

**PRESENCE AND LEVELS OF
PRIORITY PESTICIDES IN SELECTED CANADIAN
AQUATIC ECOSYSTEMS**

**Water Science and Technology Directorate
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Acknowledgments

This report represents the culmination of Canada's first National Water Quality Surveillance Program focused on current-use pesticides in vulnerable aquatic ecosystems and source waters. Funded by Environment Canada's Pesticide Science Fund, the surveillance program was conducted over a period of three years from 2003 to 2005. It was coordinated by the National Water Quality Monitoring Office, Environment Canada, and implemented in Environment Canada's regional offices. Several provincial environment ministries and other federal departments also played important roles in collecting data for this program. These partners included the Prince Edward Island Department of Environment, Energy and Forestry; the Nova Scotia Department of Environment and Labour; the New Brunswick Department of Environment, Le Ministère du Développement durable, de l'Environnement et des Parcs du Québec and Agriculture and Agri-Food Canada's Fredericton, New Brunswick, and Kentville, Nova Scotia, research centres. This report was coordinated and edited by Environment Canada's National Water Quality Monitoring Office, with substantial input from Environment Canada water quality monitoring staff across Canada. Writing assistance was obtained from Cantox Environmental Inc. of Ottawa.

Environment Canada's national Pesticide Science Fund Water Quality Surveillance team was represented on this project by the following scientists:

Janine Murray, Don Andersen, Rob Kent
National Water Quality Monitoring Office, Ottawa, ON

Taina Tuominen, Mark Sekela, Melissa Gledhill
Pacific and Yukon Water Quality Monitoring and Surveillance, Vancouver, BC

John Pasternak, Jen-ni Kuo, Mike Wan
Pacific and Yukon Environmental Protection, Vancouver, BC

David Donald¹, Nancy Glozier²
Prairie and Northern Water Quality Monitoring and Surveillance, Regina¹ and Saskatoon², SK

John Struger
Ontario Water Quality Monitoring and Surveillance, Burlington, ON

Myriam Rondeau
Quebec Water Quality Monitoring and Surveillance, Montreal, QC

Clair Murphy
Atlantic Environmental Protection, Charlottetown, PEI

Derek Muir¹, Camilla Teixeira¹, Chris Marvin¹, Allan Cessna²
National Water Research Institute, Burlington¹, ON and Saskatoon², SK

Ed Sverko¹, Richard Strub²
Analytical Laboratories, Burlington¹, ON and Vancouver², BC

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Glossary

Active ingredient	A chemical specifically designed to inhibit the proper functioning of an organism or class of organisms by a specific mode of action. A chemical pesticide is generally composed of an active ingredient and additional substances (e.g., surfactants, carriers).
Current-use pesticides	Pesticides that are currently registered for use in Canada under the Pest Control Products Act as administered by the Pest Management Regulatory Agency of Health Canada.
Detection limit	Estimate of a concentration above which it is fairly certain that the compound is present. Concentrations above this limit are almost certainly detected in the analysis. Using statistics, the certainty of detection can be quantified as 99%. Therefore, not detected indicates that the analyte may be present below the detection limit. Generally, the more interference from other compounds in the sample, the higher the detection limit.
Electrofishing	A fish survey technique that involves passing an electric current through the water to draw fish to the surface where they can be captured alive in a dip net.
Method detection limit	The method detection limit is a statistically derived expression of theoretical method detection capability. The method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. The method detection limit can vary from substance to substance and from measurement procedure to measurement procedure.
Monitoring/Surveillance	This denotes continuous or repeated observation, measurement and evaluation of health and/or environmental or technical data for defined purposes, according to prearranged schedules in space and time, using comparable methods for sensing and data collection. Evaluation requires comparison with appropriate reference values based on knowledge of the probable relationship between ambient exposures and adverse effects.
Pest Control Products Act	An Act to protect human health and safety and the environment by regulating products used for the control of pests.
Pesticide	A pesticide is a chemical mixture, or sometimes a biological agent, such as a bacterium, used to control, repel, attract or kill organisms that are considered pests.
Pests	Organisms, including insects, weeds, birds, mammals, fish and microbes that compete with humans for food destroy property, spread disease, or are considered a nuisance.
Volatilization	The process whereby a dissolved substance is vaporised.

1.0 INTRODUCTION

Canadians are concerned about the quality of their water resources (CESD, 1999; OCFP, 2004; FCM, 2006). Recent debates centred on issues ranging from the use of pesticides in urban environments to the environmental and health benefits of organically grown foods have increased societal awareness of the presence of pesticides in the Canadian environment. Pesticides enter the Canadian environment through urban and agricultural practices. In recent years, several reports (SCESD, 2000; Brimble et al., 2005) and audits (CESD, 1999; 2003) have highlighted the limited availability of data on the use, sale, occurrence, distribution and fate of current-use pesticides in Canada.

Prior to 2003, the federal government did not conduct systematic national-scale monitoring of priority pesticide residues in the Canadian environment. In a 1999 Canadian audit on toxic chemicals, the Commissioner of the Environment and Sustainable Development remarked that “there is no substitute for Canadian-based monitoring information” (CESD, 1999). Well-designed and well-equipped monitoring sites can and must serve multiple environmental issues. In May 2000, the Parliamentary Standing Committee on the Environment and Sustainable Development published an audit of Canada’s pesticide regulatory system (SCESD, 2000). During the Committee’s hearings, the issue of water contamination in both rural and urban areas emerged as a major issue. The Committee urged the Government of Canada “to substantially increase funding for research on and monitoring of the effects of pesticide products in the environment, to protect human health and the environment.” An Environment Canada report entitled *Threats to Sources of Drinking Water and Aquatic Ecosystem Health in Canada* (Environment Canada, 2001) identified pesticides as one of the 15 key threats to Canadian waters and highlighted the need for a Canadian pesticide monitoring program. Canada’s principal regulatory agency for pesticides, the Pest Management Regulatory Agency, recently identified Canadian water quality monitoring information as a top science priority to support its current regulatory decision making for pesticide re-evaluations and special reviews. The exposure profile of a pesticide product in the environment is important in determining the potential risk profile of the product. Without this information, our ability to predict or assess the potential for deleterious health and environmental effects is compromised.

