the work in a second species. We decided to investigate the use of the Tree Swallow as a suitable model. Like the starling, it is a box nester, which makes it amenable to study. Also, its aerial insect diet should render it relatively susceptible to pesticide-induced incapacitation.

One of the consequences of sublethal exposure in breeding starlings is an altered time budget (as a result of temporary incapacitation) and a reduced food intake. We suggest that it should be possible to measure the total disruption brought about by exposure to an anticholinesterase insecticide by looking at the energy expenditure of the affected birds. A method now exists to look at energy consumption in free-flying birds. It involves injecting individual birds with a mixture of deuterium and oxygen 18 (a double label) and measuring the relative disappearance of the two over time to arrive at a measure of respiration rate measured as carbon dioxide production.

Objectives and Methods. This project was a pilot study to develop the methodology to 1) investigate the effects of sublethal dosing with a cholinesterase inhibitor on the reproductive biology of the Tree Swallow and 2) evaluate the usefulness of the doubly labelled water technique to monitor disruptions in a breeding pair's time-energy budget. The insecticide fenitrothion was used as our model organophosphate.

Results and Discussion. A breeding colony of Tree Swallows was established Occupancy in this first year was low, limiting our sample size.

A calibration curve between dose and brain cholinesterase inhibition was established for the OP fenitrothion. We had considerable difficulty in establishing a valid curve because of the short residence time of the oral dose in the gut of the swallow.

We were able to test methods relating to 1) dosing of the birds, 2) injection of stable radio-isotopes for energy expenditure measurements, 3) observations of adults at the nest, 4) growth of the young, and 5) taking of blood samples for cholinesterase and radioisotope determinations

Little information was obtained on the effects of the pesticide on the breeding performance and growth rates of the young, but sample sizes were too small for us to reach any conclusions. Disturbance of the nest boxes was also a factor.

A number of pairs were injected with doubly labelled water for a measurement of their

energy expenditure. This was to be compared to time budgets established on the same pairs through intensive observation at the nest. The analysis of doubly labelled water required the samples to be sent abroad, and problems at the laboratory resulted in extended delays. Unfortunately, the samples did not yield useful results for a number of reasons, the main one apparently being cracks that developed in the seals of the sample capillaries.

Publication Medium. We do not propose to publish these results at present. Rather, the study will be reactivated when the sample analysis problems have been resolved.

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fenitrothion

3. THE EFFECTS OF SUBLETHAL ORGANOPHOSPHATE DOSING ON LEARNING AND MEMORY IN BIRDS - (P. Mineau, CWS-HQ; Staff of the Animal Resource Division, Health and Welfare Canada; Dr. P.A. Boag and Dr. R.J. Beninger, Queen's University; J. Dean and J. Oblak)

Keywords. memory, anticholinesterase, behavioural toxicology

Introduction. Considerable controversy surrounds the use of organophosphate and carbamate insecticides. At issue is the extent to which the survival of sublethally exposed individuals is compromised. This question is important to the determination of the safety of these products to wildlife because of the extent of their exposure in either forestry or agricultural applications.

Evidence from the laboratory mammal and human poisoning literature suggests that exposure to anticholinesterase agents can disrupt higher behavioural processes such as learning and memory. Furthermore, exposed animals that appear to have recovered from an acute exposure, at least in terms of gross motor function and other visible symptoms of toxicity, are often found to still be functionally impaired when tested for these more complex brain functions.

Objective and Methods. A substantial amount of work on memory in birds has been achieved through the use of food caching behaviour in certain groups, notably the family Paridae (tits or chickadees). Caching behaviour is highly repeatable and can be studied in a laboratory environment under controlled conditions. It therefore offers a natural paradigm for studying possible memory deficits resulting from exposure to anticholinesterase agents. Also, this behaviour is very important in nature because it provides a buffer against food scarcity in a variable environment.

Results and Discussion. The memory for food caches in Black-capped Chickadees (*Parus atricapillus*) was found to respond to cholinergic (anticholinesterase) and anticholinergic drugs. Pre-cache dosing with the anticholinergic scopolamine was found to impede the formation of memories for food caches, whereas the anticholinesterase eserine facilitated it. These results were expected based on reports in the literature of similar results with various working memory paradigms in rodents and in the pigeon. Having established that memories for food caches were under some cholinergic control, we then looked at the effect of acute dosing with fenitrothion, commensurate with levels of exposure reported from forest spraying programs. Despite obvious physiological symptoms of cholinergic overstimulation, no effects were seen on either memory formation or retrieval when the insecticide was given after memory formation. When the insecticide was given before memory formation, even these relatively high levels enhanced rather than impeded the future memory for food caches. Clearly, this work did not point to memory effects as the most sensitive indicators of impact following exposure to anticholinesterase pesticides.

Publication Medium. Scientific journals.

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general

4. NONTARGET PLANT TESTING AND EVALUATION OF CHEMICAL PESTICIDES: DRAFT GUIDELINES FOR REGISTRATION OF PESTICIDES IN CANADA - (C. Boutin and K.E. Freemark, CWS-NWRC; C.J. Keddy, Consulting Ecologist)

Keywords. nontarget plants, guidelines

Introduction. The Canadian Wildlife Service (CWS) is responsible for identifying and interpreting the effects of pesticides on Canadian wildlife and for providing advice and recommendations to prevent and mitigate these effects. Protection of nontarget plants is not adequately and systematically considered during the process of pesticide registration in Canada. This project will produce the nontarget plant guidelines for testing chemical pesticides in Canada.

In 1986–87, the CWS staffed a three-month term position to initiate drafting of guidelines for testing pesticide toxicity to nontarget plants.

In 1987–88, an Interdepartmental Working Committee (IWC) was established by the Commercial Chemicals Branch (CCB) and CWS to facilitate development of nontarget plant testing guidelines for registration of chemical pesticides in Canada. The Saskatchewan Research Council (SRC) was contracted to review existing international requirements for pesticide toxicity to nontarget plants, evaluate problems with currently used regulatory guidelines and tests, identify knowledge gaps regarding phytotoxicity testing, and provide conclusions and recommendations for developing guidelines in Canada.

Further contracts were let to provide a background document on aquatic plant indicator species (SRC) and to develop algal microplate testing techniques for pesticides (St. Lawrence Centre). A background document is being completed on plant-mediated effects on wildlife related to pesticide use by reviewing the scientific literature.

Objectives and Methods. In 1990–91, effort was aimed at drafting an R-memo (Memorandum to Registrants) for distribution by Agriculture Canada to pesticide registrants.

Several activities were organized to present, publish, and inform evaluators, researchers, and industries on the current status of the nontarget plant guidelines. A workshop on nontarget plant testing was held in February 1990 to stimulate exchange with people involved in pesticide registration in Canada and to generate discussion. Following the workshop, a letter was sent to pesticide proponents via the Crop Protection Institute of Canada (CPIC) explaining phytotoxicity data requirements. The document will assist companies in plant testing until the nontarget plant guidelines are completed.

In November 1989, a contract was let to Ms. Cathy Keddy to review the extensive background documentation including previous reports on nontarget plants, other guidelines and protocols, and scientific or review papers.

Results and Discussion. The first version of the nontarget plant guidelines, drafted by Ms. C. Keddy, was sent for comments within Environment Canada in March 1990.

The second version was reviewed internally in September 1990. A third version of the nontarget plant guidelines, completed in October 1990, includes test requirements, refinements/changes to existing test protocols, reporting details, as well as the rationale related to different testing. The document was sent to IWC, CPIC, IGATG (Inter-Governmental Aquatic Toxicity Group), and U.S. EPA (U.S. Environmental Protection Agency) for further reviews. A meeting with IWC members took place in March 1991 and comments were incorporated thereafter.

A report on research needs, in order of priority, has been submitted for further development of guidelines for nontarget plant toxicity testing for pesticide registration in Canada.

Publication Medium. Freemark, K., P. MacQuarrie, S. Swanson, and H. Peterson, "Development of Guidelines for Testing Pesticide Toxicity to Non-target Plants for Canada", in: *Plants for Toxicity Assessment*, W. Wang, J.W. Gorsuch, and W.R. Lower (eds.), pp. 14 to 29, ASTM Special Technical Publication 1091, American Society for Testing Materials, Philadelphia, Pennsylvania (1990).

Swanson, S., C. Rickard, K. Freemark, and P. MacQuarrie, "Testing for Pesticide Toxicity to Aquatic Plants", in: *Plants for Toxicity Assessment*, J.W. Gorsuch and W.R. Lower (eds.), ASTM Special Technical Publication 1115, American Society for Testing Materials, Philadelphia, Pennsylvania (1991).

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carbofuran, chlorothalonil, MCPA, atrazine, bromoxynil, 2,4-D, glyphosate, metolachlor, ethametsulfuron, diquat, imazethapyr

5. IMPROVEMENT OF METHODOLOGY FOR TESTING TOXICITY OF PESTICIDES TO ALGAE AND CYANOBACTERIA - (C. Boutin and K.E. Freemark, CWS-NWRC; and H.G. Peterson, Saskatchewan Research Council)

Keywords. nontarget plants, algae, methodology, toxicity tests

Introduction. A current Environment Canada initiative is to draft guidelines for testing pesticide toxicity to nontarget plants. Regulatory toxicity testing using algae produces results of questionable use because of poor selection of test species and variable test conditions.

Objective and Methods. The objective of this study is to evaluate and solve problems with current test methods and to use new test methods aimed at improving accuracy, test sensitivity, ecological relevance, predictive ability, and cost efficiency.

Three main aspects will be addressed: 1) number and classes of algal species used as indicator, 2) different toxicity endpoints, and 3) test conditions such as pH, source of nitrogen, and presence of dissolved organics.

Results and Discussion. The priority in the first year was to develop good baseline testing conditions with the different species of algae and to set up a facility where such tests could be carried out effectively.

Species

Cultures of species necessary for the entire project were obtained from different culture collections such as the University of Texas Culture Collection, American Type Culture Collection, and Cambridge Culture Collection. Out of 190 strains (green and blue-green algae, diatoms) received, 42% have performed well under good laboratory conditions over the last 6–8 months.

Green algae, cyanobacteria, and diatoms have been cultured in chemostats (nutrient limited conditions). This has been especially difficult with diatoms, of which there are 35 strains in the collection. The diatom medium has to be redesigned and is now different from the cyanobacteria and other algae. One out of five strains tested looks promising for further studies. Another 20 diatom strains have still to be tested.

Endpoints

Different endpoints have been tested for pesticide toxicity. These include the inhibition of growth, nitrate, ammonium, and phosphate uptake. Also some endpoints specific to certain groups of organisms have been tested; for instance, the inhibition of nitrogen fixation of cyanobacteria is a very sensitive endpoint, which is also ecologically very important.

Conditions

The microplate screening tests for nutrient uptake endpoints on nutrient-limited cultures were started and will continue. Most of the priority pollutants listed in our proposal have been used in these preliminary tests. One of the conclusions from this is that it is difficult to carry out microplate tests without getting large pH changes.

Much time has been spent on developing tests where pH varies within narrow limits;

these test conditions will be used to determine the pH effects of ammonium versus nitrate uptake. The difference in toxicity shown by a pH-sensitive toxicant is also being assessed when tested with our method compared with traditional methods.

Publication Medium. Peterson, H.G., C. Boutin, and K.E. Freemark, Pesticide Toxicity Testing Using Algae: Development of New Tests. Paper presented to ASTM meeting, Atlantic City, April 1991. (In preparation for publication.)

Freemark, K.E., C. Boutin, and H.G. Peterson, Nontarget Plant Hazard Assessment for Pesticide Registration in Canada. Paper presented to ASTM meeting, Atlantic City, April 1991. (In preparation for publication.)

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general

6. COMPARATIVE FIELD STUDY TO EVALUATE THE EFFECTS OF AGRICULTURAL PRACTICES ON BIRDS IN CANADA - (K.E. Freemark and B. Collins, CWS-NWRC; C. Weseloh, CWS-Ontario Region; D. Forsyth, CWS-W&N Region; C. Rogers, G. Bain, W. Harris, M. Csizy, A. Cyr, and D. Lepage, Contractors)

Keywords. cropland birds, organic/chemical farms, Ontario, Saskatchewan, Quebec, field surveys

Introduction. The Canadian Wildlife Service (CWS) is responsible for protecting and managing migratory bird species in Canada. To do this, we need field studies to assess the effects of modern agricultural practices, including habitat simplification and the use of pesticides and chemical fertilizers, on birds and their habitat. Regional information on bird use of croplands can also be used to improve CWS assessments of potential risks associated with proposed or current chemical use patterns in Canada.

Objective. The objective of the project is to compare the avifauna on organic and chemical farms in different regions of Canada in order to 1) evaluate the hazard to birds and their habitats from exposure to agricultural pesticides and chemical fertilizers, 2) provide data on bird use of croplands and adjacent habitats for improving risk assessments, and 3) examine how differences in land use patterns affect farmland birds.

The information generated by our research can be used to improve CWS advice and recommendations, not only to regulatory agencies such as Agriculture Canada, but also to the farming and conservation communities, in order to encourage sustainable agricultural practices and to prevent or mitigate adverse effects on wildlife and their habitats from practices currently used in Canada.

Methods. Literature review and field studies have been used (more details below).

Results and Discussion. In 1989, a literature review and field studies in Ontario and Saskatchewan were conducted to evaluate the feasibility of comparing organic and chemical farms in Canada. A review of existing information characterized the nature of organic farming and its extent in Canada. Sufficient numbers of organic farms to establish study sites were reported for the Maritimes, Quebec, Ontario, and Saskatchewan.

Ontario Study: In 1989, organic farms were identified and visited in eastern Ontario to determine if they were suitable for study and could be matched to chemical farms. Bird survey sites were established on three pairs of farms in eastern Ontario to compare farm types and different survey methods. Herbicides and chemical fertilizers were only used on the chemical farms. Habitat features at the bird survey sites were similar within each farm pair. A total of 64 bird species were observed on the study farms during June and early July using a variety of survey methods. Analyses indicated that birds were best surveyed using 180-degree, unlimited-distance (but on farm) point counts located at field edges. More birds and species were observed at organic sites than at their conventional twins. Analyses by

species were inconclusive due to small samples.

In 1990, ten pairs of organic/chemical farms were studied in eastern and southwestern Ontario. Thirty-six bird survey sites were paired between farms on the basis of similarity in habitat features. Organic farms were certified. Birds were surveyed twice in May and twice in June using unlimited-distance, 180-degree, 10-minute point counts located at field edges. Sixty-eight bird species were observed. The number of birds and species was significantly higher for the organic point of the pair. Ten bird species were detected significantly more often and/or were significantly more abundant on the organic point of the pair. One species occurred significantly more often on the conventional point of the pair. Bird species were classified into guilds based on food preference or foraging location. Species numbers for insectivores, aerial foragers, and ground foragers were significantly higher at organic points of the pairs. The abundance of granivores and ground foragers was significantly higher on organic points of the pairs. When food preference and feeding location were combined, species number for aerial insectivores and both species number and abundance for ground omnivores were significantly higher on the organic points of the pairs. The number of species per point did not differ for organic versus chemical points for any crop category. The number of birds per point was significantly higher at organic versus chemical points for hay, soybean, and spring grains, but not for winter grains. Habitat quantification and characterization of farm operations for each bird survey site is under way. Further analyses are planned to examine differences in birds between farm types in relation to habitat features, use of pesticides and chemical fertilizers, and tillage practices.

Saskatchewan Study: In 1989, a quarter section on each of ten pairs of organic/chemical farms was selected near Saskatoon. Quarters within farm pairs had similar spatial patterns of crop and noncrop habitat. In 1990, birds were surveyed at 40 pairs of sites on the quarter sections using the same method as the Ontario study. Waterfowl counts were also done for wetlands on each site. Habitat quantification and characterization of farm operations for each bird survey site is under way. No analyses have been done to date.

Quebec Study: In 1990, a study was initiated to select suitable farms and to compare point counts to more intensive survey methods. Point counts and mapping censuses were completed on three conventional farms during June and early July. Eight points paired between an organic and conventional farm were surveyed four times between late June and early July. The study report is currently being revised. Bird surveys of additional organic/conventional chemical farm pairs are currently under way.

Publication Medium. The 1989 feasibility study was published as a CWS technical report. The Ontario results were presented at a scientific conference in July 1991 and submitted to the *Journal of Applied Ecology*.

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MCPA, butylate

7. AN EVALUATION OF THE PHYTOTOXIC EFFECTS OF THE HERBICIDES BUTYLATE AND MCPA ON NATIVE MICRO- AND MACROFLORA - (R.A. Kent, IWD-HQ; and P.-Y. Caux and M. Taché, St. Lawrence Centre)

Keywords. thiocarbamate, *Lemna minor, Selenastrum capricornutum*, LC_{50}, LOEC

Introduction. A recent report prepared for Environment Canada summarizing pesticide use in the Quebec Region, targeted a group of compounds that, based on sales data, known fate and toxicity profiles, and proximity of use to water bodies, warranted concern regarding their potential contamination of aquatic systems. Included in this list was the thiocarbamate herbicide butylate and the phenoxy acid herbicide MCPA (solubility in water, 46 mg/L for butylate and 825 mg/L for MCPA). Butylate is used primarily against annual grasses in field and sweet corn. MCPA is effective at controlling broadleaf weeds in cereals, forage crops, peas, and flax. Since 1982, the use of these herbicides has increased dramatically in Quebec. Butylate and MCPA rank third and seventh, respectively, in terms of total herbicides applied in that province.

MCPA is currently among the top two to four most heavily used pesticides in Canada, with its principal use occuring in the prairie regions. Nationwide, MCPA has been measured in three southern Ontario watersheds and in rivers in Saskatchewan (max. 13.2 µg/L) and Alberta. Considering the high use of this herbicide in large agricultural regions in Canada, there is a surprising dearth of information regarding its effects on indigenous biota, in particular nontarget plants. A recent summary report prepared by the Western and Northern Region and a draft of the CCME Canadian water quality guideline for MCPA reviewing the toxicity data for MCPA confirmed this. This information deficiency is equally apparent for butylate. The recognized mode of action of thiocarbamate herbicides such as butylate is interference in lipid synthesis and function. These changes may occur at several levels in the plant, including alterations in lipid biosynthesis of the cuticle, which substantially increases its susceptibility to subsequent herbicide treatment; levels and composition of phospholipids and galactosides; incorporation of acetate and malonate in the lipids; biosynthesis of gibberellins; and effects on lipid-bound enzyme systems (MFO). The target site and action of MCPA is more specific than that of butylate. MCPA acts as an anti-auxin, mimicking the structures of the plant growth hormones, and in doing so, effectively interfering with normal plant growth.

Nontarget plant toxicological assessment has been recently identified by DOE as a priority area in pesticide registration and re-evaluation. Most phytotoxicological research with herbicides has been conducted on target plants (i.e., efficacy studies on weeds). There are few data on the effects these pollutants may have in aquatic systems. There is an essential need to assess the basic phytotoxicity of these herbicides on nontarget aquatic plants, which form the basis of energy flow in aquatic food webs. This report summarizes an investigation evaluating the phytotoxic potential of these high use compounds on common phytobiota models. Acute and chronic toxicity assessments with butylate and MCPA, using common green algae (*Selenastrum*

capricornutum) and the macrophyte *Lemna minor*, were conducted in the laboratory.

Objective. The objective of this project was to establish the basic phytotoxicological concentrations of butylate and MCPA to selected native aquatic biota. The designed tests that were used are representative of the mode of action of the compounds thereby enabling the most sensitive assessment of the environmental effects of these pesticides.

Methods. The test organism used was the unicellular chlorophycea *S. capricornutum* and the macrophyte *L. minor*. After exposing *S. capricornutum* to various concentrations of MCPA and butylate for a period of 96 h in microplates, an EC_{50} and a LOEC were determined by an electronic cell particle counter and compared to an EC_{50} and a LOEC obtained from a microplate fluorometer.

To determine the effect of butylate on lipids of algae, *S. capricornutum* was treated with various concentrations of butylate for a period of 96 h. Lipids were then extracted from the treated cultures and analyzed by gas chromatography.

L. minor was also treated with various concentrations of MCPA and butylate for a 14-d period. We determined an EC_{50} and a LOEC by counting the number of fronds from the whole population in each of the test flasks. Dry weight from the whole colony population was also determined.

Results and Discussion. Important measures were obtained from these observations. The growth rate EC_{50}s for MCPA and butylate for the test organism *S. capricornutum* were 18.4 µg/L and 61.0 µg/L, respectively, with LOECs of 8.9 µg/L and 8.3 µg/L, respectively. The fluorometric EC_{50}s for MCPA and butylate were 17.8 µg/L and 0.5 µg/L, respectively, with LOECs of 8.9 µg/L and 0.25 µg/L, respectively.

The data obtained from *L. minor* showed an EC_{50} of 150 µg/L for MCPA, with a LOEC of 25 µg/L. This test organism was less sensitive to butylate, with an EC_{50} of 240 µg/L and a LOEC of 120 to 240 µg/L.

These results suggested that electron transport inhibition is not a sensitive parameter for the anti-auxin acting pesticide MCPA and that, as expected, growth inhibition is a more sensitive parameter for this compound. Butylate, on the other hand, displayed a greater inhibitory effect when using fluorescence as an endpoint as compared to cell counts. This can be explained by the fact that the normal functioning of photosystems and their associated transport chains are intimately linked with lipid domain integrity.

Publication Medium. The results of the *S. capricornutum* lipids analysis along with the dry weight of butylate-treated *L. minor* will be treated in an article being prepared for the *Canadian Journal of Botany*.