Following this attention on pesticide use in Canada, from 2003 to 2005 Environment Canada conducted the country’s first nation-wide surveillance program focused on current-use pesticides (herbicides, insecticides, and fungicides) in vulnerable aquatic ecosystems and source waters. Funded by Environment Canada’s Pesticide Science Fund, which was created in 2003 to deliver on departmental priority pesticide surveillance, monitoring and research activities, and to enhance science-based decision-making regarding current-use pesticides, the program was entitled *The Presence, Levels and Relative Risks of Priority Pesticides in Selected Canadian Aquatic Ecosystems*. Using focused surveillance and monitoring, this program was designed to ascertain exposures to pesticide products in Canada. The new knowledge from this program will help the Pest Management Regulatory Agency and other federal and provincial agencies better

understand the presence and risks of in-use pesticides in Canadian aquatic environments. This report summarizes the results of this national water quality surveillance program.

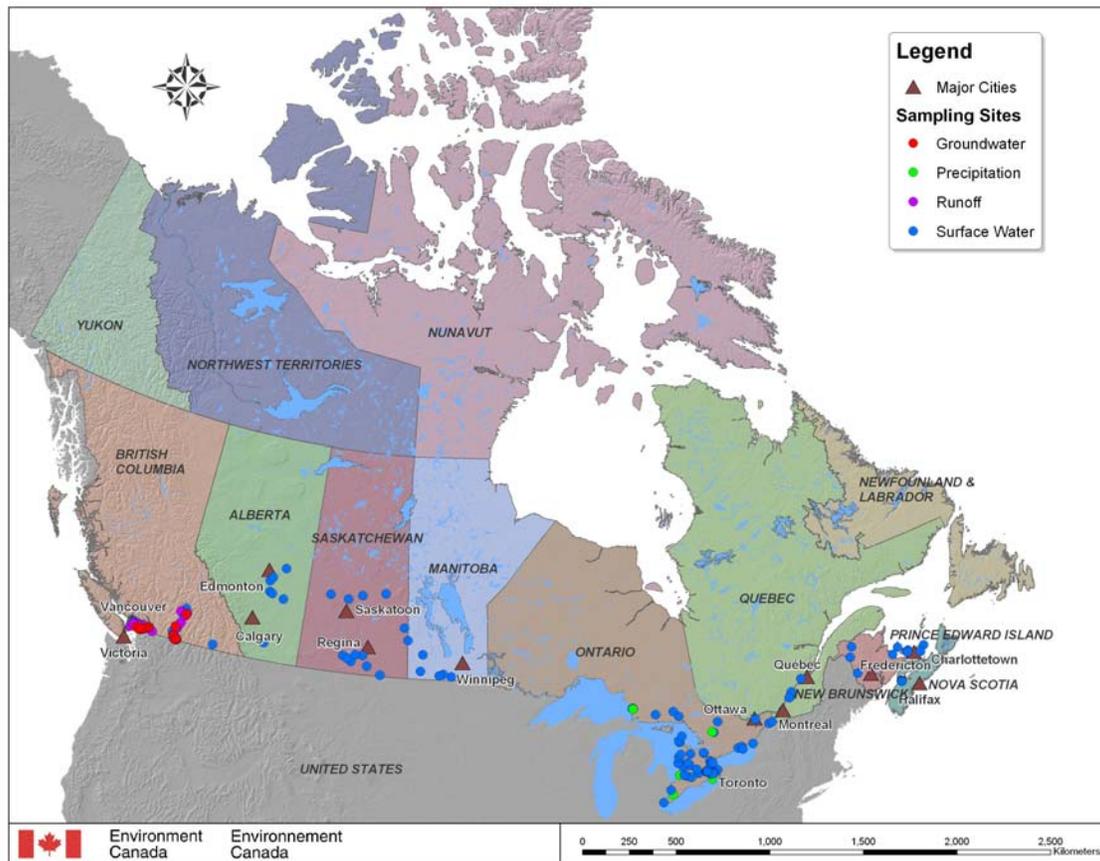


Figure 1 Pesticide Science Fund National Water Quality Surveillance Program Sites

1.1 Project Design

The Pesticides Science Fund (PSF) national water quality surveillance program consisted of a multitude of monitoring sites in every province, except Newfoundland and Labrador (See Figure 1). Short descriptions of the regional components that comprised this national water quality surveillance program are provided below. The individual regional project components were designed based on their unique aquatic environments, agricultural practices and pest management issues.

1.1.1 British Columbia

This project component focused on the detection and quantification of current-use pesticides (and their transformation products) in the aquatic environment of high-use pesticide regions of British Columbia. Areas sampled included the Lower Fraser River Valley and Okanagan Basin. Sampling was conducted in surface water, runoff from

fields, groundwater and rainwater, typically after significant rain events. Sample sites were located near agricultural and some urban areas, and in vulnerable watersheds, including drinking water sources and sensitive aquatic habitats.

1.1.2 Alberta, Saskatchewan and Manitoba

In this component, current-use pesticides in small rivers, small municipal reservoirs and wetlands in the prairie agro-ecoregion in Alberta, Saskatchewan and Manitoba were surveyed. The objective was to determine the distribution and concentration of current-use pesticides in prairie aquatic ecosystems, including reservoirs, wetlands and rivers. In addition, pesticide concentrations were assessed in drinking water supplies in small prairie communities. The drinking water reservoirs and their associated water treatment plants provided drinking water to communities that had populations ranging from 95 to 10,959. We intentionally selected communities where the source of drinking water to reservoirs was primarily snowmelt runoff from croplands, although occasionally rainfall runoff can also be a significant source of water to these reservoirs. In this region, evaporation exceeds precipitation, and rainfall runoff is a relatively rare event.

1.1.3 Ontario

A survey of surface water in selected Ontario rivers and of Areas of Concern in the Great Lakes, as defined in the Great Lakes Water Quality Agreement between Canada and the United States, was undertaken to identify and quantify the most prevalent current-use pesticides. Sampling included large-volume sampling from a limited number of Great Lakes connecting channels and small-volume sampling from smaller tributaries. Areas of focus included mainly agricultural areas and some areas of urban activity. The objectives of this component were 1) to determine spatial trends of current-use pesticides in surface waters of Ontario rivers and streams and Great Lakes Areas of Concern; 2) to develop and evaluate methods to investigate the occurrence of new pesticides; and 3) to collaborate on effects-based studies of pesticides on biota.