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atrazine, carbofuran, glyphosate, metribuzin, cyanazine, metolachlor, picloram, simazine, captan, dinoseb

8. CANADIAN WATER QUALITY GUIDELINES FOR PESTICIDES - (R.A. Kent, P.-Y. Caux, and M. Taché, IWD-HQ)

Keywords. water quality guideline, CCME, aquatic life, irrigation waters, livestock waters

Introduction. The Canadian Council of Ministers of the Environment (CCME, formerly CCREM) published the first edition of the Canadian Water Quality Guidelines in 1987 to harmonize guidelines recommended for the maintenance and protection of designated water uses. These guidelines define acceptable water quality for a number of chemical, physical, biological, and radiological parameters. The major water uses addressed are 1) raw water for drinking water supply, 2) recreational water quality and aesthetics, 3) agricultural uses including irrigation and livestock water, 4) industrial water supplies, and 5) water to support and protect freshwater and marine aquatic life.

CCME water quality guidelines are national in scope, being accepted by all provinces and territories and used in their respective water quality management programs. Guidelines do not constitute values for uniform national water quality as their use will require consideration of local conditions.

Following the release of the first edition in 1987, one group of parameters identified by the CCME Task Force on Water Quality Guidelines as urgently requiring the development of guidelines was the in-use pesticides. Although several pesticide guidelines were included in the first edition, with the exception of 2,4-D and lindane, many of these compounds are no longer registered or have widespread use in Canada. Concerns are now focused on the newer herbicides, insecticides, and fungicides currently being applied in modern agricultural and silvicultural practices.

Draft water quality guidelines for pesticides are developed by the technical secretariat of the Federal–Provincial Task Force on Water Quality Guidelines, which is provided by the Water Quality Branch, Inland Waters Directorate. These recommendations are then critically reviewed by all provincial and territorial members of the Task Force, submitted for consideration to their parent committee, the CCME Water Advisory Committee, and finally submitted for approval to the Canadian Council of Ministers of the Environment.

Methods. In 1987, the CCME Task Force compiled a priority list of pesticides urgently requiring water quality guideline development. This list was amended in 1989 with newer priorities following further consultation with Task Force members.

Guidelines are based on public documents that contain a detailed review of all the published information currently available regarding production and registered uses; physical and chemical properties; sources and pathways for entering the aquatic environment; environmental concentrations; fate and persistence; bioaccumulation; toxicity to aquatic biota; nontarget crops, livestock, and related biota; and a review of available guidelines/objectives/criteria from other jurisdictions. When sufficient information is available, maximum

numerical concentrations or narrative statements that will protect and maintain water uses in Canada are recommended.

Results and Discussion. Canadian water quality guidelines have been prepared for ten priority in-use pesticides to date, including atrazine, carbofuran, glyphosate, metribuzin, cyanazine, picloram, metolachlor, simazine, captan, and dinoseb. These guidelines have been published as updates in the original CCREM *Canadian Water Quality Guidelines*. Draft guideline documents have been prepared for organotins, diclofop-methyl, trifluralin, triallate, bromoxynil, dicamba, chlorothalonil, linuron, MCPA, aldicarb, and dimethoate. These guidelines will be published following review.

Publication Medium. *Canadian Water Quality Guidelines* and IWD Scientific Series.

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CANADIAN WATER QUALITY GUIDELINES FOR TEN PRIORITY PESTICIDES

Pesticide	Guidelines (µg/L)		
	Aquatic Life	Livestock Waters	Irrigation Waters
Atrazine	2.0	60.0	10.0
Carbofuran	1.7	45.0	-*
Glyphosate	65.0**	280.0**	-*
Metribuzin	1.0	80.0	0.5
Cyanazine	2.0	10.0**	0.5
Metolachlor	8.0	50.0**	28.0**
Picloram	29.0	190.0	-*
Simazine	10.0	10.0**	0.5
Captan	2.8	20.0	-*
Dinoseb	0.05	150.0	16.0

* No recommended guideline.
** Interim guideline.

PESTICIDES PROGRAM IN THE ONTARIO REGION

parathion, phorate, oxydemeton-methyl, dimethoate, azinphos-methyl, diazinon, imidan, malathion, naled, disulfoton, terbufos, fonofos, dursban, ethion

1. ORGANOPHOSPHORUS PESTICIDES IN WATER, SEDIMENT, AND TISSUES - (M.A. Forbes and H. Tse, NWRI).

Keywords. gas chromatographic method, water, sediment, frog tissues, organophosphorus pesticides

Introduction. A method of extraction, cleanup, and gas chromatographic analysis for 13 organophosphorus pesticides in water, sediment, and tissues was developed in the National Water Quality Laboratory in support of a study by several agencies of Environment Canada concerning contamination in the Holland Marsh area of Ontario.

Objective. The purpose of the study was to determine the levels of 13 organophosphorus pesticides in water, sediment, and frog tissues.

Methods. A method was developed for the determination of contaminants and the procedure was validated on three substrates. Degradation studies were conducted for water and a method for maintaining the integrity of the samples was implemented. Cleanup procedures were developed for all substrates and confirmation techniques for unequivocal identification and quantitation were implemented using specific detectors and gas chromatography/mass spectrometry.

Results and Discussion. A reliable analytical method was developed that enabled the investigation on pollution in the Holland Marsh area to be completed. An integrated approach was successfully implemented involving multiagency cooperation.

Publication Medium. The method will be published in the IWD *Analytical Methods Manual.*

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tributyltin

2. ACUTE TOXICITY, UPTAKE, DEPURATION, AND TISSUE DISTRIBUTION OF TRIBUTYLTIN IN RAINBOW TROUT - (M. Dixon and D.G. Dixon, University of Guelph; R.J. Maguire and R.J. Tkacz, NWRI; P.V. Hodson, Great Lakes Laboratory of Fisheries and Aquatic Science)

Keywords. rainbow trout, toxicity tests, uptake, depuration, metabolism

Introduction. Tributyltin is perhaps the chemical most toxic to aquatic organisms that has ever been deliberately added to water. Its antifouling use was regulated by Agriculture Canada under the *Pest Control Products Act* (PCPA) in 1989, but it is still registered for use as a slimicide and general lumber preservative. This study was undertaken to assess the acute toxicity and accumulation of tributyltin in representative freshwater fish. The 96-h LC_{50} value of tributyltin was determined for both rainbow trout (*Salmo gairdneri* Richardson) and lake trout (*Salmo namaycush* Walbaum). The uptake and depuration of tributyltin by rainbow trout were determined to estimate the potential for bioconcentration. Finally, the concentrations of tributyltin and its metabolites (dibutyltin, monobutyltin, and inorganic tin) were determined in 13 tissues of rainbow trout to assess tissue distribution and metabolism.

Results and Discussion. Tributyltin was highly toxic to rainbow trout. The 96-h LC_{50} was 1.4 µg Sn/L. Lake trout were more tolerant, with a 96-h LC_{50} of 5.2 µg Sn/L. Rainbow trout concentrated significant levels of tributyltin during a 64-day exposure at 0.2 µg Sn/L, with bioconcentration factors of 406 and 570 (based on tributyltin and total Sn, respectively). Rainbow trout depurated Sn slowly on transfer to tributyltin-free water. During the 32-day period following exposure, the whole-body concentration of tributyltin fell by 25%, while the total Sn concentration was reduced by 17%.

The total Sn concentrations in tissues of rainbow trout at the end of a 15-day exposure to 0.4 µg/L indicated that tributyltin partitions into rainbow trout in three main compartments. Peritoneal fat (mean concentration 9.2 mg Sn/kg) constituted one compartment; kidney, liver, and gallbladder/bile (mean concentration range 3.1–3.7 mg Sn/kg) a second; and all other tissues (mean concentration range 0.5–1.5 mg Sn/kg) a third. After 15 days of depuration the system had simplified. Only two compartments (liver plus gall-bladder/bile, and all other tissues) were apparent. Varying proportions of tributyltin and its metabolites were present in all tissue sampled. The percentage of metabolites in liver (74%) and gallbladder/bile (89%) was, however, significantly higher than the levels in all other tissues, which ranged from 10 to 43%. This suggests hepatic dealkylation and biliary/fecal excretion.

Although the sample sizes were too small to allow inclusion in the statistical analyses, appreciable quantities of tributyltin and its metabolites were present in brain and reproductive tissues of rainbow trout. Both inorganic and organic tin compounds are demonstrated mammalian neurotoxicants. The reproductive effects of organotin compounds on aquatic organisms are unknown. Although any discussion of the behavioural and reproductive effects of

tributyltin and its metabolites at this time would be purely speculative, their presence in these tissues indicates that further work on reproductive and neurological impacts is warranted.

Publication Medium. Martin, R.C., D.G. Dixon, R.J. Maguire, P.V. Hodson, and R.J. Tkacz, "Acute Toxicity, Uptake, Depuration and Tissue Distribution of Tri-n-butyltin in Rainbow Trout, *Salmo gairdneri*", *Aquat. Toxicol., 15:* 37–52 (1989).

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deltamethrin

3. ACUTE TOXICITY OF ISOMERS OF THE SYNTHETIC PYRETHROID INSECTICIDE DELTAMETHRIN AND ITS MAJOR DEGRADATION PRODUCTS TO *Daphnia magna* - (K.E. Day and R.J. Maguire, NWRI)

Keywords. isomers, degradation products, *Daphnia magna*

Introduction. The synthetic pyrethroid insecticide deltamethrin [S-a-cyano-3-phenoxybenzyl (1R,3R)-cis-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] is registered in Canada to control insect pests in large acreage crops. Like many other synthetic pyrethroids, deltamethrin has been shown to be extremely toxic to fish and aquatic invertebrates, especially crustaceans, in laboratory studies. It has been suggested, however, that the impact of deltamethrin impinging on the surfaces of aquatic ecosystems during application to nearby crops is lessened by the rapid disappearance of the chemical from the water column. The major routes of degradation or dissipation of deltamethrin from water have been reported to be 1) chemical and photochemical conversion to (2+2′)-deltamethrin stereoisomers, 2) hydrolysis with subsequent oxidation of products, and 3) partitioning into suspended solids, plants, sediment, and air.

There are eight possible stereoisomers of deltamethrin, designated as 1, 1′, 2, 2′, 3, 3′, 4, and 4′. The parent compound (1-deltamethrin), with its cis-1R, 3R configuration about the cyclopropane ring and the S configuration for the cyano group at the benzylic carbon atom, has the highest insecticidal activity. The only other isomer known to have insecticidal and mammalian toxicity is 3-deltamethrin.

There is no information on the toxicity of isomers of deltamethrin to aquatic organisms. The conversion of the parent compound to the (2+2′) isomers in natural waters as a significant transformation pathway necessitates the determination of this toxicity. In addition, deltamethrin has been shown to degrade rapidly (hours to days) under field conditions to (at least) four degradation products, namely 3-phenoxy-benzylalcohol (PBalc), 3-phenoxy-benzaldehyde (PBald), 3-phenoxybenzoic acid (PBacid), and cis-3-(2,2-dibromo-vinyl)-2,2-dimethylcyclopropane carboxylic acid (DBCA). The toxicity of these compounds to aquatic invertebrates has not been reported.

Objective. The objective of this research was to determine the acute toxicity of the stereoisomers and breakdown products of deltamethrin to *Daphnia magna*.

Methods. Young *D. magna* (<24 h) were obtained from a culture and were exposed in beakers to a range of concentrations of each isomer. Analytical standards of all eight deltamethrin stereoisomers and DBCA were provided by Roussel-Uclaf, Paris, France, and PBalc, PBald, and PBacid were obtained from Aldrich Co., Milwaukee, Wisconsin. Percent mortality in terms of immobilization was determined at 4, 24, and 48 h, and EC_{50} values were calculated by probit analysis.

Results and Discussion. Parent deltamethrin (isomer 1) was the most toxic, with EC_{50} values in the range of 0.05–1.75 µg/L, concentrations that have been observed in

the surface microlayer and subsurface water in field studies. The other isomers (2-, 3-, and 4-deltamethrin) were two to ten times less toxic than 1-deltamethrin. Isomers 1′, 2′, 3′, and 4′, plus the degradation products studied, displayed no significant toxicity. Since 1-deltamethrin can be converted by sunlight in natural water to 2′-, 3-, and 4′-deltamethrin, and since 3-deltamethrin is toxic to *D. magna*, this isomerization is only a partial detoxification step as far as some aquatic organisms are concerned.

Publication Medium. Day, K.E. and R.J. Maguire, "Acute Toxicity of Isomers of the Pyrethroid Insecticide Deltamethrin and Its Major Degradation Products to *Daphnia magna*", *Environ. Toxicol. Chem., 9:* 1297–1300 (1990).

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azinphos-methyl, fenitrothion, chlorpyrifos

4. USE OF ACETYLCHOLINESTERASE ACTIVITY TO DETECT SUBLETHAL TOXICITY IN STREAM INVERTEBRATES EXPOSED TO LOW CONCENTRATIONS OF ORGANOPHOSPHATE INSECTICIDES - (K.E. Day, NWRI; and I.M. Scott, University of Guelph)

Keywords. acetylcholinesterase, aquatic invertebrates, sublethal, insecticide, organophosphate

Introduction. Organophosphate insecticides act as nerve poisons by blocking synaptic transmission in the cholinergic portions of the nervous system. The disruption of nerve impulses in organisms following exposure is therefore caused by excessive accumulation of the neurotransmitter acetylcholine (ACh), which is normally broken down by the enzyme acetylcholinesterase (AChE). Organophosphates bind to the active site of the AChE and prevent breakdown of ACh. Recent studies have indicated that reductions in AChE in fish are probably the best general index of organophosphate poisoning, but few studies have looked at the effects of these insecticides on AChE in aquatic invertebrates.

Objective. The objective of this research was to develop methodology to measure levels of AChE in aquatic invertebrates exposed to low concentrations of organophosphate insecticides and to determine if observed changes were a good biochemical indicator of sublethal toxicity.

Methods. Several species of aquatic invertebrates were obtained from laboratory cultures or local rivers and streams. Several *in vivo* and *in vitro* exposure tests (24-h to 72-h) were performed with the organophosphate insecticides, azinphos-methyl, chlorpyrifos, and fenitrothion. Levels of AChE were measured using two methodologies based on the Ellman technique, a modified kit procedure using the spectrophotometer and a microplate assay.

Results and Discussion. Levels of AChE ranged from 12.7 milli units per milligram protein for *Daphnia magna* to 96.9 milli units per milligram protein for *Hydropsyche* spp. Exposure of invertebrates to low concentrations of azinphos-methyl and fenitrothion did not result in a significant depression. Exposure of the stonefly, *Claassenia* sp., to chlorpyrifos significantly lowered AChE levels by 30.7–45.1% at concentrations approaching lethality (≥40 µg/L). The results indicate that measurement of the activity of AChE in aquatic invertebrates exposed to field concentrations of organophosphate insecticides may be a useful biochemical technique, but only for detecting acute toxicity following exposure in the field. In addition, choice of species may be important in the detection of sublethal effects.

Publication Medium. Day, K.E. and I.M Scott, "Use of Acetylcholinesterase Activity to Detect Sublethal Toxicity in Stream Invertebrates Exposed to Low Concentrations of Organophosphate Insecticides", *Aquat. Toxicol., 18:* 101–114 (1990).

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alachlor, atrazine, metolachlor, triallate, trifluralin

5. FEDERAL INTERDEPARTMENTAL QUALITY ASSURANCE ON PESTICIDE ANALYSIS - (Y.D. Stokker, NWRI)

Keywords. reference materials, sediment extracts, quality control, quality assurance, CAPCO, neutral herbicides

Introduction. Reference sample extracts are extremely useful materials in both intra- and interlaboratory QA/QC as well as for method validation and research. The availability of such reference materials along with suitable standard solutions in ampules could reduce the cost and increase the effectiveness of laboratory quality control and analysis in monitoring and surveillance programs. This study undertook to produce some unique reference materials in the form of sediment extracts in ampules for trifluralin, triallate, atrazine, and other neutral herbicides of concern. The design values, homogeneity, and stability of these herbicides were confirmed by both in-house analyses as well as in an interlaboratory QC study.

Objectives. The objectives of this study were 1) to generate the reference extracts in ampules, 2) to verify the design values and monitor the homogeneity and stability of these samples, and 3) to conduct one interlaboratory QC study on the analysis of neutral herbicides in the sediment extracts. The purpose of the QC study was to monitor the laboratories and methodologies that contribute to the data base for these herbicides and, by so doing, establish the degree of confidence and comparability in the data upon which management decisions are made (e.g., regulatory control of atrazine in environmentally sensitive locales).

Methods. To provide the coextractives necessary as background for the sediment reference material in this study, 2.0 kg of freeze-dried sediment from Lake Erie and Lake St. Clair were crudely extracted with acetone. After filtering, the extract was fortified to approximately 1-5 µg/L with trifluralin, triallate, atrazine, alachlor, and metolachlor. 'Standard' solutions were also prepared at similar concentration ranges and sealed into glass ampules alongside the reference sediment extracts. Homogeneity of these materials was verified immediately and stability testing thereafter. For the interlaboratory QC study, 26 Canadian laboratories received sample sets consisting of two ampules of the sediment extracts, one 'blank' or unfortified sediment extract, and four different mixtures of the 'standard' solutions in ampules.

Results and Discussion. All objectives of this study were successfully completed. Homogeneity was confirmed between the ampules and stability of the five neutral herbicides of interest was verified for up to six months and is still being monitored. In all, close to 400 ampules containing the sediment extracts remain.

The quality control study using these sediment extracts was conducted under the auspices of the Canadian Association of Pesticide Control Officials (CAPCO) as the "1989 CAPCO Interlaboratory QC Study". Fifteen laboratories submitted results for the five neutral herbicides in the seven ampules. The interlaboratory medians from the submitted results agreed quite well with the design values for each herbicide, thereby offering support to the verification of the design values. Although there were a few

outlying results in this QC study, the majority of participants produced very good data. Thus it appears that one may place considerable confidence in the neutral herbicide data being generated by these same laboratories in their monitoring programs.

Publication Medium. None provided.

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general

6. EXPERT SYSTEM FOR ASSESSING THE FATE OF PESTICIDES IN THE SUBSURFACE - (A.S. Crowe and J.P. Mutch, NWRI)

Keywords. expert systems, computer simulation, groundwater contamination, pesticide regulatory assessment

Introduction. Numerous models currently exist for predicting the distribution and concentration of a pesticide in the subsurface. However, the application of these models in a regulatory framework is limited because 1) specialized knowledge is required in order to assess the transport and transformation of pesticides because they are governed by a complex set of chemical, biological, and physical processes; 2) the numerical framework upon which the models are based is generally complex and typically can only be operated by a trained modeller; and 3) the models require a specialized set of physical and chemical field data, which are not generally obtained during typical field studies.

Objective. The objective of this study is to develop an expert system that can provide regulatory personnel with a tool for evaluating the transport and transformation of pesticides in the subsurface environment in order to identify potential groundwater contamination problems. The purpose of the expert system is to provide a quick and general assessment of the potential hazards to the shallow groundwater regime associated with a particular pesticide, and to identify if further field or laboratory testing is warranted.

Results and Discussion. Specifically, the expert system known as EXPRES (Expert System for Pesticide Regulatory Evaluation Simulations) is designed to 1) choose a pesticide model based on the objective of a simulation and available data; 2) provide regulatory personnel with a method of obtaining the geological and hydrogeological data required for the models; 3) predict migration rates and concentrations of pesticides in the unsaturated zone with time and depth; 4) determine the concentration at, and the time required for, a pesticide to reach the water table; 5) be effectively used within a relatively short time by a user not trained in the use of pesticide transport models; 6) run quickly and efficiently on a personal computer; and 7) provide output that is useful and easily understood.

Two models have been chosen for EXPRES: a management model, PRZM, and a research model, LEACHM. The latter is included because the simulation of the processes involved in the transport and transformation of pesticides in the unsaturated zone makes this the preferred model when a detailed evaluation transport or transformation processes is desired. Both models simulate the transport of pesticide through the unsaturated zone only, which can be represented as a layered soil, and account for the major physical, chemical, and biological processes affecting the transport and degradation of pesticides in the unsaturated zone. A data base containing detailed descriptions of the physical, climatic, hydrogeological, and agricultural setting of typical agricultural zones across Canada is being developed.

Publication Medium. Crowe, A.S. and R.E. Jackson, An Expert System for Assessing the Migration and Transformation

of Pesticides in the Subsurface: A Project Proposal, NWRI proposal submitted to the Pesticides Division of CCB, EP/HQ (1989).

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Crowe, A.S. and J.P. Mutch, Assessing the Migration and Transformation of Pesticides in the Subsurface: The Role of Expert Systems, submitted to *Water Pollution Research Journal of Canada*.

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deltamethrin, fenitrothion

7. KINETICS OF PESTICIDE VOLATILIZATION FROM THE SURFACE OF WATER - (R.J. Maguire, NWRI)

Keywords. volatilization, surface microlayer

Introduction. Assessments of the importance of volatilization of chemicals from water are usually based on the assumption that they are uniformly distributed in subsurface water. However, some chemicals, such as pesticides, may be sprayed on water or drift to water, and volatilization will be faster from the surface of water than from subsurface water.

Volatilization from the surface microlayer was thought to be important in studies of the persistence of fenitrothion and deltamethrin in small ponds after direct aerial spraying. In these studies, the kinetics of clearance from the surface microlayer were biphasic first order, with half-lives of the fast and slow processes being of the order of minutes and hours, respectively. The fast process appeared to account for more than 90% of the loss of pesticide from water. It was hypothesized that the fast process was volatilization from the surface microlayer, while the slow process represented incorporation into subsurface water and/or chemical or photochemical reaction. Supporting evidence came from laboratory experiments that showed that the pesticides disappeared far faster from surface-sprayed water than from subsurface-injected water. In those experiments it was assumed that the kinetics of most processes would be similar in surface-sprayed water and subsurface-injected water, with the exception of volatilization. However, there were no direct measurements of volatilization. This work provides direct laboratory evidence of fast volatilization of fenitrothion and deltamethrin from the surface of sprayed water.

Methods. Experiments were performed to assess the rate of loss of fenitrothion and deltamethrin from surface-sprayed water samples and subsurface-injected water samples, and the rate of accumulation of the pesticides on air-sampling filters suspended above the solutions. Pesticide formulations were used typical of those sprayed in the field. Analyses of the subsurface-injected water samples included the parent insecticides and hydrolysis products in an effort to determine if hydrolysis was significant over the longer period that these samples were monitored.