In addition, current-use pesticides were measured in surface water, air and precipitation on a latitudinal gradient away from major agricultural (and urban) areas. This program focused on lakes along a latitudinal gradient from high pesticide use areas in Ontario and Quebec that were within a range of 1 to 500 km from intensive agricultural zones. The objectives were 1) to determine pesticide concentrations and bioconcentration over the latitudinal gradient; 2) to determine atmospheric deposition of current-use pesticides via precipitation; and 3) to use collected data and information to assist in the modification of long-range transport assessment models to assess short- and medium-range potential of polar pesticides.

1.1.4 Quebec

Lake Saint Pierre is a highly important ecological site due to its great biodiversity and its wetlands (designated a Ramsar site since 1998 and a World Biosphere Reserve by UNESCO since 2000). This lake drains watersheds with intensive agricultural activities making it important to improve our knowledge of agricultural contaminants entering the waters of Lake Saint-Pierre and eventually the St. Lawrence River. The purpose of this component was to analyze temporal variations in pesticide concentrations at the outlet of the St. Lawrence River and several of its main tributaries. Sampling was carried out between 2003 and 2005 at the mouth of three streams draining agricultural land (the Yamaska, Nicolet and Saint-François rivers), at the outlet of Lake Saint-Pierre at Port-Saint-François, and at the mouth of the St. Lawrence River at Levis (near Quebec City).

1.1.5 Prince Edward Island, Nova Scotia and New Brunswick

This component was designed to evaluate the presence, magnitude and extent of pesticide contamination in different environmental media. In Prince Edward Island, the program focused on assessing pesticide residues in ambient groundwater, surface water, sediment, finfish and shellfish, while in New Brunswick the focus was primarily surface water. In Nova Scotia, both groundwater and surface water were sampled. Samples were taken during the summer and fall periods of 2003 to 2005, both during dry weather and following runoff-inducing rainfall events. The objectives included 1) determining the presence, concentration and potential risks associated with pesticides in groundwater, surface water, stream sediments and tissue in water systems draining intensive agricultural areas; 2) generating information on the fate of commonly used pesticides in the natural environment to support decision-making processes; and 3) generating information for use in refining risk management decisions and aiding risk communication.

1.2 Report Objective

The objective of this report is to interpret the results of the national water quality surveillance program and to summarize the three years of surveillance data for pesticides. The report begins with a short overview of how pesticides are regulated in Canada. This is followed by a discussion on sales/use data for pesticide products across Canada in the context of regional differences in climate, geography and other factors. The national water quality surveillance program project design, results and discussion are then presented. Finally, data gaps and future directions are discussed.

2.0 PESTICIDES IN CANADA

2.1 Pesticide Management in Canada

In Canada, the regulation of pesticide products is achieved using pre- and post-market scientific assessment, enforcement, education and communication with the public. These

tasks are distributed among the federal, provincial/territorial and municipal governments, and are achieved using a combination of acts, regulations, guidelines, directives and bylaws. At the federal level, Health Canada's Pest Management Regulatory Agency is responsible for the regulation of pest control products under the *Pest Control Products Act*. This act controls the import, sale, manufacture and use of pesticides in Canada. The objective of the *Pest Control Products Act* is to prevent unacceptable risks to human health and the environment from the use of pesticide products. The responsibilities described in the act include registering new pest control products, re-evaluating previously registered products, enforcing compliance with the act, and establishing maximum residue limits under the *Food and Drugs Act*. In addition, other federal legislation must be considered during registration and re-registration of pesticide products (e.g., *Species at Risk Act*).

The Pest Management Regulatory Agency within Health Canada is responsible for the regulation of pest control products, including the registration of pesticide products under the *Pest Control Products Act*. Any person or company that wishes to import and/or sell a pesticide product in Canada must submit a detailed registration package to the Pest Management Regulatory Agency. The registration package must contain the following information:

- the physical and chemical properties of the pesticide in question (active ingredient and end-use product)
- the fate and behaviour of the pesticide in the environment
- methods of measuring the pesticide in different media (e.g., plants, animals and foods)
- potential impacts of the pesticide to human and animal health
- effects on non-target terrestrial and aquatic organisms
- the efficacy of the pesticide, including the economics of its use, its effectiveness and its sustainability

The Pest Management Regulatory Agency decision regarding whether to register a new product is based on an evaluation of the applicant's registration package. The pesticide product is granted registration if sufficient data demonstrate that it does not pose unacceptable risks to humans and the environment. The registration is generally valid for five years, at which time it is subject to re-evaluation. The Pest Management Regulatory Agency is in the process of re-evaluating all pesticides registered before December 31, 1994.

If new information becomes available, or a new use pattern is proposed for a registered pesticide, a special review of a pesticide or group of

Legislation Used in Managing Pesticide Products
<p>Federal <i>Pest Control Products Act</i> <i>Food and Drugs Act</i> <i>Canadian Environmental Protection Act</i> <i>Fisheries Act</i> <i>Migratory Birds Convention Act</i> <i>Species at Risk Act</i></p>
<p>Provincial/Territorial Pesticide acts and associated regulations Drinking water legislation</p>
<p>Municipal Municipal pesticide by-laws</p>

pesticides may occur. For example, in 1990, a special review of the active ingredient carbofuran occurred in response to requests from Environment Canada scientists. That special review resulted in the granular formulations of carbofuran being deregistered.

All provincial and territorial governments in Canada have passed laws designed to minimize the risk to human health and the environment from pesticide products. These laws and associated regulations provide a framework for how pesticides are sold, used, applied and licensed. For example, the *Pesticides Act* in Ontario stipulates that only licensed applicators or certified agriculturalists can apply pesticides included in Schedule 1. Schedule 1 pesticides are defined in Ontario as those pesticides that are both highly toxic and persistent in the environment. Any person may use pesticides under Schedules 3, 4 and 6 – ranging from moderate toxicity and persistence to low toxicity and no persistence – without any licensing or permitting requirements, but they must follow the pesticide label instructions. Several of the provincial/territorial pesticide acts also require the collection of pesticide product sales and/or use data and may address other issues related to pesticide use, application and licensing.

Municipal governments play a significant role in protecting human health and the environment through the management of drinking water, sewage treatment, solid waste, land use, transportation, energy planning, and pesticides (FCM, 2006). Recently, numerous municipalities in Canada have enacted by-laws restricting the use of pesticide products within municipal limits.

Thus, all levels of Canadian government play important roles in the management of pesticide products and require up-to-date information on the presence of pesticides in the Canadian environment to inform regulatory, policy and management decisions.