Results and Discussion.

Fenitrothion

Fenitrothion sprayed on the surface of water disappeared very quickly. The kinetics were first order over 90% of the disappearance, with a half-life of about 0.5 h. Fenitrothion appeared in the air filters with a similar half-life. In an attempt to determine a mass balance for the air–water system, the amount of fenitrothion in the air filters was compared to the amount in water in all of the jars, the latter being calculated from the kinetics of disappearance from one set of jars extrapolated over all the jars in the system. An average of 65 ± 18% of the fenitrothion lost from water was accounted for by volatilization.

Fenitrothion injected into subsurface water disappeared far more slowly than that sprayed on the surface. The kinetics were

first order over 85% of the disappearance, with a half-life of about 58 d. A substantial fraction of the fenitrothion volatilized, as indicated by its appearance in the air filters with similar kinetics. On average about 51% of the loss of fenitrothion from water was accounted for by volatilization. Only minor amounts of p-nitro-m-cresol were found over the course of the experiments, never amounting to more than 5% of the starting material. Therefore it appeared that hydrolysis was a negligible pathway in either distilled water or azide-poisoned natural water. The lower recovery of fenitrothion in the air filters in this set of experiments may be due to physical losses of fenitrothion or a degradation pathway other than hydrolysis.

Deltamethrin

1-Deltamethrin in water in the dark isomerizes to 2prime-deltamethrin in addition to hydrolyzing. In the experiments reported here, no other isomers were produced. Consequently deltamethrin in the water and air samples is designated as (1+2′)-deltamethrin.

Deltamethrin sprayed on the surface of water also disappeared very quickly. The kinetics of disappearance of (1+2′)-deltamethrin were first order over 85% of the disappearance, with a half-life of about 2 h. Deltamethrin appeared in the air filters with a similar half-life. An average of 71 ± 11% of the (1+2′)-deltamethrin lost from water was accounted for by volatilization.

Deltamethrin injected into subsurface water disappeared far more slowly than that sprayed on the surface. The kinetics were first order over 90% of the disappearance, with a half-life of about 5 d. (1+2′)-Deltamethrin was found only sporadically in the air filters, and in small amounts. In no case did the amount of (1+2′)-deltamethrin found in the air filters exceed 3% of that initially present in the water. The disappearance of (1+2′)-deltamethrin from subsurface water was likely due to hydrolysis. The hydrolysis product cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DBCA) accounted for 60% of the loss of deltamethrin.

This work has confirmed that volatilization is the major pathway of dissipation for fenitrothion and deltamethrin formulations sprayed on the surface of water in laboratory experiments. In each case, about 70% of the pesticide lost from water was found on the air-sampling filters, and the half-lives of volatilization were 0.7–1.7 h, as shown by rates of appearance in air filters. These findings agree well with observations of the disappearance of each pesticide sprayed on ponds. Those field observations indicated that the faster of the two processes in the biphasic dissipation from the surface microlayer accounted for over 90% of the pesticide lost, and the half-life of the faster process was 0.3 h for fenitrothion and 0.1 h for deltamethrin. The similarity of the results observed in the field and the laboratory indicates that it is likely that volatilization is the single most important pathway of dissipation from water when these pesticides are sprayed on the surface of water in the field.

Publication Medium. Maguire, R.J., Kinetics of Pesticide Volatilization from the Surface of Water, submitted to the *Journal of Agricultural and Food Chemistry,* May 1991.

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tributyltin

8. DETERMINATION OF BUTYLTIN SPECIES IN SEWAGE AND SLUDGE -

(Y.K. Chau and R.J. Maguire, NWRI; and S. Zhang, Center for Eco-Environmental Sciences, Academia Sinica, Beijing, China)

Keywords. organotin, sewage, sludge

Introduction. Tributyltin (TBT) is one of the pesticides most toxic to aquatic organisms that has ever been developed, with 24- to 96-h LC_{50} values as low as 0.01–0.1 µg/L, depending on the species. The most significant mode of entry of TBT into aquatic environments is undoubtedly from its use as an antifouling agent in paint for boats, ships, and docks. This use has now been regulated in Canada under the *Pest Control Products Act.* However, TBT is still registered for use as a general slimicide (with contact use for low-volume applications, and with batch and continual introduction for large cooling towers) and as a general lumber preservative. An investigation to determine whether these registered uses account for any significant input of TBT to water in selected locations in Canada was proposed.

This proposal was prompted by recent evidence of substantial concentrations of TBT in sewage treatment plant influents in Switzerland. The Swiss results showed concentrations of TBT and its degradation products dibutyltin (DBT) and monobutyltin (MBT) of approximately 0.2 µg/L each in sewage treatment plant influent in Zurich (pop. 350 000). About 90% of each butyltin species in the influent was associated with suspended solids, and thus was removed in primary treatment. It was concluded that untreated sewage could give rise to TBT contamination of aquatic ecosystems, and that TBT from sewage sludge might be taken up by organisms if the sludge were used as fertilizer in agriculture or disposed of at sea (a Swiss option). It should be noted that although DBT and MBT are sequential degradation products of TBT, their presence in the Swiss samples could also have been due to their (nonpesticidal) uses as poly(vinyl chloride) stabilizers. DBT and MBT have similar uses in Canada. We proposed to determine TBT, DBT, and MBT concentrations in sewage treatment plant influents and effluents and in sewage sludge in several large Canadian cities to ascertain if presently registered uses of TBT have significant inputs to aquatic systems.

Methods. Sewage and sludge samples were acidified and shaken for two hours. The various butyltin species and leachable Sn(IV) are quantitatively extracted by tropolone in toluene, followed by ethylation to their tetraalkyl-substituted forms, $BuSnEt_3$, Bu_2SnEt_2, Bu_3SnEt, and Et_4Sn, all of which can be determined by gas chromatography–atomic absorption spectrophotometry. The nonpesticidal octyltin species can also be determined by this method. Detection limits expressed as Sn are 40 ng/L and 2 ng/g dry weight for sewage and sludge, respectively.

Results and Discussion. Results are reported for sewage treatment plants in two large Ontario cities and one smaller Ontario city with heavy chemical industry. For sewage treatment plant influent and effluent,

concentration ranges were as follows: TBT, n.d.; DBT, n.d. to 2.4 µg/L for influent and n.d. to 2.0 µg/L for effluent; MBT, 3.4 to 13.7 µg/L for influent and 1.3 to 9.5 µg/L for effluent; inorganic tin, n.d. to 27.5 µg/L for influent and n.d. to 9.2 µg/L for effluent. For sewage sludges, concentration ranges were as follows: TBT, n.d. to 280 µg/kg; DBT, n.d. to 210 µg/kg; MBT, n.d. to 440 µg/kg; inorganic tin, 5.8 to 193 µg/kg. This work is continuing to assess the degree of removal of these butyltin species in sewage treatment plants, and whether further work is warranted on the degradation and bioavailability of butyltin species in sludge.

Publication Medium. Chau, Y.K., S. Zhang, and R.J. Maguire, Determination of Butyltin Species in Sewage and Sludge, submitted to *Analytical Chemistry*, June 1991.

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atrazine, hexazinone, tebuthiuron, metolachlor

9. A METHOD TO DETERMINE THE SHORT-TERM EFFECTS OF HERBICIDES ON PRIMARY PRODUCTIVITY OF PERIPHYTON IN LOTIC ENVIRONMENTS - (K.E. Day, NWRI)

Keywords. periphyton, primary production

Introduction. Herbicides may enter running water ecosystems either by accidental overspray of the stream surface during aerial or ground application or through mobilization of chemicals during periods of significant precipitation. Such contamination may result in exposure of attached algal communities (i.e., the periphyton or epilithon) to higher concentrations of herbicides than ambient for very short periods of time (i.e., exposure to pulsed doses or peaks of residues). As these organisms contribute substantially to the biological cycling of elements, as well as provide food and habitat for a variety of higher trophic organisms (e.g., invertebrates and fish), any reduction in their productivity due to the effects of herbicides could be detrimental to the entire lotic ecosystem.

Objective. This study describes a method for determining the acute short-term effects of higher concentrations of herbicides on the photosynthetic activity of naturally attached epilithic communities under field conditions using measurements of oxygen production under light and dark conditions.

Methods. The effects of single concentrations of each herbicide were measured using a specially constructed portable bankside incubator with individual chambers with simulated current. For each experiment, 12 rocks with attached algal communities were selected from the riffle area of a stream located in southern Ontario and placed in the incubation chambers filled with stream water. Three light and three dark chambers were dosed with a preselected concentration of herbicide, and three light and three dark chambers remained as controls. Primary production was determined by measuring changes in oxygen production using a digital dissolved oxygen meter in each chamber and recorded as milligrams of oxygen per square metre per hour.

Results and Discussion. All three photosynthetic inhibitors (i.e., atrazine, hexazinone, and tebuthiuron) significantly reduced net primary productivity of periphyton at several of the higher concentrations used in experiments; hexazinone was the most toxic at concentrations as low as 50 µg/L, followed by atrazine (100 µg/L) and tebuthiuron (250 µg/L), respectively. These concentrations are well within the range of residues reported in surface runoff during storm events, particularly during the spring following initial application. Metolachlor did not significantly reduce photosynthetic activity at the highest concentrations tested (i.e., 280 µg/L). However, the specific mode of action of metolachlor is thought to be inhibition of protein synthesis, terpenoid synthesis, and mitotic activity. Therefore, it is not surprising that immediate effects on oxygen production were not observed.

The methodology represents a rapid, *in situ* technique to determine the immediate effects of photosynthetic inhibitors on natural periphytic communities. A decrease in functional activity such as photosynthesis

due to the detrimental effects of a herbicide may indicate more serious effects on community structure, although the risk of permanent damage may be somewhat dependent on the duration of exposure and the composition of the community. For example, the effects of higher concentrations or "pulses" of herbicides in lotic environments is likely transitory if exposure time is limited (<24 h); once exposure has ceased, nonlethal photosynthetic inhibition may be reversed. Further research will determine if the technique described could be modified to determine recovery of photosynthetic activity by returning rocks with attached algal communities to the stream environment and then monitoring oxygen production of the same epilithic community on subsequent days following exposure.

Publication Medium. This article will be submitted to either *Freshwater Biology* or *Environmental Toxicology and Chemistry*.

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atrazine, metolachlor, terbufos, fonofos

10. A COMPARISON OF THE EFFECTS OF AGRICULTURAL RUNOFF FROM CONVENTIONAL VERSUS CONSERVATION TILLAGE ON BIOTA

- (K.E. Day, NWRI; J. Struger and J. Fischer, WQB-NWRI; R. Sallenave, University of Guelph; and C. Merkely and D. Hayman, Upper Thames River Conservation Authority, London, Ontario)

Keywords. conservation tillage, agricultural runoff, primary production, secondary production

Introduction. Agricultural runoff is one of the main contributing factors to nonpoint sources of pollution in aquatic ecosystems. In recent years, reduced tillage and no-till agricultural management practices in both Canada and the United States have been on the increase. Such tillage practices have been termed conservation tillage and can be defined as any method that leaves at least 20–30% of the soil surface protected by crop residue. The advantages of conservation tillage are control of soil erosion due to reductions in surface runoff, reduced nutrient loadings to watersheds, increased efficiency of water use by crops, and decreased labour and energy costs.

Pesticides are known to enter into aquatic ecosystems either dissolved in water or sorbed to suspended particulate matter. Therefore, considerable interest in whether conservation tillage enhances or reduces the concentrations of pesticides in overland runoff has been expressed. It is likely that both situations exist depending on a combination of conditions, which include rainfall characteristics, the time interval between pesticide application and rainfall, properties of the pesticide, rates of application, soil texture and topography, and type and amount of ground cover. There have been few studies to determine the effects of conservation versus conventional tillage on the concentrations of pesticides in agricultural runoff under realistic field conditions. In addition, little information is available on the ecotoxicological effects of differing agricultural practices on aquatic ecosystems adjacent to agricultural land. There is also a need for techniques to monitor these effects in the field (i.e., *in situ* toxicity tests).

Objectives. The objectives of this research were 1) to monitor the concentrations of two herbicides, atrazine and metolachlor, in the ambient waters of two agricultural streams adjacent to land subjected to conservation versus conventional tillage especially during storm runoff events and 2) to compare the effects of such runoff on the primary and secondary producers of both watersheds.

Methods. The study site was located on the two branches of Kintore Creek, a tributary of the Thames River, which discharges into Lake St. Clair. The west branch of the watershed has 12 out of 15 farms involved in a conservation tillage program, whereas landowners in the east branch have continued to use conventional tillage practices (i.e., corn–alfalfa rotation tillage with fall moldboard ploughing, which leaves 1–15% surface residue).

The collection of the data in the two watersheds was as follows:

1) Artificial substrates for the attachment of periphyton in the form of unglazed ceramic tiles and acrylic rods were installed in the two watersheds during the 1988, 1989, and 1990 growing

seasons. Growth of periphyton on the substrates was monitored by periodic sampling for ash-free dry weight, chlorophyll *a*, and taxonomic composition by scraping a portion of the algal biomass from replicates.

2) Annual secondary productivities of the benthic invertebrate communities (caddisflies) were estimated from quantitative field samples (replicated Surber samples) collected at monthly intervals from May 1988 to July 1989 using the size-frequency method.

3) The collection of water samples for the determination of pesticide residues and nutrient analysis (total phosphorus, soluble reactive phosphorus, nitrites-nitrates, and suspended sediment) was conducted by Water Quality Branch, Ontario Region, Burlington, and the Upper Thames River Conservation Authority.

Results and Discussion. Concentrations of atrazine and metolachlor in the two watersheds were similar and low in the ambient water throughout the fall and winter. During the growing season, when such pesticides were actively applied, concentrations of atrazine were found to be significantly higher in ambient water samples taken from the conventional tillage watershed. In addition, higher concentrations of atrazine (up to 90 µg/L) were recorded in storm runoff events in this same watershed. However, comparisons of the growth of periphyton on artificial substrates in both watersheds did not indicate that this increased input of herbicides resulted in any reductions in algal growth.

Concentrations of two organophosphate insecticides (terbufos and fonofos) were also used more heavily in the conventional tillage watershed and, although no water samples were analyzed for these two chemicals, it is possible that peak residues could be entering the water during storm runoff events. Annual secondary production of four co-existing caddisfly species were consistently lower in the watershed where conventional tillage was practiced, and a greater use of insecticides in this watershed has been suggested as a possible reason for this reduction in productivity.

Publication Medium. Sallenave, R.M. and K.E. Day, Secondary Production of Benthic Stream Invertebrates in Agricultural Watersheds with Different Land Management Practices, *Chemosphere* (forthcoming).

Further papers are being prepared for submission to the *Journal of Environmental Science and Health.*

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atrazine, triazine

11. DEVELOPMENT OF SCREENING TECHNIQUES FOR THE DETECTION OF TRACE CONTAMINANTS IN ENVIRONMENTAL SAMPLES - (J.P. Sherry and A. Borgman, NWRI)

Keywords. Elisa immunoassay (EIA), immunoassay, screening technique

Introduction. Conventional methods for the analysis of trace organic contaminants in environmental samples are generally time-consuming and expensive. Often, many contaminant-free samples are extracted and cleaned up before being analyzed using GC or GC/MS. The inclusion of screening steps in analytical protocols would, by the elimination of contaminant-free samples from subsequent analysis, greatly reduce analytical costs. Samples that test positive using the screening assay would be confirmed and quantified using conventional methods. Of the available screening tests, immunoassays (IA) appear to offer the most promise.

Current research interests in this area at the National Water Research Institute (NWRI) include the development of a radio-immunoassay (RIA) for PCDDs and the determination of its performance characteristics with a variety of environmental matrices. Eventually it is hoped to have a battery of screening tests for the detection of a range of environmental contaminants. The s-triazine herbicides, in particular atrazine, and some of their degradation products are suitable candidates for detection using IAs. An atrazine IA would facilitate the monitoring of surface water and groundwater. Environmental samples usually require less cleanup for analysis by IA than by conventional analytical methods. Thus the proposed screening technique could expedite the inclusion of atrazine in surveillance or monitoring programs. The atrazine IA is proposed as a prescreening technique that would complement, not replace, conventional analytical methods. Samples that test positive using IA would have to be confirmed using conventional techniques. The IA could contribute to the cost-effective determination of the presence, levels, trends, and environmental impacts of atrazine in freshwater bodies.

Objectives. The objectives of this study were to 1) develop and validate an immunoassay screening technique for the detection of triazine herbicides in environmental water samples, and 2) develop a rapid sample preparation procedure to facilitate the analysis of large volume water samples using the Elisa immunoassay.

Methods. Anti-atrazine antibodies were procured in kit form from ImmunoSystems and Westinghouse Bioanalytic, both located in the United States. The kits were evaluated to determine their suitability. The Westinghouse assay system required further in-house development and optimization (completed). The ImmunoSystems system required minor modifications.

The ImmunoSystems assay is tube based. Anti-atrazine antibodies are bound to the walls of plastic tubes. Both an analyte-enzyme (horseradish peroxidase) conjugate and the sample, which may contain atrazine, are added to the tube. During a five-minute incubation period,

atrazine and atrazine-enzyme compete for antibody binding sites. The sample is then rinsed from the tube. Next, substrate and chromogen are added to the tube. The antibody-bound enzyme converts the substrate to a compound, which in turn causes the chromogen to turn blue. The lighter the colour, the more atrazine is present in the sample. The tubes may be read visually, or a 500-µL portion can be transferred to a micro-well and measured spectrophotometrically.

The Westinghouse assay is micro-titre plate based (96-well plates). Protein-linked atrazine is bound to the walls of the micro-wells. Antiserum and sample are added to the wells and incubated; during this incubation period, the antibodies bind to the immobilized atrazine; binding is inhibited by free atrazine in the sample. Free antibodies and sample are then washed from the wells. In the next step, anti-rabbit gamma globulin antibodies tagged with alkaline phosphatase are added to the wells, and the plates are again incubated. After rinsing free enzyme from the wells, substrate is added to the wells; substrate conversion is determined spectrophotometrically using a micro-plate reader.

A micro-titre plate version of the ImmunoSystems assay, which is based on immobilized antibodies, was also evaluated.

Results and Discussion. The objectives have been met. The IAs for atrazine and related triazine herbicides have been modified and validated using samples from the aquatic environment. The routine laboratories at CCIW, if they so wish, now have the capability to process about 400 samples a week rather than their previous rate of about 10.

With the ImmunoSystems tube assay system it was possible to detect 0.1 µg/L of atrazine using a ten-minute test, without sample extraction or cleanup. Some problems concerning assay variability were investigated and resolved. The assay was integrated with a conventional extraction and cleanup procedure, which lowered the detection limit to the pg/L level.

The Westinghouse assay system was optimized for antiserum titre, coating antigen level, second antibody titre, and incubation time. Further evaluation of the Westinghouse and ImmunoSystems kits was undertaken in four stages: 1) assay performance using analytical standards; 2) assay performance using spiked lake and river water; 3) assay performance using spiked extracts of lake and river water; and 4) assay performance using a variety of triazine-contaminated environmental water samples; these samples are also being analyzed using the conventional method. IWD Ontario Region and NWQL participated in this evaluation.

Because of the lack of realistic support, part of the study was undertaken with the help of a volunteer research assistant.

With the micro-plate version of the ImmunoSystems assay, a detection limit of 12.5 ng/L was achieved without difficulty. An excellent dose response was achieved between 12.5 and 50 ng/L. A 15 sample set of environmental water samples was also analyzed. The samples were from a variety of locations and contained various levels of atrazine. Good agreement was observed between the IA and GC results (correlation coefficient of 0.94).

Further tests are planned with this system. The results of this study were provided to

ImmunoSystems Inc. to assist them with product development.

The IA for triazines is ready for routine use and is being transferred to IWD Ontario Region.

A rapid sample preparation technique was developed and partially validated. A more complete validation of this method is planned to complement the screening assay in the future. Personnel is the limiting factor. Lack of technical support has continued to delay this portion of the study through 1991.

Publication Medium. Results of this work were presented at the BIOQUAL '88 workshop and at the NWRI (DOE)/ Laboratory Services Branch (MOE) Method Development Seminar '89. A manuscript describing the results of this study is in preparation and will be submitted to a scientific journal.

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aldrin, alpha-*BHC*, beta-*BHC*, alpha-*lindane* (gamma-*BHC*), alpha-*chlordane*, gamma-*chlordane*, *p,p'-DDD*, *p,p'-DDE*, *o,p'-DDT*, *p,p'-DDT*, *dieldren*, alpha-*endosulfan*, beta-*endosulfan*, *endrin*, *heptachlor*, *heptachlor epoxide*, *p,p'-methoxychlor*, *mirex*

12. FEDERAL INTERDEPARTMENTAL QUALITY ASSURANCE ON PESTICIDE ANALYSIS - (Y.D. Stokker, NWRI)

Keywords. reference materials, sediment extracts, quality control, quality assurance, CAPCO, organochlorinated insecticides

Introduction. Reference sample extracts are extremely useful materials in both intra- and interlaboratory QA/QC, as well as for method validation and research. The availabilty of such reference materials along with suitable standard solutions in ampules could reduce the cost and increase the effectiveness of laboratory quality control and analysis in monitoring and surveillance programs. This study undertook to produce some unique reference materials in the form of sediment extracts in ampules for lindane, endosulfan, methoxychlor, and other organochlorinated insecticides of concern. The design values, homogeneity, and stability of these pesticides were confirmed by both in-house analyses as well as in an interlaboratory QC study.

Objectives. The objectives of this study were 1) to generate the reference extracts in ampules, 2) to verify the design values and monitor the homogeneity and stability of these samples, and 3) to conduct one interlaboratory QC study on the analysis of OCs in the sediment extracts. The purpose of the QC study was to monitor the laboratories and methodologies that contribute to the data base for these pesticides and, by so doing, establish the degree of confidence and comparability in the data upon which management decisions are made (e.g., regulatory control of lindane in environmentally sensitive locales).