2.2 Pesticide Use in Canada

There is no central registry of pesticides sales or use data in Canada. Under the authority of the Pest Control Products Sales Information Reporting Regulations, the Pest Management Regulatory Agency coordinates the development of a National Pesticides Sales Database through the National Pesticides Sales Database Working Group of the Federal/Provincial/Territorial Committee on Pest Management and Pesticides (PMRA, 2004). The goal of this working group is to determine cost effective inputs and outputs for the national pesticide sales database, taking into consideration issues and needs of provinces, territories and stakeholders. Thus, a national source of sales and use data will become available in the near future. Several Canadian provinces and territories maintain sales and/or use records within their jurisdictions, or they commission regular surveys to determine which active ingredients are being sold and used. In some cases, provincial pesticide legislation requires that this information be collected. Together, these data provide a national patchwork of sales and/or use data.

In the absence of use statistics, pesticide sales data are often employed, and, in turn, provide an indication of the potential for exposure to pesticides in the environment. This is based on the assumption that pesticide products that are sold will be applied; sales and use data are therefore often considered to be equivalent. It is also assumed that pesticides

will be used within a year of their purchase, that they will be used in the sector that they were purchased in (e.g., agriculture, domestic), and that they will be used in the province or territory in which they were purchased (Brimble et al., 2005). Limitations of using sales and use data to approximate environmental exposure include these: 1) active ingredients may no longer be registered and sold in Canada, but may still be an environmental concern (e.g., DDT and metabolites); 2) pesticide applicators may purchase large quantities of pesticides, but not actually apply them in that year; and 3) pesticides may be purchased outside the province where they are applied.

This section describes the sale and use of pesticide active ingredients in Canada. Pesticide product sales and use data were obtained from the Environment Canada report *Pesticide Utilization in Canada: A Compilation of Current Sales and Use Data* (Brimble et al., 2005). Data were most often reported for the agricultural sector and rarely available for the industrial and domestic sectors. Although the agricultural sector is generally the largest user of pesticides by volume, the domestic sector is often the most intense user (i.e., kg active ingredient/hectare). Domestic sector applications are typically for cosmetic purposes, such as lawn treatment. The intensity of urban pesticide use in Canada is estimated to be 0.97 to 3.65 times higher than agricultural use (Brimble et al., 2005).

2.2.1 British Columbia

In 2003, pesticide sales in British Columbia totalled 4,666,709 kg of active ingredient. The majority of pesticides were sold and used in the forestry sector, with anti-microbial products (e.g., wood preservatives) accounting for 71.7% of total sales. Of the remaining 28.3%, sales were distributed among insecticides (8.8%), fungicides (6.5%), herbicides (6.1%) and other pesticides (6.9%) (Brimble et al., 2005). Twenty of the 287 active ingredients registered for use in British Columbia accounted for 93% of sales. Ten pesticide active ingredients were used exclusively in the agriculture sector and accounted for 63% of total sales. They were insecticidal and herbicidal mineral oils; the herbicide glyphosate; the fungicides sulphur, mancozeb, chlorothalonil and captan; the insecticides diazinon and *Bacillus thuringiensis*, as well as the fumigants metam and methyl bromide (Brimble et al., 2005). Between 1991 and 2003, four active ingredients were consistently reported among the highest sales volumes: mineral oil (insecticidal or adjuvant), glyphosate (herbicide), sulphur (fungicide) and mancozeb (fungicide) (Brimble et al., 2005). In British Columbia, the Lower Fraser Valley and Okanagan Basin account for 46% and 44%, respectively of the agricultural and domestic-use pesticides sold in British Columbia (ENKON Environmental Ltd., 2005).

British Columbia Top 10 Active Ingredients by Sales/Use (Agricultural)
Glyphosate (Herbicide)
<i>Bacillus thuringiensis</i> kurstaki (Insecticide)
Sulphur (Fungicide)
<i>Bacillus thuringiensis</i> H-14 (Insecticide)
Mancozeb (Fungicide)
Chlorothalonil (Fungicide)
Metam (Fumigant)
Diazinon (Insecticide)
Captan (Fungicide)
MCPA (Herbicide)

2.2.2 Alberta, Saskatchewan and Manitoba

Herbicides are the most common type of pesticide sold and applied in Alberta, Saskatchewan and Manitoba (Brimble et al., 2005; Waite et al., 2004). In 1998, 9 300 508 kg of active ingredient were sold in or shipped into Alberta. Of this total volume, herbicides accounted for the majority of sales (76.4%), followed by adjuvants and surfactants (13.5%), insecticides (5.42%), fungicides (3.43%), other pesticides (0.87%), rodenticides (0.38%), and growth regulators (0.06%). Seven of the top 10 pesticides sold were herbicides. The top five pesticides sold were the herbicides glyphosate, MCPA, 2,4-D and triallate and a surfactant blend adjuvant (Brimble et al., 2005). In

Alberta, the agricultural sector accounted for 95.8% of pesticide sales, of which 77% were herbicides (Brimble et al., 2005). The commercial and industrial sector represented 3.3% of total sales. Herbicides had the highest sales and use (75%) followed by insecticides (15.1%). Insecticides were used for the control of mosquitoes and to manage pests in the forest industry. Fungicides represented 8.7% of pesticide sales in 1998, with most of these products being used on golf courses. Domestic use and other (livestock, structural) sectors accounted for only 0.9% of total pesticide sales in 1998. However, pesticide use in this sector was the most intense, with 3.1 kg of active ingredient used per hectare. As a comparison, pesticide use in the agricultural sector averaged 0.79 kg of active ingredient per hectare (Brimble et al., 2005).

Detailed information on pesticides sales and use is lacking for Saskatchewan. However, some information is available on pesticide use in Saskatchewan in Donald et al. (1999), Donald et al. (2001) and in “protected” documents from the 1990s. In Saskatchewan, commonly used pesticides include glyphosate, 2,4-D, MCPA and bromoxynil. Brimble et al. (2005) reported that Saskatchewan is the greatest user of pesticides in Canada, accounting for an estimated 36% of total Canadian sales.