Methods. To provide the coextractives necessary as background for the sediment reference material in this study, 2.4 kg of freeze-dried sediment from Lake Erie and Lake St. Clair were crudely extracted with acetone. After filtering, the extract was fortified to approximately 50 to 300 µg/L with 18 OCs, including lindane, alpha-endosulfan, beta-endosulfan, and p,p'-methoxychlor. 'Standard' solutions were also prepared at similar concentration ranges and sealed into glass ampules alongside the reference sediment extracts. Homogeneity of these materials was verified immediately, while stability testing is continuing. For the interlaboratory QC study, 45 Canadian laboratories received sample sets consisting of two ampules of the sediment extracts, one 'blank' or unfortified sediment extract, and four different mixtures of the 'standard' solutions in ampules.

Results and Discussion. All objectives of this study were successfully completed. Homogeneity was confirmed between the ampules and stability of the 18 OCs of interest was verified for up to six months and is still being monitored. In all, close to 300 ampules containing the sediment extracts remain.

The quality control study using these sediment extracts was conducted under the auspices of the Canadian Association of Pesticide Control Officials (CAPCO) as the "1990 CAPCO Interlaboratory QC Study". Thirty-four laboratories submitted results for the 18 OCs in the seven ampules. The

interlaboratory medians from the submitted results agreed quite well with the design values for each pesticide, thereby offering support to the verification of the design values. Although there were a few outlying results and some relatively high blank values for certain participants in this QC study, the majority of laboratories produced very good data. Thus it appears that one may place considerable confidence in the organochlorinated insecticide data being generated by these same laboratories in their monitoring programs.

Publication Medium. None provided.

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general

13. EXPERT SYSTEM FOR ASSESSING THE FATE OF PESTICIDES IN THE SUBSURFACE - (A.S. Crowe and J.P. Mutch, NWRI)

Keywords. expert systems, computer simulation, groundwater contamination, pesticide regulatory assessment

Introduction. Currently, regulatory personnel who are required to assess the potential for pesticides to contaminate groundwater do not have the technical expertise to use the complex numerical models designed to simulate the migration and transformation of pesticides within the subsurface. An expert system known as EXPRES is being developed to aid regulatory personnel with their assessment of the potential for pesticides to contaminate groundwater.

Objectives. The objective of this expert system is to provide the Pesticides Division, Environment Canada, with the capability of simulating the transport and transformation of pesticides in the subsurface by providing all the necessary hydrogeological and modelling knowledge required to undertake these simulations. Specifically, the expert system will aid in the registration of pesticides.

Results and Discussion. The development of the expert system has been an ongoing task. Specific tasks completed during 1990–91 included 1) Phase 2: the incorporation of two pesticide transport models (LEACHM and PRZM) into the knowledge-based system; 2) Phase 3: the construction of a data base of the chemical characteristics of a pesticide aldicarb) and a second data base of values that characterize the physical, pedological, hydrological, and meteorological settings, as well as the agricultural practices of a potato-growing region in Prince Edward Island that was used to test and verify the operation of the expert system; 3) Phase 4: the verification and validation of EXPRES and the modified pesticide transport codes (LEACHM and PRZM) within EXPRES; 4) the finalization of the user-system "help" module (part of Phase 6); 5) finalization of the user-system interface or "screens" (part of Phase 6); and 6) approximately 75% of the data base characterizing the agricultural zones (Phase 5). Also, during 1990–91, a working, but prototype, version of EXPRES was submitted to the staff of the Pesticides Division for their examination of the applicability and suitability of EXPRES for their use.

Publication Medium. Crowe, A.S. and J.P. Mutch, EXPRES: An Expert System for Assessing the Fate of Pesticides in the Subsurface, *Environ. Monit. Assess.* (forthcoming).

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cresols, monochlorophenols, dichlorophenols, trichlorophenols, tetrachlorophenols, pentachlorophenol

14. BIODEGRADATION AND TOXICITY ASSESSMENT OF PESTICIDES - (D. Liu, R.J. Maguire, Y.K. Chau, B.J. Dutka, and G.J. Pacepavicius, NWRI)

Keywords. bacterial culture, resazurin reduction method, cyclone fermentor system

Introduction. Biodegradation is one of the major processes for the elimination of a contaminant from the aquatic ecosystem. Toxicity assessment, on the other hand, is one of the few important parameters commonly used in the characterization of a chemical's behaviour in the environment. The fate and impact of a pesticide on the environment usually can be approximated from the analysis of its biodegradability and toxicity data.

Objectives. The objectives of this study were 1) to systematically investigate microbial degradation of priority pesticides under a well-controlled laboratory environment and 2) to assess the microbial toxicity of pesticides. The biodegradability and toxicity of a pesticide formulation were also studied.

Methods. The biodegradation experiments were conducted in the cyclone fermentor system under both aerobic and anaerobic conditions. The toxicity of a pesticide to microorganisms was estimated at the population (agar plate method) and the enzyme level (dehydrogenase activity).

Results and Discussion. Aerobic and anaerobic biodegradation processes for 18 chlorophenols and 3 cresols were evaluated using an acclimatized mixed culture of pentachlorophenol-degrading bacteria. The results indicate that nonspecific generalization, such as the degree of a chemical's chlorination, cannot be reliably used to predict the persistence of chemicals in the environment. However, the position of chlorine substitution on the phenolic ring appears to be more useful in predicting the environmental fate of existing and new chemicals.

The potential of using the co-metabolic technique to degrade stable pesticides was demonstrated using three persistent chlorophenols. Studies are in progress to check the ultimate potential of this new technique in accelerating the biodegradation of other stable pesticides such as 2,4,5-T.

Publication Medium. Liu, D., "Assessment of the Interaction between Microorganism and Chemical Mixture Using Resazurin Reduction", *Toxic. Assess., 4:* 463–471 (1989).

Liu, D. and G. Pacepavicius, "A Systematic Study of the Aerobic and Anaerobic Biodegradation of 18 Chlorophenols and 3 Cresols", *Toxic. Assess., 5:* 367–387 (1990).

Liu, D., R.J. Maguire, G. Pacepavicius, and B.J. Dutka, "Biodegradation of Recalcitrant Chlorophenols by Co-metabolism", *Toxic. Assess., 6:* 85–95 (1990).

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TCMTB, MBT

15. AQUATIC ENVIRONMENTAL CHEMISTRY OF 2-(THIOCYANOMETHYLTHIO)-BENZOTHIAZOLE AND RELATED BENZOTHIAZOLES - (J.H. Carey, and B.G. Brownlee, NWRI)

Keywords. anti-sapstain chemical, photolysis

Introduction. Previous work supported by PESTFUND in 1988–89 and 1989–90 concentrated on the environmental dynamics of 2-(thiocyanomethylthio)benzothiazole (TCMTB), which is a replacement for chlorinated phenols as an anti-sapstain agent in the lumber industry in British Columbia. Further laboratory studies on 2-mercaptobenzothiazole (MBT) photolysis were the focus of our A-base funded 1990–91 studies.

Objectives. The objectives of the study were to 1) predict the rates of disappearance by sunlight photolysis of TCMTB and its primary photoproduct, MBT, under conditions typical of receiving waters in southern Canada; 2) identify photolytic degradation products of MBT; and 3) develop a unified pathway for the fate of TCMTB, MBT, and related benzothiazoles in aquatic environments.

Methods. Laboratory studies in 1990–91 concentrated on quantitative measurements of sunlight photolysis rates for MBT and identification of products.

Results and Discussion. Sunlight quantum yields of 0.01 and 0.002 were estimated for TCMTB and MBT, respectively. Using these values, sunlight photolysis half-lives were calculated for TCMTB and MBT. Sunlight photolysis of MBT gave two identifiable products: benzothiazole and 2-hydroxybenzothiazole in 30 to 50% and 4 to 5% yields, respectively. On the basis of our results and literature reports on benzothiazoles, a pathway for the fate of TCMTB and MBT in aquatic environments has been proposed.

Publication Medium. This work is being published as NWRI Contribution #91-62, and a manuscript has been submitted to *Environmental Toxicology and Chemistry.*

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chlorothalonil

16. FUNGICIDE USE OPTIMIZATION ON FIELD TOMATOES AND ITS RELATIONSHIP WITH CLIMATIC VARIABILITY

- (B. Srivastava, AES-Ontario Region; T.J. Gillespie, University of Guelph; and R.E. Pitblado, Ontario Ministry of Agriculture and Food)

Keywords. Ridgetown, Ontario, Essex and Kent counties, agrometeorological index, tomato spray schedules

Introduction. A multidisciplinary/ multiagency project conducted in Essex and Kent counties has developed a weather-based fungicide management scheme for tomato disease control with minimized environmental threat. The scheme has the potential to change the use patterns of fungicides by the growers so as to maintain disease control while minimizing the number of sprays required.

Objectives. The specific objectives were 1) to ensure good quality maximum and minimum temperature observations at sites by providing good radiation shields, 2) to improve the models and test their effectiveness and to evaluate the accuracy and robustness for climatic variability, and 3) to compare results on control plots for different models

Results and Discussion. Good quality data were collected at eight sites in the 1990 growing season. The analysis included the transferability of temperature/dewpoint criteria from one growing season to the other. It was found that the improved daily model performed as well as the hourly model and with a scheme of calibration from a master site in each county, the agrometeorological index that computes the disease severity index (DSI) and spray schedules could be made robust enough to account for the year-to-year climatic variability. Field experiments on control plots were conducted.

Publication Medium. Srivastava, B., R.E. Pitblado, and T.J. Gillespie, Development of an Agrometeorological Index for Fungicide Use on Field Tomatoes Using Standard Meteorological Data, paper presented at the Canadian Society of Agrometeorology Symposium, 70th Annual Conference of the Agricultural Institute of Canada, Penticton, B.C., July 22–26, 1990.

Srivastava, B., T.J. Gillespie, and R.E. Pitblado, Coping with Growing Season Climate Variability in a Weather-based Plant Disease Prediction for Tomatoes, paper presented at the ECA/CSAM/AIC Symposium on Changing Climate in Relation to Sustainable Agriculture, July 29–30, 1991, Fredericton, New Brunswick.

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atrazine, metolachlor

17. ATRAZINE AND METOLACHLOR IN AGRICULTURAL RUNOFF FROM A PAIRED WATERSHED UNDERGOING CONSERVATION TILLAGE - (J. Struger and J. Fischer, WQB-Ontario Region; and Upper Thames River Conservation Authority)

Keywords. runoff, streams, paired watershed, pesticide loadings, conservation tillage, storm event sampling, continuous flow proportional sampler, pesticide questionnaire

Introduction. Contamination of surface runoff with pesticide residues is a problem in many areas of agricultural activity in North America. Large amounts of atrazine and metolachlor are used in the production of corn and soybeans in southern Ontario, especially in the Thames River watershed. The Water Quality Branch (WQB), Ontario Region, in co-operation with the Upper Thames River Conservation Authority (UTRCA), undertook a study to determine the potential for harm of neutral herbicides in surface water from a small paired watershed in Kintore Creek near Thamesford, Ontario.

Objective. The major objective of this study is to monitor and compare the concentrations of herbicides in agricultural runoff from conservation versus conventional tillage practices in a paired watershed. The project will also link up with another project by K. Day of the National Water Research Institute that is attempting to describe the ecotoxicological effects of agricultural runoff on stream biota, as well as primary and secondary productivity.

Methods. The streams were sampled in three ways: 1) at regular two-week intervals, 2) during periods of rain when the stream discharge was increasing, and 3) on a continuous flow proportional basis. Water samples were collected with an Isco automatic water sampler (Model #2700) fitted with glass sample bottles. Events were monitored at eight sampling intervals during a ten-hour period. The water samples were analyzed for seven neutral herbicides. Flow proportional continuous samplers were installed in both watersheds to estimate loadings. Other information was also collected, including other chemical constituents and water flow. Sediment samples were collected and analyzed for neutral herbicides and organochlorine pesticides.

A pesticide usage questionnaire was completed by each landowner in the watershed, which documented field crops and the types of pesticides used.

A fisheries assessement and an aquatic macrophyte survey were carried out on both watersheds by the Ontario Ministry of Natural Resources, UTRCA, and WQB.

Results and Discussion. Preliminary results from 1989 indicate that atrazine concentrations in the continuous flow proportional samples were consistently higher from the watershed undergoing conventional tillage than from the watershed undergoing conservation tillage. For the most part, this occurred during the precipitation events as well. During the event on June 22, concentrations of 90.0 µg/L of atrazine were found in the conventional till watershed, while the highest concentration in the conservation till watershed was 12.9 µg/L. Biweekly water

samples collected from both watersheds indicated significant carryover of atrazine from the previous growing season, confirming that atrazine does not degrade completely from one year to the next. Grab samples from a catch-basin associated with a tile drain indicated subsurface movement and/or groundwater flow of atrazine during low precipitation periods. Metolachlor concentrations were generally low or nondetectable in many of the samples, and were lower in the conservation till watershed than the conventional till watershed.

Twenty-two different pesticides (primarily herbicides) were used in the watersheds. Pesticide application rates, field acreages, and crop information were also documented.

Publication Medium. A poster was presented at the 1989 Society of Environmental Toxicology and Chemistry meeting in Toronto. A written summary of the poster is available.

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azinphos-methyl, diazinon

18. ORGANOPHOSPHORUS PESTICIDES IN SURFACE WATERS OF THE NIAGARA PENINSULA - (J. Struger and D. Johnson, WQB-Ontario Region)

Keywords. organophosphorus insecticides, Niagara Peninsula, streams, fruit crops

Introduction. Large amounts of organophosphorus (OP) pesticides are used throughout the fruit belt of the Niagara Peninsula to control pests in the production of apples, cherries, peaches, and grapes. During the course of a growing season, up to 12 pesticide applications can occur. There is very little information on the fate of OPs in surface waters. Sampling activities were coordinated with a Canadian Wildlife Service PESTFUND project investigating the biological effects of OPs on nesting songbirds in orchards.

Objective. The Water Quality Branch, Ontario Region, undertook a study to determine the presence of organophosphorous pesticides in surface waters of the fruit-growing region of the Niagara Peninsula.

Methods. A total of five sampling sites, including four creek sites and one tile-drain site, were selected representing different types of fruit assemblages. The sampling was initiated in early May and continued on a biweekly basis up until September. Water samples were analyzed for 14 OP pesticides. Sediment samples were also collected and analyzed for organochlorine pesticides to determine past organochlorine pesticide use. Six large-volume (4-L) samples were collected from a site with a known spraying history. These samples will be submitted for GC/MS investigative screening scans for OP pesticide confirmation.

Results and Discussion. Initial results from this field season indicate that azinphos-methyl (Guthion) and diazinon are present in surface waters. Guthion was detected in seven out of 50 samples and the maximum concentration was 2.92 µg/L. Diazinon was detected in four out of 50 samples and the maximum concentration was 3.53 µg/L. Six out of the 11 Guthion and diazinon detections occurred at the same site. The GC/MS investigative screening scan results were unavailable.

Publication Medium. None provided.

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atrazine, metolachlor

19. PESTICIDE CONTAMINATION IN REGIONALLY SIGNIFICANT WETLANDS IN SOUTHERN ONTARIO - (J. Struger and J. Merriman, WQB-Ontario Region; CWS; and Ontario Ministry of Natural Resources)

Keywords. wetlands, Rondeau Harbour, Long Point

Introduction. Some wetlands situated in watersheds with agricultural row crops (corn and soybeans) are subject to inputs of agricultural pesticides (primarily herbicides, atrazine and metolachlor). A joint Water Quality Branch–Lands project completed in 1988–89 identified three wetland areas in southern Ontario subject to high pesticide use.

Objectives. In 1989–90, the Water Quality Branch, Ontario Region, in conjunction with the Canadian Wildlife Service (CWS) and the Ontario Ministry of Natural Resources (OMNR), undertook a study to determine the presence of atrazine and metolachlor in wetlands associated with the Big Creek National Wildlife Area (BCNWA) near Long Point/Port Rowan and Rondeau Harbour near Blenheim, Ontario.

Methods. Two sampling sites in the Big Creek National Wildlife Area were selected. One location was inside the marsh proper, while the other site was an impoundment cell. Three small agricultural watersheds with associated estuary wetlands were sampled in Rondeau Harbour. Water samples were collected on a biweekly basis from May until September and during runoff events.

Results and Discussion. Water samples were collected on approximately ten sampling surveys from both locations. atrazine and metolachlor concentrations were very low (<1 µg/L) in the BCNWA and consistently greater in the open marsh than in the impoundment cell. atrazine and metolachlor concentrations were >1 µg/L in the three creeks from Rondeau on the first two sampling surveys (June 23 and July 11). After a precipitation event on June 23, atrazine concentrations in Indian Creek were 17.0 µg/L, while metolachlor concentrations were 9.6 µg/L. From July 26 on, 95% of the Rondeau samples were below the detection limit for atrazine and metolachlor.

Publication Medium. None provided.

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2,4-D, atrazine, metolachlor

20. HERBICIDES IN BIG CREEK - (J. Merriman and J. Struger, WQB-Ontario Region)

Keywords. Big Creek, tobacco, surface water, groundwater

Introduction. Big Creek is located in a mixed agricultural area in southwestern Ontario that is dominated by tobacco production. There is extensive use of herbicides in the watershed, which extends from north of Delhi, at the upstream end, to its mouth, where it empties into Long Point Marsh. The Big Creek basin has an area of approximately 728 km^2 and a length of 56 km.

Objectives. In 1989, the Water Quality Branch, Ontario Region, undertook a pilot study to evaluate the presence/absence of herbicides in both surface water and groundwater in the Big Creek watershed. The main objective of the study was to determine concentrations and spatial distribution of herbicides, and from the results of the pilot study and other land use information, design an ongoing monitoring program for the basin.

Methods. Eight sampling sites (five surface water and three groundwater) were selected in the Big Creek watershed for monitoring. The sampling commenced in April 1989 at a sampling frequency of every two weeks until October. One-litre samples were collected in precleaned glass bottles and analyzed for base-neutral and phenoxy acid herbicides. The phenoxy acid herbicides were preserved on site with sulfuric acid. Detection limits ranged from 0.005 to 0.1 µg/L for the neutral herbicides and from 0.03 to 0.05 µg/L for the acid herbicides.

Results and Discussion. Preliminary analysis of the data indicates that phenoxy acid herbicides are present in trace amounts. All detections were at or slightly above the analytical detection limits, with the exception of one sample. On June 27, 2,4-D was detected at one station near the bottom end of Big Creek at a concentration of 0.11 µg/L. This sampling date was after a storm event and the water was very turbid, which may explain the higher than usual value. All detections of 2,4-D were well below the freshwater aquatic life guideline of 4 µg/L.

Base neutral herbicides, namely atrazine and metolachlor, were detected regularly throughout the study, with atrazine being detected almost three times as often as metolachlor. Concentrations were for the most part below 1 µg/L, except for the survey completed on June 27. atrazine was found at concentrations as high as 19.3 µg/L, while metolachlor was detected as high as 3.5 µg/L. Levels of atrazine found during this survey exceed the freshwater aquatic life guideline of 2 µg/L, while the highest metolachlor concentrations detected were below the interim freshwater aquatic life guideline of 8 µg/L.

Based on these preliminary results, it appears as though phenoxy acid herbicides do not pose a problem in the Big Creek watershed. Future monitoring will address base neutral herbicides that have been shown to exceed suggested freshwater aquatic life guidelines.

Publication Medium. None provided.

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1,3-D, 1,2-D

21. NEMATOCIDES IN SURFACE WATERS AND GROUNDWATERS OF THE BIG CREEK WATERSHED - (J. Merriman and J. Struger, WQB-Ontario Region)

Keywords. nematocides, surface water, groundwater, Big Creek, fumigants

Introduction. Big Creek flows through Ontario's major tobacco-producing belt in the southwestern part of the province. The area is characterized by sandy soils with low water-holding capacity.

Soil fumigants are used for the control of nematodes and black root rot, which stunt tobacco growth. Fumigants are injected into the soil at a depth of about 15 cm in the spring, approximately two weeks before planting. The compound of interest, 1,3-dichloropropene (1,3-D), is composed of a cis-and trans-isomer, has a relatively high water solubility, and is moderately toxic to aquatic life. 1,2-Dichloropropane (1,2-D) is present in small quantities as a manufacturing by-product.

Data provided by the Ontario Ministry of Agriculture and Food indicate that in 1988, 677 370 kg of 1,3-D were applied to 16 300 ha, which represents a reduction of about 50% from 1983 statistics. On a Canada-wide basis, 1,3-D sales totalled 1 441 823 kg in 1987, of which 98% of sales were in Ontario.

Objectives. In 1989, the Water Quality Branch, Ontario Region, undertook a study to determine the presence/absence of 1,3-dichloropropene and 1,2-dichloropropane in the Big Creek watershed. Because of the highly volatile nature of these compounds, it was not known whether they would be present in surface waters or groundwaters. The primary objective of the study was to determine environmental concentrations and spatial distribution of the compounds and to relate this to other land use information so that an ongoing monitoring plan for the watershed could be developed. This project also provided data on environmental concentrations in waters that could be useful to Agriculture Canada in its reevaluation of registered pesticide products.

Methods. Samples were obtained at seven locations, consisting of four surface water and three groundwater sites. Water was collected in 40-mL glass bottles with Teflon septa and analyzed using a purge and trap technique. Weekly sampling began in late April before application of 1,3-dichloropropene and 1,2-dichloropropane and increased to twice weekly sampling during the application period in the area, which was around the second and third weeks of May. This continued until the third week in May when weekly sampling was recommenced until mid-June. This was followed by one collection in July. Sampling was carried out over a variety of climatic conditions, including dry periods and during and after rain events. One duplicate sample was collected during each sampling run.