Pesticide sales and use data for Manitoba were reported by the Manitoba Crop Insurance Corporation for the years 2001–2003 (Manitoba Crop Insurance Corporation, 2003). Pesticide use is estimated by the number of hectares (ha) for which farmers report pesticide use and not by the quantity of pesticides applied. Thus, the data reported are only an estimate of pesticide use. Herbicides are the most frequently used pesticides, accounting for 84.9% of the province’s total use. Insecticides and fungicides each account for less than 10% of pesticide use (Brimble et al., 2005). The five most frequently used pesticides in Manitoba are the

Prairies

Top 10 Active Ingredients by Sales/Use (Agricultural)

- Glyphosate (Herbicide)
- 2,4-D (Herbicide)
- MCPA (Herbicide)
- Triallate (Herbicide)
- Ethalfuralin (Herbicide)
- Flucarbazone (Herbicide)
- Bromoxynil (Herbicide)
- Trifluralin (Herbicide)
- Imazamethabenz-methyl A/B (Herbicide)
- Chlorpyrifos (Insecticide)

Ontario

Top 10 Active Ingredients by Sales/Use (Agricultural)

- Glyphosate (Herbicide)
- Atrazine (Herbicide)
- s-metolachlor (Herbicide)
- 1,3-Dichloropropene (Fungicide)
- Dimethanamid (Herbicide)
- Dicamba (Herbicide)
- MCPA/MCPB (Herbicides)
- 2,4-D (Herbicide)
- Pendimethalin (Herbicide)
- Chloropicrin (Nematocide)

herbicides 2,4-D, glyphosate, MCPA/MCPB, bromoxynil and ethalfluralin. The intensity of pesticide use in Manitoba is low, at 0.41 kg of active ingredient applied per hectare (Brimble et al., 2005).

2.2.3 Ontario

In 2003, herbicides accounted for 79.4% of the 4 218 238 kg of pesticides used in the Ontario agricultural sector, followed by nematocides (7.9%), fungicides (7.4%), growth regulators (3.4%) and insecticides (1.9%) (McGee et al., 2004; Brimble et al., 2005). The five pesticides used in the greatest quantity were the herbicides glyphosate, atrazine, s-metolachlor and metolachlor and the nematocide 1,3-dichloropropene. Between 1998 and 2003, the use of glyphosate increased by 58% in Ontario. Conversely, the use of atrazine in Ontario declined by 20% during the same period, and the use of metolachlor and s-metolachlor declined by an average of 61% (Brimble et al., 2005). A 14% increase in herbicide use was reported from 1998 to 2003. This was attributed to an increase in the amount of land used to grow winter wheat (Brimble et al., 2005). Between 1998 and 2003, overall pesticide use on fruit and vegetable crops decreased by 20%. This trend was attributed to decreased crop acreage and the use of alternative pest management strategies (Brimble et al., 2005).



Application of herbicides on row crops in southern Ontario (Photo: John Kraft)

Table 1 presents figures on the intensity of pesticide use on different crops over time. The data show that the intensity of pesticide use for most crops decreased from 1983 to 2003 (Brimble et al., 2005). Tobacco requires the highest intensity of pesticide use, followed by fruit, vegetables and field crops. The majority of Ontario's agricultural output consists of field crops, where the intensity of pesticide application is relatively low, compared to other crops. (Brimble et al., 2005).

Table 1 *Intensity of pesticide use on major crops in Ontario (kg active ingredient/ hectare)*

Crops	1983	1988	1993	1998	2003
Tobacco	39.77	31.56	18.78	9.65	19.14
Fruit	19.81	20.64	20.73	20.34	9.87
Vegetables	4.89	6.01	6.01	4.72	2.65
Field corn	3.47	2.90	2.90	2.28	1.77
Soybeans	3.52	3.27	1.65	1.50	1.48
Total field crops, fruit & vegetable	2.10	1.85	1.85	1.35	1.09
Field crops	1.92	1.63	1.63	1.15	1.00
Grains	0.44	0.58	0.72	0.56	0.58

Source: McGee et al. (2004).

The Province of Ontario does not collect data on domestic pesticide use. However, Struger et al. (2002) reported pesticides commonly used by professional applicators in lawn care (Table 2). Ten pesticides accounted for 95% of total applications.

Table 2 *Pesticides most often used by Ontario professional lawn care applicators in 1993*

Active ingredient	Proportion of total used (%)
Mecoprop	19.34
2,4-D	17.28
Dicamba	14.61
Diazinon	9.80
Chlorpyrifos	9.66
Dichlorprop	8.04
2,4-D butyric acid	7.82
MCPA	3.72
<i>Bacillus thuringiensis</i>	3.08
Glyphosate	1.43

Source: Struger et al. (2002).

2.2.4 Quebec

In 2001, 3 276 257 kg of pesticide active ingredients were sold in the province of Quebec (Brimble et al., 2005). Herbicides accounted for 52.3% of pesticide sales, followed by insecticides (18.7%) and fungicides (16.5%) while other pesticides (e.g., biocides, rodenticides) make up the remaining 12.5% of sales. The quantities of specific pesticide active ingredients sold were not reported for reasons of confidentiality. However, the type of pesticide (i.e. herbicides, fungicide, and insecticides) and ranking of active ingredient sales were disclosed. Among the top five pesticides sold were the herbicides glyphosate, atrazine and s-metolachlor and the insecticides naphthalene and mineral oil. Data from 1992 to 2001 showed a decline in sales of herbicides, insecticides, adjuvants and plant growth regulators. During this period, there was an increase in the sales of fungicides, biocides, soil fumigants and rodenticides. The use of atrazine and metolachlor decreased while the use of glyphosate increased (Brimble et al., 2005).

Quebec Top 10 Active Ingredients by Sales/Use (Agricultural)
Glyphosate (Herbicide)
Atrazine (Herbicide)
Insecticidal Mineral Oil (Insecticide)
S-metolachlor (Herbicide)
Naphthalene (Insecticide)
Mancozeb (Fungicide)
2,4-D Amine (Herbicide)
Metiram (Fungicide)
Bentazon (Herbicide)
Pendimethalin (Herbicide)

The agricultural sector was the primary user of pesticides, accounting for 79.1% of sales. The domestic sector accounted for 10.8% of pesticides active ingredients sold (355 212 kg), of which insecticides were the most common products (262 933 kg), followed by herbicides (53 313 kg), fungicides (36 422 kg) and rodenticides/repellents (2 544 kg). Other sectors (e.g., Green space maintenance, Industrial, Forestry) account for the remaining 10.1% of sales (Brimble et al., 2005).