Results and Discussion. Over the sampling period, 1,2-dichloropropane was not detected in any of the samples above the detection limit of 0.16 µg/L. This is not surprising, considering it is only a manufacturing by-product of 1,3-dichloropropene and is present in very low concentrations in the formulation.

The active ingredient, 1,3-dichloropropene, which includes both cis- and trans-isomers, was found to be present at four of the seven sites sampled. This compound was found only at the surface water stations and was not found above the detection level at any of the groundwater sites. Concentrations ranged from 0.15 to 4.12 µg/L for 1,3-dichloropropene (total cis- and trans-). The detection limits are 0.12 and 0.14 µg/L for cis- and trans- 1,3-dichloropropene, respectively.

All detectable concentrations of 1,3-dichloropropene occurred either during or very shortly after application of the soil fumigants. There were no detectable levels found after the May 18 survey, which suggests that 1,3-D is not very persistent in surface waters.

Concentrations of 1,3-dichloropropene tended to be higher at the upstream sites, which were located in smaller tributaries of Big Creek and adjacent to tobacco crops, compared to the downstream station, which was located outside of the tobacco-growing area but still influenced by it.

The results of this pilot study show that soil fumigants can be detected in river water if sampled in a timely manner. The compounds of interest do not remain in the aquatic environment for very long periods. Further work is required to establish a monitoring program for the watershed, with the possibility of looking for other active ingredients in soil fumigants.

Publication Medium. None provided.

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PESTICIDES PROGRAM IN THE WESTERN AND NORTHERN REGION
(Alberta, Saskatchewan, Manitoba, Northwest Territories)

carbofuran

1. EFFECTS OF CARBOFURAN ON BEHAVIOUR AND SURVIVAL OF MALLARD DUCKLINGS - (D.J. Forsyth, CWS, Saskatoon; and P. Martin, University of Guelph)

Keywords. Manitoba, mallard ducklings, approach-response, cholinesterase

Introduction. Ducklings of the dabbling species, such as Mallards, must be led by brood hens from nest sites in upland habitat to a suitable wetland within 48 hours of hatching. This overland journey varies from about 5 to 500 m through remnants of prairie habitat, cropland, rights-of-way, or pasture, any of which may be sprayed with carbofuran for grasshopper control. Spraying for grasshopper control takes place from early June through mid-July, which overlaps with the peak hatching period of mallards and pintails in June. Spraying for alfalfa weevil takes place during mid-June through early July. Carbofuran is extremely toxic to waterfowl, and ducklings are probably more sensitive than adults because of their small size.

Objective. The objective of this study was to determine the effects on mallard duckling survival and brood cohesiveness of walking increasing distances through prairie grassland sprayed with carbofuran at the rates registered for control of grasshoppers and alfalfa weevils.

Methods. Mallard ducklings 24–36 hours old were led, after imprinting on technicians, through carbofuran-sprayed vegetation over distances of 50, 150, and 300 m. Spray rates of 132 g a.i./ha (grasshopper control) and 264 g a.i./ha (alfalfa weevil control) were tested. Ducklings were allowed to swim for 5 minutes immediately following exposure, then 8 of the 15 test birds per group were selected for testing of their approach-response behaviour. The stimuli used in these tests were a group of five ducklings caged at the end of a runway plus a recording of a simulated hen vocalization. Samples of blood and whole brains were collected from ducklings within 15 minutes of behavioural testing and frozen in liquid nitrogen for cholinesterase analysis. Sprayed vegetation and deposit samplers were analyzed for carbofuran residues.

Results and Discussion. No mortality occurred from exposure of ducklings to the sprayed vegetation, but symptoms of poisoning were observed among some birds exposed to 300 m of the 132-g/ha treatment and by some birds in each exposure-distance group of the 264-g/ha treatment. There was a significant dose-related slowing of response to the behavioural stimuli, and brain cholinesterase activity was 82 and 64% of control in birds exposed to 150 and 300 m of vegetation sprayed at 132 g/ha. Brain cholinesterase activity of birds exposed to 50, 150, and 300 m of the 264-g/ha treatment was 70, 46, and 29% control, respectively. Growth of ducklings was not affected in a dose-related manner during four weeks after treatment.

Reductions in brain cholinesterase activity and retarded response of ducklings to the stimuli of brood cohesiveness could decrease their ability to walk from nest sites to water over distances greater than 300 m and might increase susceptibility to predation. A field-scale study of mallard brood survival with brood hens, following exposure to sprayed vegetation, is needed to provide data

about the potential impact of carbofuran spray programs.

Publication Medium. To be submitted to *Environmental Toxicology and Chemistry*.

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dimethoate, carbofuran, deltamethrin, trichlorfon

2. ALFALFA IN THE PRAIRIE PROVINCES: DISTRIBUTION, INSECT PEST CONTROL, AND ATTRACTIVENESS TO BIRDS - (D.J. Forsyth, CWS, Saskatoon)

Keywords. alfalfa, insecticides, nesting habitat, prairies

Introduction. Alfalfa is attractive to some species of migratory birds as cover for nesting or foraging. The extent to which it is sprayed for insect control, its attractiveness as cover for birds, and its availability as habitat in the prairie provinces have not been documented; hence, the potential for insecticide use on alfalfa to adversely affect migratory birds is difficult to assess.

Objective. The objective of this study was to determine the geographic distribution of alfalfa grown for seed and forage in the prairies, the size of fields, the insecticides sprayed, and the use of alfalfa by birds.

Methods. Alfalfa producers in the three prairie provinces were surveyed by telephone to obtain information about acreage of alfalfa grown as a seed crop and as hay, insect problems encountered and insecticides used, and wetlands and wildlife in these crops. Published and unpublished literature was reviewed for information about insect control practices and use of alfalfa by wildlife.

Results and Discussion. There were 9634 ha of alfalfa grown for seed in 1988 by 104 producers surveyed in Saskatchewan; however, some producers were missed by the survey. Statistics of Saskatchewan Agriculture indicated that 14 164 ha of alfalfa were grown for seed in 1987.

There were 7813 ha of alfalfa seed crops sprayed for insect control in 1988 according to the surveyed producers. The Lygus bug and the alfalfa plant bug were the most serious pests, and the insecticides used most often were deltamethrin and dimethoate. Carbofuran was not used by any surveyed producers in Saskatchewan in 1988. Approximately 55% of the application of insecticide was made by aircraft. Fifty-one of the surveyed producers grew 3927 ha of alfalfa hay in 1988, and all reported that hay is not sprayed for insects.

In Alberta, only 22 producers sprayed. Total area planted to alfalfa for seed in 1987 was estimated to be 2560 ha by Alberta Agriculture. The insect pests that were sprayed in 1988 were the Lygus beg and the alfalfa weevil. Trichlorfon and deltamethrin were used on over 70% of the crops in the survey. Aerial application accounted for 90% of spraying. Carbofuran was used only to a minor extent in 1988, but it had been used extensively in previous years and was considered to be as effective as, and cheaper than, deltamethrin. Fifteen of the producers grew alfalfa for hay, primarily on irrigated land, and several reported that they had sprayed hay in the past for control of aphids or alfalfa weevils.

Eight Manitoba producers were surveyed. They grew alfalfa for seed on 590 ha, and all of them sprayed their crops at least once in 1988, primarily for alfalfa plant bug. The Lygus bug was also a problem, but the alfalfa weevil does not occur in Manitoba. Dimethoate was the most commonly used material as a spring "cleanup" spray. Five of the eight producers sprayed a second time with deltamethrin or trichlorfon, and the other three sprayed with dimethoate the

second time. Alfalfa grown for hay had never been sprayed for insects by these producers.

Further survey information is needed from producers in Alberta and Manitoba. Spraying of alfalfa seed crops with insecticide may pose a risk to birds using these crops for nesting or foraging. Wildlife in hay is generally not at risk, however, there may be some risk in irrigated areas of Alberta. The effects of dimethoate on birds in alfalfa should be investigated. This compound is highly toxic to birds, according to acute oral LD_{50} data, but very few field data are available. It has been shown to kill sage grouse in alfalfa sprayed at the rate used in Canada against the alfalfa plant bug, the Lygus bug, and the sweet clover weevil (560 g a.i./ha).

Publication Medium. To be published in the Canadian Wildlife Service Technical Report Series (pending data from Alberta and Manitoba).

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carbofuran, dimethoate, chlorpyrifos, demeton, 2-4D, picloram

3. REPRODUCTIVE SUCCESS OF BLUEBIRDS AND TREE SWALLOWS NESTING IN NEST BOX TRAILS IN PRAIRIE CROPLAND - (D.J. Forsyth, CWS- Saskatoon; and L. Horstman, Pecan Resources Inc., Morinville, Alberta)

Keywords. bluebirds, Tree Swallows, nest box trails, insecticides, prairies

Introduction. Songbirds can be poisoned by insecticides such as carbofuran, chlorpyrifos, dimethoate, and demeton, which can be ingested by birds eating sprayed insects or vegetation, by inhalation, by preening of feathers, or by absorption through the feet. Some insecticides used in granular formulations for flea beetle control in Canada are attractive to birds as grit and have resulted in large kills of species such as Lapland Longspurs during spring migration through canola cropland in Saskatchewan.

Volunteer naturalists who maintain bluebird nest boxes in trails across the prairie provinces make regular visits to prepare the boxes for bluebird nesting, to monitor the reproductive success of the birds, and to band the young. These amateur naturalists are potentially a source of valuable information about the reproductive success of birds using nest boxes in a variety of agricultural croplands and could report bird kills in cropland that might otherwise go unnoticed. Bluebird trails are potentially useful for an ongoing monitoring program to detect adverse effects of pesticides, especially insecticides, on bluebirds and swallows as indicator species.

Objectives. The objectives of this study were to 1) evaluate the effectiveness, in 1989, of a data collection system to monitor effects of pesticides on Mountain Bluebirds and Tree Swallows in bluebird nest box trails, using the services of volunteer trail operators; and 2) begin a program of monitoring reproductive success of birds in nest boxes located close to selected types of crops in 1990.

Methods. In 1989, six trail operators were provided with data collection notebooks designed by the project coordinator (Pecan Resources Inc.) in a pilot study to elucidate any problems that might occur in collecting data. Landowners in the vicinity of monitored nest boxes were contacted for information about pesticide use. The pilot study demonstrated that volunteer trail operators were generally very effective in recording weekly data from nest boxes and that several revisions to the data collection notebooks were required. In 1990, data notebooks were distributed to 51 volunteer trail operators in Alberta and Saskatchewan in an effort to enlist cooperators with nest boxes adjacent to four crop types: canola, wheat, seed alfalfa, and pasture or hay. The objective was to obtain 60 occupied nest boxes (30 bluebird and 30 Tree Swallow) adjacent to each crop type. Landowners and municipal officials were contacted to determine what pesticides were applied to crops and roadside adjacent to all nest boxes reported in the data notebooks.

Results and Discussion. The rate of participation by trail operators to whom data notebooks were given was 79% in 1990. Data adequate for analysis were provided from 184 Tree Swallow, 167 Mountain Bluebird, and 19 House Wren nests. Fledging success of bluebird nesting near wheat was not significantly different from

those near pasture. Similarly, fledging success of Tree Swallows nesting near alfalfa hay did not differ from those near pasture. Hatching and fledging success of Western Bluebirds nesting adjacent to crops treated with herbicide were not significantly affected, compared to nests adjacent to pasture or hay. There were only two applications of insecticide to crops near the nest box trails in the 1990 monitoring program. Five nest boxes were located within 300 m of a wheat field sprayed with dimethoate, which is highly toxic to songbirds. Two broods of Mountain Bluebirds and two broods of Tree Swallows fledged successfully, but a brood of five Eastern Bluebirds died. The bluebird nestlings died about two weeks after the dimethoate was applied. Spraying of methamidophos on a field next to one nest box did not affect fledging success.

Three cases, two in 1989 and one in 1990, of nestlings dying in nest boxes that had been exposed to roadside spraying of Tordon 101, a 2,4-D/picloram brush killer mixture (4:1 ratio), were reported. Two broods of Western Bluebirds and one brood of Tree Swallows were found dead within several days of spraying.

This project will be continued to obtain a minimum of three years of data for reproductive success in nest boxes located adjacent to crops treated with a variety of insecticides.

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carbofuran

4. EFFECTS OF CARBOFURAN ON SURVIVAL OF MALLARD DUCKLINGS: A POND ENCLOSURE STUDY - (D.J. Forsyth, CWS–, Saskatoon; and P. Martin, University of Guelph).

Keywords. Saskatchewan, mallard ducklings, brood behaviour, cholinesterase, thermoregulation

Introduction. In 1989, mallard ducklings that walked 150 or 300 m through vegetation sprayed with carbofuran exhibited depressed brain cholinesterase activity and retarded response to the stimuli of brood cohesiveness. Reduced capability of ducklings to maintain body temperature has also been shown to result from exposure to carbofuran. The potential for these sublethal effects to influence survival of ducklings in a pond is not known.

Objective. The objective of this study was to determine the effects of exposure to carbofuran-sprayed vegetation on the survival of mallard ducklings in pond enclosures.

Methods. A series of trials was conducted between June 20 and July 17, 1990, to assess the effects on mallard broods (24 h old) with hens of walking 200 m to a pond enclosure through grassland habitat sprayed with carbofuran at two rates of application: 132 g a.i./ha and 164 g a.i./ha. Five trials were conducted at the lower rate and four at the higher rate. Each trial consisted of a control brood and an experimental brood that were placed at the end of an enclosed 200-m walkway, 2 m wide, that had been sprayed 1.5 h previously, in the case of the experimental brood, with carbofuran by sprayer mounted on an all-terrain vehicle. The walkways led to two of ten fenced enclosures in a prairie pond. Each enclosure included 30 m of pond edge and extended 50 m into the water. Two ducklings per brood of eight were marked with radio transmitters implanted under the skin of the back to monitor body temperature and assist in locating the birds for subsequent collection. The broods were watched from observation towers in the pond for behavioural effects for three days after walking to the pond. Deposit of carbofuran was assessed for each trial by analysis of Rhodamine B dye, mixed with the spray formulation, deposited on Petri dish samplers placed at the height of the vegetation (which was mowed to 15–20 cm). A group of eight ducklings (24 h old) was oversprayed with carbofuran at 132 g a.i./ha and immediately moved into a 1.2-m square enclosed area of unsprayed grass for observation of effects during the subsequent 2 h. Two ducklings were sacrificed at 1 h post-spray and the rest of the group were sacrificed at 2 h. All were frozen for analysis of brain cholinesterase.

Results and Discussion. The majority of ducklings walked through sprayed vegetation and survived three days on the water without apparent adverse effects. Several were unable to walk the full 200 m and were left behind by the hens; several were lost to predators after reaching the pond. Brain cholinesterase analysis of ducklings that did not reach the water showed that enzyme depression had occurred. The ducklings oversprayed and observed for 2 h showed no apparent adverse effects and did not feed or preen during that time. Most ducklings walking to the water with hens did not feed, but tended to move

quickly with the hen or to brood if the hen stopped walking. There was no evidence of effects of carbofuran affecting ability to maintain body temperature. The results indicate that exposure to carbofuran-sprayed vegetation only affected the few ducklings that ingested insects during the walk to water.

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lindane

5. LETHAL AND SUBLETHAL TOXICITY OF LINDANE TO *Pimephales promelas* AND *Ceriodaphnia dubia* - (M. Constable, EP-W&N Region; and P. Orr, Beak Consultants Limited)

Keywords. bioassay, *Ceriodaphnia*, *Pimephales*, lethal, sublethal

Introduction. Lindane, the gamma isomer of hexachlorocyclohexane (HCH), is frequently detected in western Canadian rivers at levels of 0.001–0.02 µg/L. The source of contamination is thought to be from the long-range aerial transportation of the insecticide from other parts of the world where it is used in a spray formulation or where it can readily volatilize. The use of lindane on the prairies is primarily as a seed treatment that would not readily contaminate large rivers in remote areas.

This low, but continuous level of contamination could pose a sublethal toxic threat to freshwater life. The survival of *Daphnia* sp. continuously exposed to 19 µg/L of lindane for three generations was significantly reduced in the third generation compared to the controls, indicating that the effects on daphnids are cumulative. Populations of rotifers, primarily *Polyarthra* sp., were reduced 75% in numbers at a concentration of 20 µg/L after exposures of six days. Lindane has been shown to have sublethal effects on sensitive aquatic arthropods at concentrations less than 10 µg/L. The midge *Chironomus tentans* exhibits larval mortality, severe developmental retardation, and a reduction in the number of emerging adults when exposed over two generations to 7.3 µg/L of lindane. At 5.0 µg/L, lindane still caused a significant delay in emergence of adults. Freshwater scud, *Gammarus fasciatus*, do not successfully reproduce at lindane concentrations of 2.6 µg/L and have a 96-h LC_{50} of 10 µg/L.

The toxic threat to freshwater life from concentrations of lindane in western Canadian rivers needed to be assessed with more sensitive, up-to-date toxicity tests than have been applied in the past. An early life stage (ELS) toxicity test requires less cost, time, and effort than a life-cycle toxicity test, and can generate values comparable to those from life-cycle tests. The seven-day lethal and sublethal tests with *Ceriodaphnia dubia* and *Pimephales promelas* are a rapid means of estimating the sublethal effects of a chemical.

Methods. The lethal and sublethal toxicity of lindane was determined using the seven-day *P. promelas* survival and growth test and the seven-day *C. dubia* survival and reproduction test. For effects on the survival of both species, seven-day LC_{50}s were estimated. For effects on the growth rate of *P. promelas* and reproduction of *C. dubia*, 50% inhibition concentrations (IC_{50}s) and maximum acceptable toxicant concentrations (MATCs) were estimated.

Results and Discussion. Using *P. promelas* and *C. dubia*, sublethal and lethal toxicity values were estimated for lindane in water. The growth rate of *P. promelas* was reduced by 50% at 58.5 µg/L; the seven-day LC_{50} was 112 µg/L. The maximum acceptable toxicant concentration for growth was determined to be 31 µg/L. *C. dubia* are more sensitive to the toxic effects of lindane; their reproduction was reduced by 50% at

13 µg/L; the seven-day LC_{50} was 45.5 µg/L. The maximum acceptable toxicant concentrations were determined to be 15 µg/L for survival and 8.3 µg/L for reproduction. *C. dubia* has been shown to be more sensitive than *P. promelas* in seven-day static renewal tests for a variety of chemicals.

The Canadian guideline for protection of aquatic wildlife from hexachlorocyclohexane (HCH) isomers is 0.01 µg/L. The combined levels of alpha- and gamma-HCH isomers found in Canadian prairie rivers occasionally exceed the CCME guideline concentration. This is due primarily to the high levels of alpha-HCH in western Canadian river water. Alpha-HCH has little insecticidal activity and is not a toxic threat to aquatic life at the levels detected in western Canada. The maximum detected ambient levels of HCH isomers was 0.039 µg/L, of which 0.009 µg/L was the gamma isomer. This lindane concentration is 900 times lower than the estimated MATC for *C. dubia* reproduction, and 3000 times lower than the MATC for *P. promelas* growth. Based on this evidence, aquatic resources in western Canadian rivers are likely not at risk from lindane.

Publication Medium. Submitted to *Aquatic Toxicology* in January 1991.

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6. REVIEW OF ENVIRONMENTAL INFORMATION PERTAINING TO THE USE OF DIMETHOATE IN CANADA - (M. Constable and J. Bharadia, EP-W&N Region)

Keywords. re-evaluation, toxicity, environmental behaviour, environmental fate

Introduction. Re-evaluation is a review of all registered uses of pesticide active ingredients and the data supporting these uses in the light of current knowledge and concerns. The purpose of reevaluation is to 1) identify and fill data gaps, thus bringing older data bases up to modern standards; 2) identify and examine concerns regarding human safety or adverse environmental effects; 3) ensure continued efficacy; and 4) take the appropriate regulatory steps to remove those products that are no longer effective or no longer meet the regulatory requirements of the *Pest Control Products Act.*

Objective. It is the mandate of EP, Western and Northern Region, to ensure the protection and preservation of the quality of the environment in the prairie provinces and the Northwest Territories. The objective of the regional mandate is to ensure that regional priority pesticides do not pose a hazard to the environment under present application practices by reviewing the databases on pesticides for the Agriculture Canada re-evaluation program. Where it is determined that a pesticide may pose a threat to the environment, information pertaining to the potential hazard is relayed to EP, Ottawa, and subsequently to Agriculture Canada.

Results and Discussion. On the basis of the literature reviewed, it was concluded that dimethoate is very toxic to three groups of species: insects (including aquatic insects), birds, and fish. In general, mammals are not at risk from the direct, or likely even the indirect, effects of dimethoate use in Canada. Field mice are repelled by dimethoate; in laboratory experiments, the mice starved to death rather than eat dimethoate-treated food.

Insects are the principal target of dimethoate, but there are a great many beneficial and benign insects in a crop when it is sprayed with dimethoate. The environmental impact of this sudden eradication of many of these nontarget insects has yet to be properly addressed.

The use of bran baits was hailed to be less environmentally harmful than a broadcast spray of dimethoate to control grasshoppers, but there is considerable doubt that the bran-bait formulations are less hazardous to wildlife just because they contain three times less active ingredient. The bran delivers more insecticide to the insect than does a spray formulation, making a poisoned grasshopper a toxic food source for many birds. The bran may be an attractive food source for small birds, whereas the spray formulations pose no such risk.

Bees of many species are an important economic resource that are at risk from the use of dimethoate. The often recommended precautions of spraying in the evening or early morning to avoid foraging bees does not work, as dimethoate is taken in by plants and is partitioned into the nectar that the bees are feeding on. Toxic nectar can be encountered several days after a spray.

Upland game birds, such as grouse and partridge, are potentially at risk from the use

of dimethoate. Preliminary research done on the chronic effects of dimethoate on quail identified the increased incidence of egg shell thinning in birds that were exposed to low levels of dimethoate. Sage grouse inhabiting sprayed potato fields in Idaho have a high incidence of dimethoate intoxication and death. This has serious implications for upland game birds inhabiting areas of southern Alberta where irrigated crops may be frequently sprayed with dimethoate.