2.2.5 Prince Edward Island, Nova Scotia and New Brunswick

A total of 814 103 kg of pesticide active ingredients were sold in Prince Edward Island in 2002. Fungicides accounted for 82% of sales, followed by herbicides (13.7%) and insecticides (4.3%) (Brimble et al., 2005). The fungicides chlorothalonil and mancozeb accounted for 74% of total pesticides sales. Other frequently used pesticides included the herbicides MCPA, diquat and sodium metaborate tetrahydrate and the fungicides metaxyl-m and metiram (Brimble et al., 2005). Prince Edward Island has a higher intensity of pesticide application than other provinces. Between 1993 and 2001, the intensity of pesticide application ranged from 2.8 to 4.1 kg of active ingredient per hectare.

Prince Edward Island, Nova Scotia and New Brunswick Top 10 Active Ingredients by Sales/Use (Agricultural)
Mancozeb (Fungicide)
Mecoprop (Herbicide)
Glyphosate (Herbicide)
Chlorothalonil (Fungicide)
Linuron (Herbicide)
Hexazinone (Herbicide)
Metiram (Fungicide)
MCPA (Herbicide)
Diazinon (Insecticide)

Sales and use data for Nova Scotia indicate 441 609 kg of pesticide active ingredients were sold in 2003. Herbicides accounted for 67.7% of sales, followed by fungicides (13.4%), other pesticides (9.6%; not defined), insecticides (8.6%) and adjuvants (0.56%) (Brimble et al., 2005). The highest selling pesticide was mecoprop, followed by mineral and vegetable oils, hexazinone, glyphosate and metiram.

Sales data for New Brunswick indicate that 781 923 kg of pesticide active ingredients were sold in 2003 (New Brunswick Department of the Environment and Local Government, 2005; Brimble et al., 2005). Within New Brunswick, fungicides accounted for 52.4% of sales, followed by herbicides (25.7%), growth regulators (13.3%), insecticides (5.8%), anti-microbials (2.32%) and other pesticides (e.g., surfactants, rodenticides). The top five active ingredients sold were the fungicides mancozeb and chlorothalonil and the herbicides glyphosate, linuron and MCPA (Brimble et al., 2005).

2.3 Identifying Priority Pesticides

Pesticides are formulated to have specific effects on particular classes of biota. They are generally classed as herbicides, insecticides, fungicides and vertebrate pest toxicants and are used to control target species of plants, insects, moulds and fungi, and vertebrate pests, respectively. Unintentional impacts on non-target species can occur (e.g., fish kills in Prince Edward Island; (PEI, 2006)). Impacts are influenced by both the toxicity of the chemical and the exposure scenario (amount, timing and method of application). Direct exposure in farm fields, field margins and urban environments has the potential to impact biota. Contributions from soil erosion, surface runoff, spray drift and atmospheric deposition are also important sources to aquatic habitats and resident biota.

Why Sample for Transformation Products?

Transformation products are an important consideration when designing sampling plans for pesticide product surveillance. Transformation products, often called degradation products, are chemicals that occur as a result of a change to the parent pesticide. These changes may occur due to biological processes (e.g., microbial metabolism), physical processes (e.g., photolysis), or chemical processes (e.g., hydrolysis). The presence of transformation products in environmental media is therefore an indicator that the parent pesticide was present and may also help estimate in what quantities. They also provide information on the fate of a pesticide in environmental media. Some transformation products are known to be more toxic to biota than the original pesticide product.

Pesticide products may migrate to environmental media other than that to which the product was applied (i.e., urban lawns, agricultural soils, crop foliage). The major mechanisms involved in pesticide transport to non-target areas include volatilization, spray drift, leaching to groundwater, and surface runoff containing both dissolved and particle-associated pesticides (Figure 2).

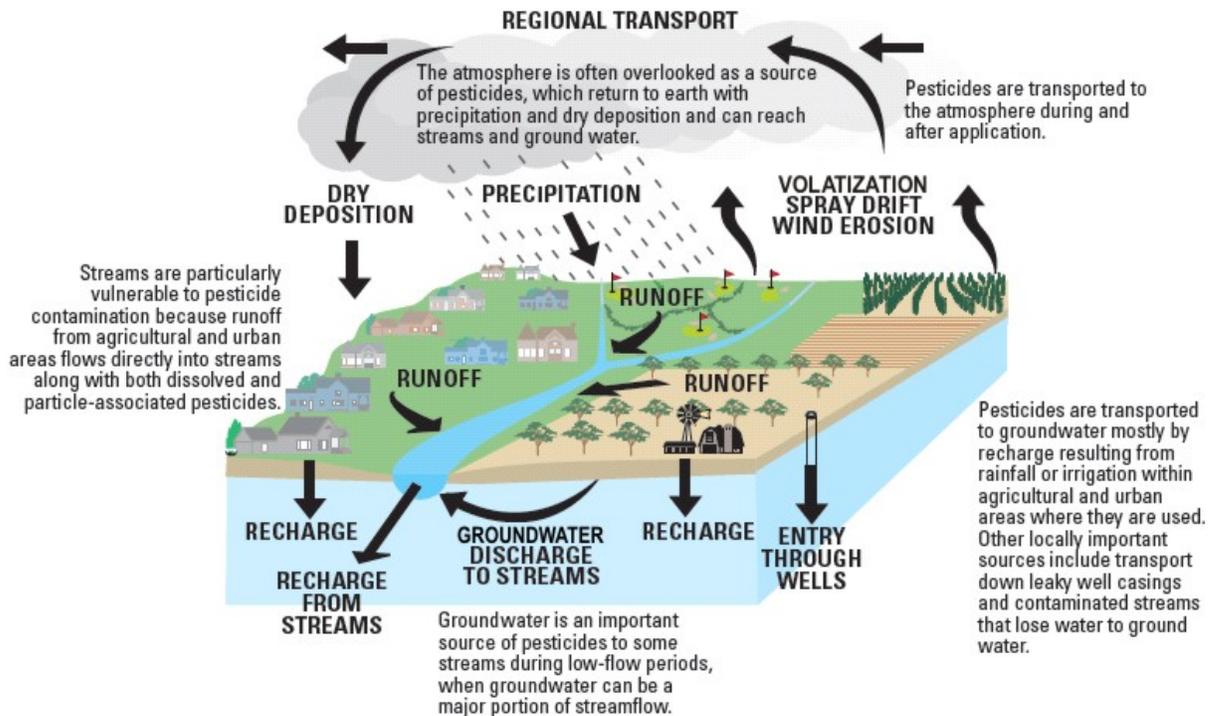


Figure 2 Pesticide transport in the environment. Modified from Gilliom, 2005

A common problem in many agricultural regions related to the application of pesticides is migration to local surface and ground water bodies, although some pesticides can also migrate into the local airshed via processes such as volatilization and spray drift. When pesticides migrate to non-agricultural media, there is the potential for adverse effects on non-target organisms. This potential is generally highest for pesticides applied directly to farmland soil or foliage, and is considerably lower for seed treatment pesticides. Surface runoff, spray drift/atmospheric deposition and soil erosion are typically the predominant means by which pesticides applied in agricultural systems reach surface waters. However, the amount of pesticide lost from agricultural systems, and how it is lost, is highly variable. Pesticide loss is influenced by a number of factors, including:

- the quantity of pesticide applied
- the physical-chemical properties and the environmental fate and transport of the pesticide
- the site-specific factors that influence the environmental fate and transport of the pesticide (e.g., topography, soil type and texture, soil chemistry, water chemistry, geology, hydrogeology)
- local meteorological factors such as precipitation and winds
- the frequency of pesticide applications and the time between treatments
- crop production practices
- the use of beneficial management practices (e.g., buffer zones, soil and water conservation, setbacks, application during appropriate weather conditions, etc.)

With respect to the environmental impacts of agricultural pesticides, there has been an emphasis on evaluating surface water impacts, as agriculture occurs within watersheds, and its practices often interact with various watershed processes (Gregorich et al., 2000). Agriculture is generally practised over large land acreages, for many months of the year, and multiple pesticide applications may be required (e.g., insecticide, herbicide and fungicide applications) (Gregorich et al., 2000).

More than 500 pesticides are currently registered for use in Canada (Brimble et al., 2005). It would be extremely costly to survey for all registered pesticides at all sampling sites. More importantly, not all registered pesticides are considered to be of equal environmental concern. Given that different regions of Canada have unique aquatic environments, agricultural practices and pest management issues, priority pesticides were identified for surveillance on a region-by-region basis. Existing knowledge of pesticide product sales and use, agricultural practices and known environmental effects provided the basis for this priority-setting exercise. A total of 141 pesticides and transformation products were included in this surveillance program; however, in each regional component, a subset of this list was monitored, reflecting the unique agricultural and pest management practices in that region of Canada (Table 3).

Table 3 List of active ingredients and transformation products monitored in each of during the 2003–2005 national water quality surveillance program

Pesticide or transformation product ^a	CAS RN ^b	Class ^c	Registration status ^d	Geographic region ^e					
				Atl	QC	ON ₁	ON ₂	Prairie	BC
<i>1-naphthol</i>	90-15-3	--	T		X				
2,3,6-TBA	50-31-7	Herbicide	UNK			++		++	
2,4,5-T	93-76-5	Herbicide	H		X	++		++	
2,4-D	94-75-7	Herbicide	R	X	++	++		++	++
2,4-DB	94-82-6	Herbicide	R		++	++		X	
<i>2,4'-DDD</i>	53-19-0	Insecticide	T						++
<i>2,4'-DDE</i>	3424-82-6	Insecticide	T						++
2,4'-DDT	789-02-6	Insecticide	H						++
2,4-DP (Dichlorprop)	120-36-5	Herbicide	R		X	++		++	
<i>4,4'-DDD</i>	72-54-8	Insecticide	T						++
<i>4,4'-DDE</i>	72-55-9	Insecticide	T						++
4,4'-DDT	789-0-6	Insecticide	H						++
Alachlor	15972-60-8	Herbicide	H				++		X
Aldrin	309-00-2	Insecticide	H						++
Ametryn	834-12-8	Herbicide	H				++		++
<i>AMPA</i>	1066-51-9	--	T			X			
Atrazine	1912-24-9	Herbicide	R	++	++	++	++	++	++
Azinphos-methyl	86-50-0	Insecticide	R	++	X	++	X	X	++
Azoxystrobin	131860-33-8	Fungicide	R	X					
Bendiocarb	22781-23-3	Insecticide	R		X				
Bentazone	25057-89-0	Herbicide	R		++				
Benzoylprop-ethyl	22212-55-1	Herbicide	UNK			X		++	
Bromoxynil	1689-84-5	Herbicide	R		++	++		++	++
Butralin	33629-47-9	Herbicide	R				++		++
Butylate	2008-41-5	Herbicide	H		X	X	++	++	++
Captan	133-06-2	Fungicide	R				X		++
Carbaryl	63-25-2	Insecticide	R	X	X				
Carbofuran	1563-66-2	Insecticide	R	X	++				
Chlordane, alpha (cis)	5103-71-9	Insecticide	H						++
Chlordane, gamma (trans)	5103-74-2	Insecticide	H						++
Chlorfenvinphos	2701-86-2	Insecticide	H		X				
Chlorothalonil	1897-45-6	Fungicide	R	++	++	X	++		++
Chloroxuron	1982-47-4	Herbicide	H		++		X		
Chlorpyrifos	2921-88-2	Insecticide	R		++	++	++	++	++
<i>Chlorpyrifos-oxon</i>	5598-15-2	--	T						++
<i>Chlorpyrifos-methyl</i>	5598-13-0	--	T						++
Clopyralid	1702-17-6	Herbicide	R		++	++		++	
Cyanazine	21725-46-2	Herbicide	R		++				++
Cycloate	1134-23-2	Herbicide	H				X		
Cypermethrin	52315-07-8	Insecticide	R	++					++
Dazomet	533-74-4	Nematocide	R				++		

Table 3 List of active ingredients and transformation products monitored in each of during the 2003–2005 national water quality surveillance program