This literature review also found a lack of some basic information on dimethoate, the most serious being a lack of data on the persistence and fate of dimethoate in Canadian water systems, a lack of soil degradation rates from typical Canadian soils, few data on the toxicity of dimethoate to soil organisms, and highly variable data on the vapour pressure at ambient temperatures.

Publication Medium. Government report series.

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carbofuran

7. REVIEW OF ENVIRONMENTAL INFORMATION PERTAINING TO THE USE OF CARBOFURAN IN CANADA - (M. Constable and J. Bharadia, EP-W&N Region)

Keywords. re-evaluation, toxicity, environmental behaviour, environmental fate

Introduction. Re-evaluation is a review of all registered uses of pesticide active ingredients and the data supporting these uses in the light of current knowledge and concerns. It is a substantially different process from the review and registration of a new product. The purpose of reevaluation is to 1) identify and fill data gaps, thus bringing older data bases up to modern standards; 2) identify and examine concerns regarding human safety or adverse environmental effects; 3) ensure continued efficacy; and 4) take the appropriate regulatory steps to remove those products which are no longer effective or no longer meet the regulatory requirements of the *Pest Control Products Act.*

Objective. It is the mandate of EP Western and Northern Region, to ensure the protection and preservation of the quality of the environment in the prairie provinces and the Northwest Territories. The objective of the regional mandate is to ensure that regional priority pesticides do not pose a hazard to the environment under present application practices by reviewing the databases on pesticides for the Agriculture Canada reevaluation program. Where it is determined that a pesticide may pose a threat to the environment, information pertaining to the potential hazard is relayed to EP, Ottawa, and subsequently to Agriculture Canada. Environmental concerns may be addressed directly by either the manufacturer or by Agriculture Canada. EP's role is limited to supplying information that demonstrates a reasonable potential for a pesticide to harm the environment. It is the responsibility of the pesticide industry to prove that their products are safe and to refute any information provided to the contrary.

Results and Discussion. The insecticide carbofuran is a systemic, contact, and stomach poison. It is a potent cholinesterase inhibitor with an extreme acute oral toxicity to most animals. Carbofuran acts by inhibiting acetylcholinesterase (AChE) by contact or ingestion. Carbofuran is a direct inhibitor of AChE, which means that it does not require metabolic alterations to become active. The inhibitory effects of carbofuran are reversible. Exposure to carbofuran results in the development of typical ChE poisoning symptoms, which include muscle tremors, excessive salivation, and perspiration. Other possible symptoms include constriction of the bronchial tree and increased mobility of the alimentary tract. All metabolites of carbofuran have toxicities lower than the parent compound.

Aerial application of 560 g/ha of Furadan 3G to a rice field in Texas resulted in the deaths of several fish, bird, and nontarget invertebrate species. Mortality of earthworms and several aquatic invertebrates occurred in less than 2.5 hours after application. Cricket frogs were paralyzed or were exhibiting unusual behavior within 15 minutes of aerial application.

The literature review and evaluation of the information are not yet complete, so no discussion of the results is available. The data base on carbofuran is massive and will

take a considerable effort to summarize and evaluate.

Publication Medium. Government report series.

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triallate

8. EXPERIMENTAL DETERMINATION OF TRIALLATE BIOCONCENTRATION IN FISH - (G.R. Craig, D.R. Hart, and P. L. Orr, Beak Consultants Limited)

Keywords. bioconcentration, rainbow trout, Avadex-BW, herbicide, continuous flow-through bioassay

Introduction. Triallate has been measured in Canadian surface waters in concentrations of up to 0.15 µg/L. Detectable residues have been found in the bottom sediments of the LaSalle River, Manitoba, at levels of 16.9 to 119 ng/g and in fish at levels from 3.3 to 9.2 ng/g. The bioconcentration factor for triallate has been estimated to range from 150 to 282 based on K_{ow} and water solubility.

Objective. The objective of the study was to determine a bioconcentration factor for rainbow trout exposed to a triallate concentration of 0.14 µg/L.

Methods. Rainbow trout were exposed to triallate (acetone carrier) at a mean measured concentration of 0.14 µg/L in a continuous-flow system for 21 days. The bioconcentration factor was determined by both a kinetic and static model.

Results and Discussion. A bioconcentration factor of 789 was established for rainbow trout exposed to triallate concentrations of approximately 0.14 µg/L.

The objective of the study was met. The information obtained from the study is significant to Agriculture Canada's pesticide reevaluation program by providing data on the bioaccumulation of this pesticide.

Publication Medium. The work will not be published. Results are available in the original report form submitted by the contractor.

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dimethoate, chlorpyrifos, carbaryl

9. BRAN-BAIT INSECTICIDE FORMULATIONS USED IN GRASSHOPPER CONTROL: EFFECTS ON NONTARGET ORGANISMS

- (D. Gregory and Dr. D. Johnson, Lethbridge Research Station, Agriculture Canada; and Dr. B.H. Thompson, EP-W&N Region)

Keywords. grasshoppers, nontarget populations, bran bait, delivery systems

Introduction. For several generations, grasshopper infestations have posed a significant problem for agricultural operations on the Canadian prairies. In 1986, for example, during the most recent cyclical infestation, over 170 000 L of insecticide chemicals were applied in Alberta alone.

Agriculture Canada and Alberta Agriculture are currently assessing the effectiveness of various strategies for grasshopper control. Bran-bait formulations (i.e., bran particles impregnated with insecticides or other control agents) appear promising from an environmental viewpoint as well from an effectiveness perspective. The bran-bait approach promises to reduce the amount of chemical necessary to achieve control by about 60%, virtually eliminate residue levels on crops, and reduce wind-assisted spray drift. Furthermore, because the bran particle is eaten by the target insect, this approach will decrease the risk to nontarget (i.e., harmless or beneficial) organisms. Nontarget organisms with feeding habits similar to grasshoppers, however, are likely to be adversely affected. To confirm that bran-bait formulations indeed represent an environmentally superior alternative to conventional spray formulations, the significance of such effects must be determined.

In order to identify the potential environmental consequences of this control strategy early in its development, Environmental Protection (W&NR) and Agriculture Canada embarked on a partnership initiative to determine the extent of the nontarget impact. The two-year project was carried out mainly at the Agriculture Canada Research Station in Lethbridge, Alberta. Alberta Agriculture also contributed an operating grant under its Farming for the Future program.

Objective and Methods. Laboratory and field studies were performed to estimate the lethal and sublethal effects of exposure (either dietary or contact) of representative nontarget organisms to bran-bait formulations using three insecticide chemicals as examples. Bran-bait formulations were also compared with conventional spray formulations using the same active ingredient at operational dose rates.

Results and Discussion. Bran-bait formulations of two of the chemicals (i.e., carbaryl and dimethoate) had minimal or undetectable effects on field mice, adult and larval beetles, leafcutter bees, and fish when applied at dose rates effective in controlling grasshoppers. The third chemical (chlorpyrifos) led to significant lethal and nonlethal effects in some cases, whether applied as a spray or as branbait. When both conventional (liquid spray) and bran formulations were tested simultaneously, the conventional

formulation displayed significantly greater mortality than the bran-bait formulation. Laboratory trials were carried out to estimate the leaching rate of active ingredient from the bran particle in water under various conditions of temperature and pH.

Bran baits appear to represent an alternative to conventional spray applications against grasshoppers in being effective and at the same time reducing the loading of toxic chemicals in the environment, a goal of the federal government's Green Plan. Agriculture Canada and provincial agriculture departments are promoting the use of bran-bait formulations as an effective and environmentally sound means of controlling grasshoppers. The partnership research has thus served to remove possible environmental constraints from an otherwise environmentally favorable pest management strategy.

Publication Medium. A copy of the final report can be obtained from the contact person identified below.

The results have been prepared as three publications for the *Journal of Agricultural Entomology*.

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glyphosate, difenzoquat, dichlorprop, 2,4-D, bromoxynil, clopyralid

10. OFF-TARGET MOVEMENT OF PESTICIDES USED UNDER A ZERO-TILL REGIME IN A SMALL MANITOBA WATERSHED - (K. Best and W. Nickolaichuk, NHRI, IWD-W&N Region; and W. Tibbatts, EP-W&N Region)

Keywords. Manitoba, lysimeter, H-flume, spring runoff

Introduction. Soil and wildlife conservationists actively promote reduced or zero-tillage agricultural practices to protect the soil resource and provide nesting habitat. The shift to zero-tillage from more conventional practices may involve a corresponding shift in type and volume of herbicides used. Under zero-tillage, improved soil tilth may make groundwater contamination with herbicides more likely. Decreased soil erosion and better water-holding capacity of the soil may make off-target surface migration of herbicides less likely. This study examines those two transport pathways on a working zero-till farm in Manitoba.

Objective. The objective of the study was to examine off-target movement of herbicides through the soil and through spring surface runoff under zero-tillage agricultural practices.

Methods. The study area is a small (6.9 ha) privately owned and operated watershed near Minnedosa, Manitoba, which had been under zero-tillage practices for seven seasons at the start of the study. The watershed contains portions of the two fields, which drain into a small dugout. An H-flume with automatic sampler and gauge recorder was installed at the end of a clearly defined flow channel in the east field to collect samples of spring runoff for analysis of fall-applied herbicides. Suction lysimeters were installed at six locations throughout the watershed, at depths of 30, 60, 90, 150, and 180 cm, with duplicate tubes installed at the three shallower depths. Water samples were collected from the lysimeters following post-emergent herbicide application. Water and bottom sediment samples were collected from the dugout throughout the season.

Results and Discussion. Runoff began March 30, 1990, and continued to April 19, 1990. Fall-applied glyphosate and its primary metabolite, AMPA, were detected in all runoff samples, at levels ranging from 0.0007 to 0.002 µg/L for glyphosate and 0.0004 to 0.001 µg/L for AMPA in the first 24 hours following the onset of runoff. As water flows decreased, the concentrations ranged from 0.001 to 0.003 µg/L for both glyphosate and AMPA. These data will be used with gauging data to calculate total loss through spring runoff. Volumes collected from lysimeters were often insufficient for analysis at acceptable detection limits, and some samples were pooled. The duplicate lysimeter tubes were moved further apart to prevent overlap of the suction radius for the next season.

Publication Medium. None provided.

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trifluralin

11. ACCUMULATION OF TRIFLURALIN AND RELATED COMPOUNDS IN SEDIMENTS AND BENTHIC FAUNA OF PRAIRIE FARM DUGOUTS - (M.E. Fox, NWRI; and E.E. Prepas and C. Van Tol, University of Alberta)

Keywords. farm dugouts, northern Alberta, sediments, leeches

Introduction. Earlier studies established that trifluralin added to northern Alberta farm dugouts accumulated in the sediments and indigenous leeches along with two stable reductive degradation products α,α,α-trifluoro-N^4,N^4-dipropyltoluene-3,4-diamine (R1TRF) and α,α,α-trifluoro-N^4,N^4- dipropyltoluene-3,4,5-triamine (R2TRF), and persisted for at least one year.

Objective. The objective of the study was to use convenient integrating and sensitive markers (surficial sediments and leeches) to determine whether episodic, but potentially harmful, pollution of farm dugouts with trifluralin and its reductive degradation products has occured after application of trifluralin to the surrounding land.

Methods. Artificial substrates to collect resident leeches were installed in 15 farm dugouts in northern and central Alberta in June 1990. Leeches were removed for identification and analysis along with surficial sediment samples. The leeches were identified and one species (*Nephelopsis obscura*) was analyzed for trifluralin, R1TRF, and R2TRF along with the sediment samples. A survey of trifluralin use on adjacent farms was conducted in 1990.

Results and Discussion. The leech collection substrates worked well, producing several species from 11 of the 15 sites. One detritus feeding species (*N. obscura*) was found at all 11 sites and was thus selected for analysis.

Despite the use of trifluralin on farms adjacent to some of the dugouts, trifluralin and the degradation products were found only in the sediment and/or leeches of the two dugouts that had been directly treated with trifluralin a year earlier. Maximum sediment concentrations were 525 ng/g R2TRF, 100 ng/g trifluralin, and 5 ng/g R1TRF. Maximum leech concentrations were 340 ng/g R2TRF, 10 ng/g trifluralin, and 10 ng/g R1TRF.

The survey of trifluralin use indicated that 8 of the 15 farms used trifluralin in the previous ten years, with only four treatments in the immediate area of the dugouts and none since 1987. The failure to find any trace of trifluralin in the sediments and resident leeches of any dugout other than these two experimentally treated ones may be a negative finding of significance to farming practices in the prairie provinces where trifluralin is widely used, although the absence of trifluralin in *N. obscura* may also be accounted for by their average life cycle of only two years. A reasonable inference from this study is that trifluralin, as currently applied, does not appear to be a threat to human or animal health through the ingestion of water from farm dugouts, even when applied to adjacent fields. The absence of residues of trifluralin and its persistent reductive metabolites from sediments and leeches at these locations may be due to low transport rates in surface and subsurface water, or complete degradation,

with the former explanation appearing more likely from the results of this and related studies.

Publication Medium. NWRI Contribution.

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difenzoquat, sethoxydim

12. THE FATE AND EFFECTS OF THE HERBICIDES DIFENZOQUAT AND SETHOXYDIM IN PRAIRIE WETLAND ENCLOSURES - (R.A. Kent, IWD-HQ; and G.G. Goldsborough, University of Brandon)

Keywords. phytotoxicity, prairies, conservation tillage, littoral enclosures, periphyton

Introduction. The entry of agricultural herbicides to aquatic ecosystems via spray drift, surface runoff, groundwater flow, or sediment transport is well established. There are, however, relatively few data on the environmental chemistry and aquatic phytotoxicity of these chemicals. The herbicides difenzoquat (Avenge) and sethoxydim (Poast) are heavily used on the Canadian prairies in cereal and broadleaf crops. Very few data, however, exist on the environmental chemistry, fate, and toxicology of these popular herbicides. Considering the extensive use of these herbicides in prairie agriculture today (and anticipated expanded use in conservation tillage), critical information is required for adequately evaluating the environmental risk in the aquatic environment.

Methods. Bioassay experiments on the effects of difenzoquat and sethoxydim on short-term carbon fixation by intact periphyton communities from the Delta Marsh, Manitoba, were carried out between May and August 1990. Ten littoral enclosures were deployed in the marsh in early June 1990. Four were treated once with two concentrations of difenzoquat (5.0 and 50 mg/L) and four were treated once with two concentrations of sethoxydim (1.0 and 10 mg/L). Two additional enclosures and two sites outside the enclosures were maintained as untreated controls. Water samples for nutrient analysis were collected from each enclosure at two- to three-day intervals for four weeks prior to herbicide treatment, and for four weeks after treatment. Water samples were collected at weekly intervals after treatment for analysis of herbicide residues. Samples of artificial substrata (acrylic rods) colonized by periphyton were collected at weekly intervals for three weeks before treatment and eight weeks after treatment. Levels of periphyton biomass (chlorophyll concentration) and rate of photosynthesis (radiocarbon uptake) for these samples were measured.

Results and Discussion. The availability of aquatic toxicological and environmental fate information was surveyed and few data pertinent to this project were found.

Field dissipation studies on the parent compounds yielded half-lives in marsh water ranging from 7.1 to 25.4 days for sethoxydim and 2.9 to 29.0 days for difenzoquat. Although variability existed between enclosure locations, both herbicides had measurable effects on algal photosynthesis during short-term (3–4 hours) exposures. Inhibition of carbon-fixation rates occurred with EC_{50} ranges of 2.5–8.6 and 38.1–66.6 mg/L for sethoxydim and difenzoquat, respectively. Alterations in species composition were also observed in treated enclosures suggesting dominance profile shifts and secondary community effects.

Publication Medium. Two manuscripts are expected to be submitted for publication.

One will deal with the results of short-term laboratory bioassays conducted before and during the enclosure experiment. A second publication will present water chemistry data, herbicide residue data, and periphyton biomass and productivity data arising from the enclosure experiment.

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alpha-*BHC, lindane, heptachlor, heptachlor epoxide, aldrin,* alpha-*chlordane,* gamma-*chlordane, endrin, dieldrin,* alpha-*endosulfan,* beta-*endosulfan, p,p'-DDT, p,p'-DDE, p,p'-DDD,/o,p'-DDT, mirex, p,p'-methoxychlor, MCPA, dicamba, 2,3,6-TBA, 2,4-D, 2,4-DP, 2,4-DB, 2,4,5-T, silvex, picloram, bromoxynil, trifluralin, triallate, diclofop-methyl, diallate, atrazine, barban, benzoylprop-ethyl, metolachlor*

13. QUALITY CONTROL DATA: A REVIEW OF ORGANICS DATA FROM SAMPLING IN TRIPLICATE DURING THE PERIOD MARCH 1985 TO SEPTEMBER 1989 - (H. Block, WQB-W&N Region)

Keywords. quality control, reproducibility, spatial patterns, temporal patterns

Introduction. The Water Quality Branch, Western and Northern Region (WQB-W&R), has for many years operated and participated in a number of quality control programs to obtain information and feedback on the quality of the data being produced. One such program has consisted of the collection in triplicate of water samples from selected rivers for selected parameters.

Objectives. The objectives of this study were to 1) quantify the precision of sampling and analytical practices; and 2) determine the value to the WQB-W&N and to its clients of this triplicate sampling program in terms of quality control.

Methods. Since April 1984, the WQB-W&N has been collecting triplicate samples for pesticide analysis at selected sites for quality control purposes. For this report, the regional triplicate data records for organics for the period April 1984 to March 1990 were examined. The proportion of results above detection limit was tabulated for all compounds. Reproducibility was reported for each compound.

Results and Discussion. The triplicate program has helped determine precision of sampling and analytical practices for a few compounds. However, the majority of compounds were never detected. This type of program, when applied to a pesticide monitoring program for ambient surface waters has only limited value. As a result of this evaluation, WQB-W&N will redesign its quality assurance program. This work has long-term significance in relation to the scientific validity of the branch's routine monitoring data.

Publication medium. Western and Northern Region report.

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glyphosate

14. SHORT-TERM EFFECTS OF GLYPHOSATE (ROUNDUP FORMULATION) ON PRIMARY PRODUCTIVITY OF PRAIRIE PONDS - (P. Shaw, WQB-W&N Region)

Keywords. primary productivity, wetlands, herbicides

Introduction. Traditional agricultural practices are gradually being supplanted in some areas of the prairies by minimum-tillage systems. Under these regimes, crop residues are left on the soil surface, with resulting improved soil moisture and reduced topsoil losses from wind and water. A beneficial side effect of minimum-till farming is enhanced availability of nest cover for waterfowl and greatly improved nest success and production. For this aspect alone, these systems are being actively promoted by waterfowl management agencies in Canada and the United States. A shift from conventional-tillage farming carries with it an increased reliance on herbicides to control perennial weeds that would have been managed through tillage operations. This elevated use of agricultural chemicals in wetland areas carries with it the potential for contamination of these important aquatic habitats and possible adverse effects.

Objectives. The objectives of this work were, 1) to assess the possible effect of glyphosate on wetland phytoplankton productivity; and, 2) to determine degradation rates in a prairie wetland setting.

Methods. Pairs of enclosures (surface area 20 m^2) were constructed in three ponds on farmlands near Stettler, Alberta, in late May 1990. One of each pair of enclosures was selected at random and sprayed with Roundup (Monsanto) to provide an application rate of 2.5 L/ha (0.890 kg/ha glyphosate). Commercial Roundup was mixed with pond water and applied evenly to the water surface using a portable hand-sprayer. At intervals of 1, 3, 5, 10, and 15 days after herbicide application, each of the enclosures was sampled for chlorophyll *a* and glyphosate in water and sediment. Primary productivity was also measured by ^{14}C uptake during 4-h *in situ* incubations.

At four pond sites in the study area, *in situ* bioassay trials were conducted to determine the response of primary production rates to levels of Roundup. Dilutions of commercial Roundup (356 g/L) were prepared from natural pond water to provide a 1000 mg/L stock solution. Pond water samples were then spiked from this stock to provide final concentrations of 0.01, 0.1, 1, 10, and 100 mg/L glyphosate. ^{14}C uptake was then determined as with the enclosure experiments.

Results and Discussion. Phytoplankton biomass and productivity in the enclosure experiments showed no effects that could be unequivocally attributed to herbicide application. Bioassay trials showed a 50% reduction in ^{14}C uptake at glyphosate concentrations of 0.1 to 1.0 mg/L. In several of the trials, enhanced production was found at glyphosate concentrations below 0.1 mg/L, a result possibly due to use of the glyphosate phosphorus moeity as a nutrient by phytoplankton.

Decline of glyphosate concentration in water closely followed a first-order decay, with a calculated half-life of 6.8–17.0 days.

Environmental levels of glyphosate from normal use on crops in a minimal-till system are likely to remain orders of magnitude below levels that would seriously impair phytoplankton primary productivity in wetlands.

Publication Medium. None provided.

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1,2-dichloropropane

15. ABBOTSFORD OUTWASH AQUIFER PESTICIDE STUDY - (G. Grove and H. Liebscher, NHRI; and B. Zebarth and S. Szeto, Agriculture Canada)

Keywords. Abbotsford, groundwater, outwash aquifer

Introduction. A sampling program of 21 wells conducted in 1985 by the National Hydrology Research Institute (NHRI) indicated that measurable quantities of the organochlorine compound 1,2-dichloropropane (1,2-DCP) were detectable in wells and standpipes drilled into the Abbotsford outwash aquifer. The aquifer is an unconfined body of sand and gravel that straddles the international boundary and is used extensively in Canada and the United States as a source of water for drinking, agriculture, fisheries, and light industry.

Objectives. The objectives of the study were 1) to determine the degree of contamination of the Abbotsford aquifer by pesticides; 2) to determine the hydrogeologic controls on the temporal and spatial variation in concentration of selected pesticides in the Abbotsford aquifer; 3) to determine potential mitigation of pesticide contamination of the Abbotsford aquifer by changing pesticide use practices; and 4) to identify alternative solutions to problems resulting from pesticide contamination in the Abottsford aquifer.

Methods. This project was essentially a survey. As yet, no intensive study has been dedicated to processes or mechanisms. Water samples were collected from various wells and analyzed for target compounds. More intensive work is being initiated.

Results and Discussion. Resignation of the principal investigator for this project has curtailed activities. Nevertheless, work has concentrated on documentation of results from past drilling and sampling programs. Planning is currently under way for more detailed studies to examine mechanisms controlling distribution of 1,2-DCP in the Abbotsford aquifer.

Publication Medium. McNaughton, D.C., Pesticides in Groundwater: An Investigation of the Abbotsford Aquifer, Fraser Lowland, British Columbia, NHRI Draft Report (1990).

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MCPA, 2,4-D, bromoxynil, trifluralin, triallate, atrazine, simazine, diclofop-methyl, lindane

16. DRY LAKES STUDY - (D.B. Donald, WQB-W&N Region)

Keywords. herbicides, bioaccumulation

Introduction. The prairie provinces were subjected to drought conditions throughout the 1980s, with an extreme drought during 1988. Consequently, many large lakes in southern Saskatchewan completely dried out. For example, Old Wives Lake covers about 43 000 ha at 668.5 m above sea level, but was dry in the fall of 1988.

In years with normal precipitation, lakes in southern Saskatchewan provide critical breeding habitat for shorebirds, such as the American Avocet, and are critical staging habitat for a variety of shorebirds and waterfowl. As indication of its importance, the Old Wives–Chaplin Lake complex has been targeted as as a Hemispheric site within the Western Hemisphere Shorebirds Reserve Network. For the shorebirds, these lakes provide a rich food resource critical for their successful migration to and from the Gulf of Mexico and South America. The invertebrates forming the bulk of this food resource often have a dessication-resistant stage and would be relatively unaffected by dry periods.

Strong adsorbtion of many pesticides to soil particles and organic matter is well documented, and a number will persist as bound residues for some period after initial application. For example, as much as 10% of applied trifluralin can remain in the soil to the following year. As much as 12% of applied triallate was detected in soils 17 months after application. In addition, residues of other commonly used herbicides have been detected in spring snowmelt. These two sources, soil-bound contaminants and melt waters, could be major factors in loading of pesticides to prairie waters.

Pesticide residues in water may reduce the abundance of aquatic plants and invertebrates, which are the principal food supply of migratory birds utilizing these habitats. The plants and invertebrates accumulate pesticides from sediment and/or water. This study will assess pesticide residue levels in the first and second steps of this chain from water and sediments to biota.

Objective. The objective of the study is to assess the levels and significance of pesticide residues in sediment, spring runoff, and aquatic invertebrates in terminal prairie lakes that are critical shorebird and waterfowl staging habitat.

Methods. Ten "dry" lakes and ten permanent lakes will be sampled to assess pesticide residue levels in water, sediment, and biota. Samples will be analyzed for pesticides in common use in southern Saskatchewan including MCPA, 2,4-D, bromoxynil, trifluralin, triallate, atrazine, diclofop-methyl, and lindane.

Results and Discussion. This study began in 1989 and will be completed in 1992. Results and prelimary analyses are available for samples collected in the winter of 1988 and spring of 1989. Of the sediment-borne herbicides analyzed, only triallate and simazine were commonly encountered. For simazine, levels to 190 µg/kg were found in three of the eight "dry" lakes and three of ten permanent lakes. Triallate was detected in 14 of 30 sediment samples. atrazine was the only other pesticide found in sediments. It

was present in a single sample from a permanent lake at 169 µg/kg.

In water samples, lindane, alpha-BHC, and 2,4-D were encountered at near detection limits in more than 50% of both permanent and "dry" lake sites. No relationship is evident between the presence of contaminants in sediment and in water.

Two herbicides were detected in invertebrate tissues. Diclofop-methyl was recorded from one permanent lake at 6.7 µg/kg and one "dry" lake at 4.8 µg/kg. Triallate was encountered in three "dry" lakes and four permanent lakes at concentrations from 2.3 to 10.2 µg/kg.

From these preliminary results, it is clear that the principal contaminants of prairie lakes are lindane, alpha-BHC, 2,4-D, and triallate.

Publication Medium. None provided.

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PESTICIDES PROGRAM IN THE PACIFIC AND YUKON REGION
(British Columbia and Yukon Territory)

TCMTB

1. LEACHING OF 2-(THIOCYANOMETHYLTHIO)BENZOTHIAZOLE (TCMTB) FROM SURFACE-TREATED LUMBER - (P.K. Krahn and R. Strub, EP-P&Y Region)

Keywords. Fraser River, North Arm, leaching, leachate, toxic plumes, bioassay, anti-sapstain, wood protection, wood preservation, salmonids, chinook salmon, rainbow trout, sawmill, 2-(thiocyanomethylthio)benzothiazole, 2-mercaptobenzothiazole, 2-(methylmercapto)benzothiazole, benzothiazole, 2-methylbenzothiazole, chloromethylthiobenzothiazole, spray booths

Introduction. TCMTB, or 2-(thiocyanomethylthio)benzothiazole, is a fungicide registered for use an anti-sapstain chemical to protect dimensioned lumber during transport to export markets. TCMTB is toxic to fish and has a 96-h flow-through fish bioassay LC_{50} of approximately 15 µg/L for chinook salmon in fresh water and 6 µg/L in seawater. The leaching of TCMTB from treated wood was monitored during rainfall events at a sawmill located on the tidally influenced section of the North Arm of the Fraser River from October 1989 to January 1990.

Objectives. The objectives of the study were to determine the concentration of TCMTB and its degradation products in 1) rainwater leachate from surface-treated lumber and in 2) the Fraser River adjacent to stormwater outfalls that drain treated lumber storage yards.

Methods. Samples of rainwater, leachate dripping from the wood, yard runoff discharging from the storage yards, and Fraser River water were collected as 1/2-h to 6-h composite samples and analyzed by high performance liquid chromatography. Concentrations were correlated to rainfall and tidal conditions.

Results and Discussion. Freshly treated wood had less than 11 minutes covered storage time before exposure to rainfall. The average concentration of TCMTB in leachate dripping from freshly treated lumber was 89 000 µg/L, which was diluted on the yard to 7500 µg/L before discharge to the Fraser River. The average concentration of TCMTB in leachate dripping from treated lumber that had at least 12 hours of covered storage time was 5400 µg/L, which was diluted to 340 µg/L before discharge to the Fraser River.

The average sawmill located on the lower Fraser River has an uncovered treated lumber inventory of 6 000 000 board feet (treated with TCMTB). It will discharge an average of 450 000 L/d of contaminated effluent at least 30 days per year and 700 000 L/d on at least 5 days per year. The average chemical concentration will depend on the application rate to the lumber and will normally range from 240 µg/L to 340 µg/L. This is 16 to 23 times the allowable concentration in the British Columbia Provincial Anti-sapstain Chemical Waste Control Regulation.

The effluent plume discharged from a TCMTB-treated lumber storage yard will stratify in the top metre of the water column. The plume will extend 10 m into the river at least 30 days per year and 20 m into the river at least 5 days per year. Within the plume, the concentration of TCMTB will be three to

five times the regulated limits for a period of 5 to 10 h (or as long as rainfall continues).

Because of the high concentrations in the runoff and sublethal toxicity, the allowable limit of TCMTB in stormwater runoff from treated lumber storage yards was reduced from 15 µg/L to 6 µg/L. This has effectively removed TCMTB products from the marketplace for this application.

Publication Medium. Leaching of 2-(thiocyanomethylthio)benzothiazole (TCMTB) from Surface-treated Lumber, Regional Program Report 90-10, Environment Canada, Conservation and Protection, Environmental Protection, Pacific and Yukon Region (1990).

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DDAC

2. LEACHING OF DIDECYLDIMETHYL AMMONIUM CHLORIDE FROM TIMBERCOTE II-TREATED LUMBER - (E.C. Mendoza and P.K. Krahn, EP-P&Y Region)

Keywords. Fraser River, North Arm, leaching, leachate, toxic, anti-sapstain, wood protection, wood preservation, salmonids, chinook salmon, rainbow trout, sawmill, spray booths

Introduction. Didecyldimethyl ammonium chloride (DDAC) is a fungicide registered for use an an anti-sapstain chemical to protect dimensioned lumber during transport to export markets. DDAC is toxic to fish and has a 96-h static fish bioassay LC_{50} of approximately 700 µg/L for rainbow trout in fresh water. The leaching of DDAC from treated wood was monitored during rainfall events at a sawmill located on the tidally influenced section of the North Arm of the Fraser River from October 1 to October 18, 1990.

Objectives. The objectives of the study were to 1) determine the concentrations of DDAC and its degradation products in rainwater leachate from surface-treated lumber, and 2) to estimate the concentrations of DDAC in treated lumber storage yard runoff that drains to the Fraser River.

Methods. The protocol "Standard Leaching Test for Anti-sapstain Chemicals" (Environment Canada, Regional Program Report 90-10) was used to determine the concentration of DDAC in leachate from treated lumber. Packages of treated lumber were mounted on leachate collection trays. Leachate was collected using only natural rainfall over the study period. A rainfall cycle consisted of one dry day followed by a day of rainfall. The average rainfall was 13 mm/d, which compared to the 15-mm/d predicted standard. Composite samples of leachate were analyzed for DDAC using the modified Lonza Standard Analytical Method NR-171 for determination of concentrations in milligrams per litre using dichloromethane and bromophenol blue for colorimetric determination. The Environmental Protection Service (EPS) and Pacific Institute capillary column gas chromatographic procedure was used for resin acid determination.

Results and Discussion. Concentrations of DDAC were adjusted to the 15-mm/d standard predicted rainfall. DDAC leached from Timbercote II-treated lumber at a concentration of 73 200 µg/L during the first cycle, which decreased to 6000 µg/L by the seventh cycle. The average leachate concentration over the standard 15 cycles was estimated to be 15 900 µg/L. The leachate is diluted as it migrates across the storage yard and discharges through an outfall to the Fraser River. The concentration of DDAC in the yard runoff was estimated to be 1060 µg/L, which is 1.5 times the British Columbia provincial regulated level of 700 µg/L. Other chemicals that were registered for use as anti-sapstains (before DDAC) have yard effluent concentrations that were 15 to 23 times the regulated limits. Formulations containing DDAC appear to be replacing these chemicals in the marketplace. Resin acids were present in the leachate. It was not possible to determine any significant trends in the concentrations of resin acid as the data set was too small and the concentrations had a high variability.

Publication Medium. A report will be published: Leaching of Didecyldimethyl Ammonium Chloride from Timbercote II Surface Treated Lumber", Regional Program Report 91-01, Environment Canada, Conservation and Protection, Environmental Protection, Pacific and Yukon Region.

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DDAC, IPBC

3. LEACHING OF DIDECYLDIMETHYL AMMONIUM CHLORIDE (DDAC) AND 3-IODO-2-PROPYNYL BUTYL CARBAMATE (IPBC) FROM NP1-TREATED LUMBER

- (H. Martin, MacMillan Bloedel Limited; P.K. Krahn, E.C. Mendoza, and R. Strub, EP-P&Y Region; and Dr. H. Ward, Kopcoat Ltd.)

Keywords. Fraser River, North Arm, leaching, leachate, toxicity, anti-sapstain, wood protection, wood preservation, salmonids, chinook salmon, rainbow trout, sawmill, spray booths

Introduction. DDAC and IPBC are fungicides registered for use as anti-sapstain chemicals to protect dimensioned lumber during transport to export markets. DDAC is toxic to fish and has a 96-h static fish bioassay LC_{50} of approximately 700 µg/L for rainbow trout in fresh water. IPBC is also toxic to fish and has a 96-h LC_{50} of 120 µg/L for chinook salmon in fresh water. The leaching of DDAC and IPBC from treated wood was monitored during artifical rainfall events from March 4 to March 21, 1991.

Objectives. The objectives of the study were to determine the concentration of DDAC and IPBC in 1) rainwater leachate from lumber treated with a commercial formulation, and in 2) treated lumber storage yard runoff that drains to the adjacent stormwater outfalls and into receiving waters.

Methods. The protocol Standard Leaching Test for Anti-sapstain Chemicals (Environment Canada, Regional Program Report 90-10) was used to determine the concentration of DDAC and IPBC in leachate from treated lumber. Packages of treated lumber were mounted on leachate collection trays. Leachate was collected using only artificial rainfall over the study period. A rainfall cycle consisted of one dry day followed by a day of rainfall; the wood was subjected to eight cycles. The average rainfall was 15 mm/d. Composite split samples of leachate were analyzed for DDAC using the modified Lonza Standard Analytical Method NR-171 for determination of concentrations in milligrams per litre using dichloromethane and bromophenol blue for colorimetric determination, the MacMillan Bloedel proprietary colorimetric method, and the Environment Canada method using a surfactant/formaldehyde preservative and nitrogen-phosphorus detection capillary gas chromatography (HRGC-LRMS). The samples were analyzed for IPBC using the Environment Canada method for determination by high performance liquid chromatography (HPLC). The Environmental Protection Service (EPS) and Pacific Institute capillary column gas chromatographic procedure was used for resin acid determination.

Results and Discussion. Concentrations of DDAC and IPBC will be reported based on the standard artificial rainfall rate of 15 mm/d. Preliminary results indicate that when lumber is treated with the commercial formulation containing DDAC and IPBC, the concentrations of both active ingredients are likely to be within limits regulated under the British Columbia Provincial Anti-sapstain Chemical Waste Control Regulation. The contribution to toxicity by natural leachable wood extractives could not be definitively determined. The commercial formulation has gained a substantial portion

of the anti-sapstain chemical market in British Columbia.

Publication Medium. A report is currently in the draft stage.

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2,4-D BEE, 2,4-DP BEE

4. ACUTE TOXICITY TO JUVENILE PACIFIC SALMONIDS AND RAINBOW TROUT OF BUTOXYETHYL ESTERS OF 2,4-D, 2,4-DP, AND THEIR FORMULATED PRODUCT WEEDONE CB AND ITS CARRIER - (M.T. Wan, R.G. Watts, and D.J. Moul, EP-P&Y Region)

Keywords. butoxyethyl esters (BEE) of 2,4-dichlorophenoxyacetic acid, 2-(2,4-dichlorophenoxy)propionic acid, Aquatic Toxicity Laboratory, North Vancouver, juvenile Pacific salmonids, static acute toxicity, Weedone CB

Introduction. 2,4-D BEE and 2,4-DP BEE are base chemicals manufactured by Rhone-Poulenc Agriculture, Mississauga, Ontario, for formulating Weedone CB. The use of this product for forestry conifer release and industrial rights-of-way programs in coastal British Columbia may result in the accidental introduction of BEE of 2,4-D and 2,4-DP into water bodies inhabited by anadromous fish.

Objective. The purpose of the study was to evaluate the acute toxicity of BEE of 2,4-D and 2,4-DP, Weedone CB, and its carrier to juvenile salmonids of the Pacific northwest.

Methods. A series of 96-h static acute toxicity tests were conducted in fresh water using several species of juvenile salmonids obtained from British Columbia hatcheries. The tests were undertaken from February to July 1989 in accordance with the procedure outlined by Environment Canada.

Results and Discussion. 2,4-D, 2,4-DP, and Weedone CB are highly toxic to salmonids (96-h LC_{50} values, 0.8–5.7 µg/L). They are also more toxic to young salmon than their carrier and diesel oil, irrespective of water types (soft, reconstituted, and hard). As well, the carrier of 2,4-D and 2,4-DP is much more toxic to salmonids than diesel oil, which is usually added at the rate of 10% oil and 90% product v/v to enhance adhesion on vegetation. During the 96-h exposure, the LC_{50} values remained almost unchanged after 24 h, except for Weedone CB in soft water and diesel oil in the three water types. Between fish species, the data suggest that 2,4-D, 2,4-DP, diesel oil, and Weedone CB are most toxic to pink salmon, irrespective of water types. The 96-h LC_{50} values of diesel oil for salmonids in different water types vary considerably (32–33 216 µg/L). The cause of this wide range of variation is not known. Diesel oil is most toxic to pink salmon when compared to coho salmon and rainbow trout irrespective of water types.

This bioassay study indicates that butoxyesters of 2,4-D, 2,4-DP, Weedone CB, and its carrier are highly toxic to juvenile salmonids of the Pacific Northwest. The acute toxicity to salmonids of 2,4-D, but not 2,4-DP, is affected by the characteristics of water. At the manufacturer's recommended rate of application (50 L/ha), the potential to generate concentrations acutely toxic to salmonids of Weedone CB is high in streams unintentionally oversprayed.

Publication Medium. Wan, M.T., R.G. Watts, and D.J. Moul, "Acute Toxicity to Juvenile Pacific Salmonids and Rainbow Trout of Butoxyethyl Esters of 2,4-D, 2,4-DP and Their Formulated Product Weedone CB and Its Carrier", *Bull. Environ. Contam. Toxicol., 45:* 604–611 (1990).

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creosote

5. RAILWAY RIGHT-OF-WAY CONTAMINANTS IN THE LOWER MAINLAND OF BRITISH COLUMBIA: POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) - (M.T. Wan, EP-P&Y Region)

Keywords. PAH, contaminants, railway right-of-way, British Columbia (lower mainland)

Introduction. In 1989, Environment Canada carried out a study to determine the levels of 16 selected PAH residues in the ballast and the right-of-way ditches of five railways operating in the lower mainland of British Columbia.

Objectives. The objectives of the study were 1) to determine the occurrence and levels of PAHs in right-of-way ditches and 2) to evaluate their significance and potential impact, if any, to aquatic invertebrates and Pacific salmon and trout in streams receiving discharges from the railway.

Methods. Sediment and water samples were taken at random from railway ballasts and ditches at six study sites. The selecting criteria of ditches were ditches that a) flowed directly into fish habitat or other waterbodies; b) did not receive industrial effluents, farm runoffs, or residential sewage; c) were situated within 5 m of the railway ballast; and d) contained water about 0.25 m in width and 0.1 m in depth. Reference and background levels of PAHs in ditches leading to fish streams were obtained for comparison from 'pristine' parklands and agricultural lands.

Results and Discussion. PAHs such as acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)-perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno-(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene were found in the ballast and ditch sediment/water of five railway rights-of-way. In the ballast, total levels of the 16 PAHs varied from 1.6 to 58.8 g/m^2, averaging 18.1 g/m^2. The mean concentration of the 16 PAHs in ditch sediments was 213.5 µg/g (range, 1.9 to 1168.7 µg/g). PAHs were not consistently found in ditch water at all study sites, but at sites where they occurred, the selected 16 compounds had an average total concentration of 606.3 µg/L (range, 1 to 3515.9 µg/L). PAHs were not detected in the ditches of 'pristine' parklands, but low concentrations were detected in some agricultural samples. Some biological implications of PAH-contaminated sediments and water from railway ditches discharging into fish habitats are discussed.

This study indicates that railway rights-of-way are a potential source of PAHs to the aquatic environment. The levels of these contaminants in ditch sediments and water varied, with the highest concentrations occurring where power/telecommunication line poles are erected in railway ditches. Although the PAH levels found in the ditch water were not acutely toxic to fish, chronic exposure of aquatic invertebrates and salmonid fish to low levels may be a concern.

Publication Medium. Wan, M.T., "Railway Right-of-Way Contaminants in the Lower Mainland of British Columbia: Polycyclic Aromatic Hydrocarbons (PAH)", *J. Environ. Qual., 20(1):* 228-234 (1991).

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Basacid Blue, 2,4-DA, 2,4-DE, glyphosate, triclopyr

6. ACUTE TOXICITY TO JUVENILE PACIFIC NORTHWEST SALMONIDS OF BASACID BLUE NB755 AND ITS MIXTURE WITH FORMULATED PRODUCTS OF 2,4-D, GLYPHOSATE, AND TRICLOPYR - (M.T. Wan, R.G. Watts, and D.J. Moul, EP-P&Y Region)

Keywords. Aquatic Toxicity Laboratory, North Vancouver, triphenylmethane dye, juvenile Pacific northwest salmonids, static acute toxicity, Roundup, Garlon 4

Introduction. Basacid Blue (BB) is a triphenylmethane dye manufactured by BASF Corporation, New Jersey. This product is used in British Columbia mainly as a marker by aerial and ground herbicide spray operators in forestry. Concerns were raised about the acute toxicity to young salmon of this dye and its mixture with several common herbicides.

Objective. The purpose of the study was to determine the acute toxicity to juvenile Pacific northwest salmonids of BB and its mixture with formulated products of 2,4-D, glyphosate, and triclopyr in different sources of dilution water.

Methods. A series of 96-h static acute toxicity tests were conducted in fresh water using several species of juvenile salmonids obtained from British Columbia hatcheries. The tests were conducted from February to June 1990 in accordance with the procedure outlined by Environment Canada, using three different types of dilution water: soft, intermediate, and hard.

Results and Discussion. Mixtures of BB at the rate of 100 mg/L with 2,4-DA, 2,4-DE, and Garlon 4 (respective mean 96-h LC_{50} values: 156, 49, 1.3 mg/L) are 2 to 3 times more toxic to salmonids than 2,4-DA, 2,4-DE, irrespective of water types, and to Garlon 4 in soft and hard water. The use of BB as a dye indicator with these herbicides has to be treated with caution, as it has the potential to greatly increase the toxicity to salmonids of these products, particularly at rates higher than 100 mg BB/L. BB (100 mg/L) mixture with Roundup does not increase the toxicity (96-h LC_{50}, 23 mg/L) to young salmonids of the herbicide. BB indicator for Roundup herbicide spray should not be greater than 100 mg/L (equivalent 8 mL BB per 100-L load), as the effects of this dye on young salmon at concentrations greater than the rate stated earlier have not been evaluated.

BB dye is quite toxic to salmonids, particularly in soft water. This dye (with no herbicides) is not likely to have an acute impact on salmonids at rates commonly used by foresters. However, the use of this dye as an indicator at the rate of 100 mg/L in spray mixtures increases the toxicity to young salmon of formulated products of 2,4-D amine, 2,4-D ester, Garlon 4 (except in intermediate water), but not Roundup, irrespective of water types. It is suggested that the use of Basacid Blue dye indicator for Roundup ground and aerial operations should not exceed 100 mg/L (equivalent to 8 mL Basacid Blue NB755 per 100 L spray mixture) per spray mixture load of 100 L.

Publication Medium. Wan, M.T., R.G. Watts, and D.J. Moul, "Acute Toxicity to Juvenile Pacific Northwest Salmonids of Basacid Blue NB755 and its Mixture with Formulated Products of 2,4-D, Glyphosate, and Triclopyr", *Bull. Environ. Contam. Toxicol., 47:* 471–478 (1991).

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pentachlorophenol

7. UTILITY AND RAILWAY RIGHTS-OF-WAY CONTAMINANTS IN THE LOWER MAINLAND OF BRITISH COLUMBIA: CHLOROPHENOLS (CPs) - (M.T. Wan, EP-P&Y Region)

Keywords. utility right-of-way, railway right-of-way, contaminants, chlorophenols, British Columbia (lower mainland)

Introduction. In 1990, Environment Canada carried out a study to determine the occurrence and levels of chlorophenols (CP) in selected utility and railway rights-of-way ditches in the lower mainland of British Columbia.

Objectives. The objectives of the study were 1) to determine the occurrence and levels of CPs in selected ditches of utility and railway rights-of-way and 2) to evaluate in a general way the significance of CPs found in these ditches to aquatic invertebrates and juvenile salmonids (*Oncorhynchus* spp.) in streams receiving the discharges.

Methods. Sediment and water samples were obtained from utility and railway rights-of-way ditches at 14 sites. The selecting criteria were ditches that a) were located near (0–1 m) poles treated in the 1980s and recently (1990); b) flowed directly into fish habitat; c) did not receive industrial effluents, farm runoff, or residential runoff/sewage; and d) contained water averaging less than 0.3 m in width, 0.05 m in depth, and with a flow rate averaging 0.025 m^3/s. Reference and background levels of CPs in ditches leading to fish streams were obtained for comparison from pristine watershed areas, parks, and agricultural lands.

Results and Discussion. CPs were found in both water and sediments of utility and railway rights-of-way ditches. In utility ditches, CP levels for water and sediments ranged, respectively, from 13.6 to 1408 µg/L and from 0.3 to 139 mg/kg. For railway right-of-way ditches containing utility timbers, CPs in water and sediments ranged, respectively, from 3.8 to 225 µg/L and from 0.4 to 49.7 mg/kg. CPs were not detected in ditch water and sediments from watershed areas and parklands, but low levels of CPs were found in some farm ditch sediments. Some biological implications of CP-contaminated sediments and water from utility and railway ditches discharging into fish habitats are discussed.

This study indicates that wood utility poles and railway ties are a potential constant source of CPs and possibly other contaminants, such as dioxins, furans, and PAH contaminants, to the aquatic environment. The levels of CPs varied, with the highest concentrations occurring where utility timbers and railway ties are installed close to the ditches. CP levels found in ditch water near the utility structures and railway ties exceed the 96-h LC_{50} of salmonids by about 1.5 order of magnitude. Those occurring downstream are within the range demonstrated to be harmful to the well-being of not only salmonids but also to benthic invertebrates. Feasible and practical options exist to reduce/eliminate the source of CP contaminants in utility and railway drainages.

Publication Medium. Submitted to the *Journal of Environmental Quality* in June 1991.

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TCMTB

8. ENVIRONMENTAL DYNAMICS OF BENZOTHIAZOLE-BASED PESTICIDES - (J.H. Carey and B.G. Brownlee, NWRI)

Keywords. anti-sapstain chemical, hydrolysis, photolysis

Introduction. Pesticides containing 2-(thiocyanomethylthio)benzothiazole (TCMTB) are being used as replacements for chlorinated phenols as anti-sapstain agents in the lumber industry in British Columbia. This study was carried out to provide information on the fate of TCMTB in receiving waters in British Columbia, and was part of a PESTFUND 1989/90 multi-agency study between DFO, EP-(P&Y) and NWRI entitled "TCMTB (Woodstat 30WB) Anti-sapstain Chemical: Levels in Receiving Waters and Sublethal Effects on Juvenile Salmon."

Objectives. The objectives of the study were to 1) predict the rates of disappearance of TCMTB by hydrolysis and photolysis under conditions typical of receiving waters in British Columbia; 2) identify degradation products of TCMTB; and 3) develop methods for analysis of TCMTB and metabolites in salmon bile.

Methods. High performance liquid chromatography was used to measure TCMTB and its breakdown product, 2-mercaptobenzothiazole (MBT). This was used to measure hydrolysis rates in buffer and natural waters, sunlight photolysis rates in buffer, and TCMTB and MBT in salmon bile.

Results and Discussion. The half-life for hydrolysis of TCMTB in British Columbia seawater at pH 7.8–8.0 and 24°C was about 750 hours. TCMTB readily underwent direct sunlight photolysis to give MBT and traces of benzothiazole. Analysis of bile of TCMTB-exposed salmon showed high concentrations of MBT, but TCMTB was not detected.

Publication Medium. This work was published as NWRI Contribution #90-58. Copies are available by contacting B. Brownlee at the address below.

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tributyltin, dibutyltin, monobutyltin

9. DETERMINATION OF ORGANOTIN COMPOUNDS IN SEDIMENT, WATER, AND BIOTA FROM BRITISH COLUMBIA MARINAS, SALMON FARMS, SHIPBUILDING/REPAIR FACILITIES, HEAVY BOATING TRAFFIC AREAS, AND CONTROL SITES - (C. Garrett and J. Shrimpton, EP-P&Y Region)

Keywords. British Columbia, sediment, mussels, clams, fish, organotin

Introduction. Tributyltin (TBT) is widely used as an antifouling agent in marine paints and coatings. Leaching of this compound from boat hulls can result in contamination in harbour and marina areas. Preliminary sampling of British Columbia harbours by Environmental Protection indicated that elevated levels of organotin were present in sediments, particularly in the vicinity of shipbuilding/repair facilities. Organotins were also present in fish from Vancouver Harbour.

In addition, several British Columbia salmon farms have used this compound as an antifouling agent on net pens. TBT is not registered for this use in Canada and, in 1987, Agriculture Canada issued orders to detain all TBT antifouling products being marketed for use in aquaculture. Previous studies have indicated that salmon from treated net pens accumulate TBT.

TBT is considered to be among the most toxic of all commercial chemicals released to the aquatic environment, and oyster spat have demonstrated especially high sensitivity. Because many marinas, active boating areas, and salmon farms in British Columbia are located in important oyster-growing areas, the potential release of TBT from these facilities is of particular concern.

Objectives. The objectives of the study were 1) verify the results of previous work at British Columbia salmon farms and to confirm that significant levels of TBT remain in the salmon and other environmental media despite the discontinuation of this compound in aquaculture; 2) determine the levels of TBT and other organotins in the biota, sediments, and water in the vicinity of British Columbia shipbuilding/repair facilities and marinas; 3) determine whether organotin levels vary seasonally in the biota and water in areas of known contamination; 4) determine the influence of organism size (mussels) on the level of organotin in the tissue; 5) determine the background level of organotins in shellfish from control areas; and 6) determine the influence of seasonal boating activity on organotin levels in shellfish from important oyster rearing areas.

Methods. Between February 1988 and March 1990, Environmental Protection conducted sampling at eight marinas, four salmon farms, six shipbuilding/repair facilities, three heavy boating traffic areas, and three control sites to determine the levels of organotins and other environmental contaminants in sediment, water, fish muscle and liver tissues, and where available, groundfish and shellfish (mussels, clams, and oysters). Analyses were performed by Seakem Analytical Services Ltd. in Sidney, British Columbia. Split samples were analyzed by the Environmental Protection Atlantic Laboratory.

Results and Discussion. Analytical data and specific methodologies have now been

provided by the two laboratories. Data analyses is ongoing.

Publication Medium. Pacific and Yukon Region Program Report is in preparation.

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creosote, pentachlorophenol, arsenic, copper

10. LEVELS OF CHEMICAL CONTAMINANTS IN SEDIMENTS AND FLATFISH COLLECTED IN THE VICINITY OF WOOD PRESERVATION SITES ON THE FRASER RIVER - (C. Garrett and J. Shrimpton, EP-P&Y Region)

Keywords. Fraser River, wood preservation, sediments, starry flounder, chlorophenols, chlorinated anisoles, organochlorine pesticides, PCBs

Introduction. Wood preservation refers to the pressure or thermal impregnation of chemicals into wood to a depth that will provide effective long-term resistance to attack by fungi, insects, and marine borers. The chemicals predominantly used in British Columbia for wood preservation are creosote, pentachlorophenol, and aqueous formulations of arsenic, copper and chromium, or copper and ammonia. The toxic nature of the chemicals makes them effective in preventing the attack of wood by live organisms, but can also be toxic to nontarget aquatic organisms. Consequently, the release of these chemicals to the receiving environment is cause for concern.

Objective. The purpose of the study was to determine the presence of chemicals such as chlorophenols, chlorinated anisoles, organochlorine pesticides, PAHs, metals, PCBs, and phthalate esters in sediments and flatfish in the vicinity of wood preservation facilities on the Fraser River.

Methods. Sediments were collected by Environmental Protection at five wood preservation industry sites (three using creosote, three using PCP, three using CCA, and one using ACA) in September 1990. In addition to analysis for select contaminants and particle size, SVR and SFR tests are being run on sediment samples. Contaminants in fish tissue will be determined on a whole-body basis. In addition, livers were taken from some of the fish for histopathological examination and MFO analysis. Gall bladders were removed for PAH metabolite analysis. All fish collected were examined externally for lesions and are being aged by otolith examination.

Results and Discussion. Sampling was completed at the five sites in the fall of 1990. The samples have been prepared and submitted to the analytical laboratories involved; however, analyses are not yet completed.

Publication Medium. Pacific and Yukon Region Program Report is in preparation.

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chlorophenols, organotin

11. LEVELS OF SELECT CONTAMINANTS IN WILD AND HATCHERY SALMON - (C. Garrett and J. Srimpton, EP-P&Y Region)

Keywords. British Columbia, salmon hatcheries, salmon (wild), *Oncorhynchus kisutch, Oncorhynchus tschawytscha, Oncorhynchus keta,* PCBs, chlorophenols, organotin

Introduction. Degradation of the environment has been cited as a major factor in the decline of Pacific salmon stocks. In fact, spills of various toxic chemicals and the resultant fish kills have been well documented. It is suspected that the long-term chronic discharge of toxic chemicals to the aquatic environment causes fractional but cumulative losses. Little information is available concerning "background" levels of industrial-based contaminants in Pacific salmon or on the levels of these contaminants in salmon from particular streams.

Objective. The objective of the study was to determine the level of specific contaminants in various tissues of several species of adult wild and hatchery salmon in British Columbia.

Methods. Salmon were collected by Environmental Protection in 1989–90 from nine salmon hatcheries and in the wild at three different locations. Samples of muscle, liver, milt, and egg tissues were obtained from these fish and are being homogenized by Environmental Protection before submission to the analytical laboratories involved in the study

Results and Discussion. Various salmon species have been collected as wild fish and at a number of salmon hatcheries in British Columbia just prior to spawning. Samples of muscle, liver, milt, and eggs were obtained for contaminants analysis. Samples are currently being homogenized in preparation for submission to the analytical laboratories.

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diazinon, quintozene, thiophanate-methyl

12. HAZARDS TO WILDLIFE OF GOLF COURSE TURF-CARE CHEMICALS -

(J.E. Elliott and I.E. Moul, CWS-P&Y Region)

Keywords. British Columbia (lower mainland), golf courses, waterfowl

Introduction. There are many golf courses in the lower mainland and Saanich Peninsula of British Columbia. A 1988 ruling by the British Columbia government to permit golf course development on land in the Agricultural Land Reserve (ALR) has resulted in many applications for new golf courses on ALR lands, particularly in the lower mainland. Turf maintenance requires heavy input of nutrients and pesticides, including insecticides such as diazinon, which are known to be highly toxic to birds, especially waterfowl (LD_{50} for mallard ducks is 3.5 mg/kg). In the United States, more than 100 kills of waterfowl have been attributed to the use of diazinon on golf courses and turf farms.

The lower mainland and the Saanich Peninsula are staging sites for migrating birds that are of international importance. The lower mainland also supports the highest concentrations of over-wintering birds in Canada. Initial surveys showed that waterfowl make extensive use of golf courses, attracted by grass, shelter, and wet areas.

Objectives. The objectives of the study were to 1) determine the usage patterns of turf care chemicals on British Columbia golf courses, and 2) describe the birds found on lower mainland golf courses and assess the hazard of pesticides to those birds.

Methods. Information on the use of turf care chemicals was gathered by distributing a five-page questionnaire to 75 golf courses throughout British Columbia. The questionnaire asked for information about the types and quantities of turf care products used, along with target areas (greens, tees, fairways, and roughs) and frequency of application. Bird use of golf courses was surveyed biweekly throughout one year at eight lower mainland locations by periodically recording all birds seen or heard while walking three or four 100-m wide transects through each course.

Results and Discussion. Questionnaires were returned by 33 golf courses (44% return). Three courses reported the use of diazinon on greens, while five courses reported its use on ornamental trees. The most commonly used fungicides were quintozene and thiophanate-methyl, also used primarily on greens. Most golf course superintendents reported decreased insecticide use in recent years. While there is considerable use of fungicides and herbicides, they are not particularly toxic to birds, but may pose a threat if runoff enters critical fish habitat such as salmon spawning streams.

During the summer, 4140 birds representing 70 species were recorded during 32 counts. Four species (European Starling, Barn Swallow, Northwestern Crow, and American Robin) accounted for over half of the birds counted. During the winter of 1990–91, 5890 birds representing 54 species were recorded on 44 counts. Three of the four species dominated the counts in winter, with the Mallard replacing the Barn Swallow as the fourth. No incidence of pesticide-related

bird mortality was observed on golf courses during the study.

The diversity of birds on golf courses appears to be related to the quality of habitat offered. Golf courses provide a park-like setting. The birds observed were commonly nonspecialized species that can adjust to a wide range of conditions and are found throughout North America. Preliminary results indicate a relationship between bird diversity and the quality of habitat observed on individual golf courses.

Publication Medium. The results will be published initially in a CWS technical report. The data will eventually be published in a scientific journal, probably *Agriculture, Ecosystems and Environment.*

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DDT, dieldrin

13. WILDLIFE AND AGRICULTURAL PESTICIDES IN THE OKANAGAN VALLEY: ORGANOCHLORINES AND REPRODUCTIVE SUCCESS OF CAVITY-NESTING PASSERINES IN ORCHARD AREAS, 1990 - (J.E. Elliott, CWS-P&Y Region)

Keywords. Okanagan Valley, Tree Swallow, House Wren

Introduction. The uses of persistent organochlorine insecticides, including DDT and dieldrin, were severely restricted by legislation in Canada and the United States during the early 1970s. Before that, DDT was used throughout the fruit-growing area of the Okanagan Valley for control of a wide variety of insect pests at an average application rate of 13.45 kg/ha.

In recent years there have been a number of reports of continuing high levels of DDE in wildlife inhabiting orchard areas of North America. Samples of prey species of the Peregrine Falcon, particularly robins and meadowlarks, collected and analyzed in 1983 contained mean DDE levels greater than 1.0 ppm, which precludes active reintroduction of falcons into the valley.

Objectives. The objectives of the study were 1) to determine residue levels of organochlorine pesticides in eggs of cavity-nesting birds breeding in the Okanagan Valley and 2) to investigate the utility of cavity-nesters as sentinel species for studying the effect of pesticide use on wildlife in the valley.

Methods. Nest boxes were set out in the late winter, 1990, prior to the return of migrant songbirds, in central British Columbia. Boxes were nailed to posts or trees in many mixed fruit orchards in two regions of the Okanagan Valley and in two areas of mixed, non-orchard agriculture. The orchard areas included farms around and south of Penticton and those around and north of Naramata, along the southeast portion of Lake Okanagan. The nonorchard areas were north of the Okanagan region and included White Lake and Kamloops. Nests were checked periodically during the early spring for occupancy, and if occupied, species was ascertained. After at least three eggs had been laid in a box, one egg was removed for analysis of organochlorine pesticides and PCBs. Eggs were pooled within species and area giving a total of eight samples. The nests were monitored throughout incubation and the nestling stage to determine parameters of reproductive success.

Results and Discussion. Eggs were analyzed for organochlorines at the National Wildife Research Centre (NWRC). Results for two species (Tree Swallows and House Wrens) indicated that DDE levels were much higher in eggs from the Okanagen Valley than from other areas in British Columbia.

Nest success of Tree Swallows using nest boxes in control and orchard areas was compared. Preliminary results indicate that productivity of Tree Swallows was higher in orchards than in control areas, possibly as a result of lower nest predation.

Further work is currently under way to investigate the possible effect of pesticide use on a resident ground-nesting species, the California Quail, and to collect eggs for organochlorine analysis from quail and other resident birds.

Publication Medium. The detailed data will be published in a CWS technical report with eventual publication in a scientific journal, probably the *Archives of Environmental Contamination and Toxicology.*

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DDT, dieldrin, chlordane, heptachlor, mirex, HCH, HCB

14. PATTERNS AND TRENDS OF CHLORINATED HYDROCARBON CONTAMINANTS IN SEABIRDS FROM THE PACIFIC COAST OF CANADA -

(J.E. Elliott and P.E. Whitehead, CWS-P&Y Region; and D.G. Noble and R.J. Norstrom, CWS-HQ)

Keywords. Pacific Coast, Double-crested Cormorant, Pelagic Cormorant, Leach's Storm-Petrel, Fork-tailed Storm-Petrel, Glaucous-winged Gull, Rhinoceros Auklet, Ancient Murrelet

Introduction. The oceans are the ultimate sink for many toxic substances via runoff and discharges from land-based sources, atmospheric transport, and direct dumping. Seabirds feed at high trophic levels in marine food webs and thus can integrate lipophilic contaminants over wide areas. Seabird eggs can be collected at low cost and with minimal effect on populations. The seabirds of the Pacific coast of Canada constitute a rich and diverse natural resource. Several million birds of more than 40 species breed or winter along the coast. Little is known of the effect of toxic chemicals on the health of those populations, especially relative to other human activities such as logging, oil transportation, and introduction of mammalian predators.

Objectives. The objectives of the study were 1) to determine organochlorine levels in representative seabird species from the Pacific coast of Canada and to assess possible effects on the health of populations and 2) to determine trends in chemical contamination of the marine environment using seabirds as indicators.

Methods. Eggs of Double-crested Cormorants (inshore, subsurface feeder), Rhinoceros Auklets (continental shelf, subsurface feeder), and Leach's Storm-Petrels (offshore, surface feeder) were collected at irregular intervals from 1970 to 1990 (regular monitoring at four-year intervals began in 1985) from colonies in the Strait of Georgia (Mandarte Island), the west coast of Vancouver Island (Cleland Island), the north mainland coast (Lucy Island), and the Queen Charlotte Islands (Hippa Island). Eggs have also been collected at a number of sites and in several years from colonies of Fork-tailed Storm-Petrels, Glaucous-winged Gulls, and Ancient Murrelets. Samples were analyzed at the National Wildlife Research Centre for DDT-related compounds, dieldrin, chlordane-related compounds, mirex, HCH, HCB, and PCBs.

Results and discussion. During the early years of the sampling, DDE may have adversely affected the breeding success of Double-crested Cormorants through effects on eggshell thickness. In recent years, Double-crested Cormorant populations have generally increased on the Pacific coast. Organochlorine levels were generally not high enough to have a serious effect on the health of the species sampled, although the body burden of some chemicals may influence the survival of birds during periods of severe stress.

DDE levels declined by about one-half between 1970 and 1990 in eggs of Leach's Storm-Petrels from the west coast of Vancouver Island; none of the other organochlorines in storm-petrel eggs showed any significant change with time. Levels of DDE, but not the other organochlorines,

declined significantly between 1970 and 1990 in Rhinoceros Auklet eggs from Lucy Island. With the exception of HCH, organochlorine levels generally declined between 1970 and 1990 in eggs of Double-crested Cormorants from Mandarte Island in the Strait of Georgia. Levels of the beta isomer of HCH tend to be much higher in seabird species from the Pacific coast of Canada than in fish-eating birds reported from other locations. In particular, both the eggs of the Ancient Murrelet and the Peregrine Falcon, a main predator of this seabird, collected from Langara Island on the northern tip of the Queen Charlotte Islands, have high levels of beta-HCH. The source of the HCH pollution is not clear, but may be a result of atmospheric transport from areas of current use in Asia.

Continuation of this monitoring program is planned to complement a similar program under way in Atlantic Canadian seabirds.

Publication Medium. The results from this work have been published in the following articles:

Noble, D.G. and J.E. Elliott, "Environmental Contaminants in Canadian Seabirds, 1968–85: Trends and Effects", *Canadian Wildlife Service Technical Report Series*, No. 13, Ottawa, 275 pp. (1986).

Elliott, J.E., D.G. Noble, R.J. Norstrom, and P.E. Whitehead, "Organochlorine Contaminants in Seabird Eggs from the Pacific Coast of Canada, 1971–1986", *Environ. Monit. Assess., 12:* 6782 (1989).

Elliott, J.E., D.G. Noble, R.J. Norstrom, P.E. Whitehead, M. Simon, M., P.A. Pearce, and D.B. Peakall, "Patterns and Trends of Organic Contaminants in Canadian Seabirds, 1968–1990", in: *Persistent Pollutants in the Marine Environment*, C.H. Walker (ed.), Pergamon Press (forthcoming).

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