Pesticide or transformation product ^a	CAS RN ^b	Class ^c	Registration status ^d	Geographic region ^e					
				Atl	QC	ON ₁	ON ₂	Prairie	BC
		Fungicide Herbicide							
Dacthal (DCPA)	1861-32-1	Herbicide	R				++		++
<i>Desethylsimazine</i>	--	--	T			++		++	
<i>Deisopropylatrazine</i>	--	--	T		++				
<i>Desethylatrazine</i>	6190-65-4	--	T		++	++	++	++	++
Diallate I	17708-57-5; 2303-16-4	Herbicide	H			X		X	
Diallate II	17708-58-6; 2303-16-4	Herbicide	H			X		X	
Diazinon	333-41-5	Insecticide	R		X	++	++	X	++
<i>Diazinon-oxon</i>	962-58-3	--	T				++		++
Dicamba	1918-00-9	Herbicide	R	X	++	++		++	++
Dichlorvos	62-73-7	Insecticide	R		X				++
Diclofop-methyl	51338-27-3	Herbicide	R		X	X		++	
Dieldrin	60-57-1	Insecticide	H						++
Dimethenamid	87674-68-8	Herbicide	R		++		++		++
Dimethoate	60-51-5	Insecticide	R	++	++	++	++	++	++
Dinoseb	88-85-7	Herbicide	H		X				
Disulfoton	298-04-4	Insecticide	R		++	X	++	X	++
<i>Disulfoton-sulfone</i>	2497-06-5	--	T						++
Dithiocarbamate (total) (e.g., mancozeb, maneb, etc.)	--	Fungicide	R	++					
Diuron	330-54-1	Herbicide	R		++				
Endosulfan a	959-98-8	Insecticide	R	++		++	++		++
Endosulfan b	33213-65-9	Insecticide	R	++			X		++
<i>Endosulfan-sulphate</i>	1031-07-8	--	T			++	++		++
Endrin	72-20-8	Insecticide	H						++
<i>Endrin-aldehyde</i>	7421-93-4	--	T						++
<i>Endrin-ketone</i>	53494-70-5	--	T						++
EPTC	759-94-4	Herbicide	R		++		++		
Ethalfuralin	55283-68-6	Herbicide	R			X	++		++
Ethametsulfuron ME	97780-06-8	Herbicide	R					++	
Ethion	563-12-2	Insecticide	R			X		X	++
Fenitrothion	122-14-5	Insecticide	R		X				++
Fenoprop (Silvex)	93-72-1	Herbicide	H		X	++		++	
Fluazifop	69335-91-7	Herbicide	R						++
Flufenacet	142459-58-3	Herbicide	R				X		X
Flumetsulam	98967-40-9	Herbicide	R		++				
Flutriafol	76674-21-0	Fungicide	R				++		++
Fonofos	944-22-9	Insecticide	H	X	X	++	++	X	++
Glyphosate	1071-83-6	Herbicide	R			++			

Table 3 *List of active ingredients and transformation products monitored in each of during the 2003–2005 national water quality surveillance program*

Pesticide or transformation product ^a	CAS RN ^b	Class ^c	Registration status ^d	Geographic region ^e					
				Atl	QC	ON ₁	ON ₂	Prairie	BC
HCH, alpha	319-84-6	Insecticide	H						++
HCH, beta	319-85-7	Insecticide	H						++
HCH, delta	319-86-8	Insecticide	H						++
HCH, gamma (Lindane)	58-89-9	Insecticide	H				++		++
Heptachlor	76-44-8	Insecticide	H						++
<i>Heptachlor-epoxide</i>	1024-57-3	--	T	X					++
Hexachlorobenzene	118-74-1	Insecticide	H						++
Hexazinone	51235-04-2	Herbicide	R	++					++
Imazamethabenzmethyl (A)	81405-85-8	Herbicide	R			++		++	
Imazamethabenzmethyl (B)	81405-85-8	Herbicide	R			++		++	
Imazethapyr	81335-77-5	Herbicide	R		++	++		++	
Imidacloprid	138261-41-3	Insecticide	R	++		X			
Linuron	330-55-2	Herbicide	R	++	++		++		++
Malathion	121-75-5	Insecticide	R		X	++	X	++	++
MCPA	94-74-6	Herbicide	R	++	++	++		++	++
MCPB	94-81-5	Herbicide	R		X	++		++	
Mecoprop (MCP)	7085-19-0; 93-65-2	Herbicide	R	X	++	++		++	++
Metalaxyl	57837-19-1	Fungicide	R	++					
Metolachlor	51218-45-2	Herbicide	R		++	++	++	++	++
Methamidophos	10265-92-6	Insecticide	R						++
Methidathion	950-37-8	Insecticide	H		X				
Methoprene	40596-69-8	Insecticide	R						++
Methoxychlor	72-43-5	Insecticide	R						++
Metobromuron	3060-89-7	Herbicide	R	X					
Metribuzin	21087-64-9	Herbicide	R	++	++	++	++	++	++
Metsulfuron ME	74223-64-6; 5585-64-8	Herbicide	R					++	
Mevinphos	298-01-1	Insecticide	H		X				
Mirex	2385-85-5	Insecticide	H						++
Myclobutanil	88671-89-0	Fungicide	R		++	++	++		
Naled (Dibrom)	300-76-5	Insecticide	R			X	++	X	++
Napropamide	15299-99-7	Herbicide	R				++		
Nicosulfuron	111991-09-4	Herbicide	R		X				
Nonachlor, cis-	3734-49-4; 5103-73-1	Insecticide	H						++
Nonachlor, trans-	39765-80-5	Insecticide	H						++
<i>Oxychlorane</i>	26880-48-8; 27304-13-8	--	T						++
Parathion	56-38-2	Insecticide	R		X	X		X	
<i>Parathion-ethyl</i>	--	--	T						++
<i>Parathion-methyl</i>	298-00-0	--	T		X		X		X
Pendimethalin	40487-42-1	Herbicide	R			++	++		++

Table 3 *List of active ingredients and transformation products monitored in each of during the 2003–2005 national water quality surveillance program*

Pesticide or transformation product ^a	CAS RN ^b	Class ^c	Registration status ^d	Geographic region ^e					
				Atl	QC	ON ₁	ON ₂	Prairie	BC
Permethrin	52645-53-1	Insecticide	R	++					++
Phorate	298-02-2	Insecticide	R		X	X	++	X	X
Phosalone	2310-17-0	Insecticide	R		X	++	++		
Phosmet (Imidan)	732-11-6	Insecticide	R			X	++	X	++
Picloram	1918-02-1	Herbicide	R		X	++		++	
Pirimiphos-methyl	29232-93-7	Insecticide	NR						++
Propiconazole	60207-90-1	Fungicide	R			++	++		
Quintozene	82-68-8	Fungicide	R						++
Quizalofop-ethyl	76578-14-8	Herbicide	R			X	++		
Rimsulfuron	122931-48-0	Herbicide	R		X				
Simazine	122-34-9	Herbicide	R		++	++	++	++	++
Sulfosulfuron	141776-32-1	Herbicide	R					++	
Tebuconazol	107534-96-3	Fungicide	R				++		++
Tebuthiuron	34014-18-1	Herbicide	H		X				
Tecnazene	117-18-0	Fungicide	H				X		++
Tefluthrin	79538-32-2	Insecticide	R			X	++		
Terbacil	5902-51-2	Herbicide	R	X			X		
Terbufos	13071-79-9	Insecticide	R		X	X	++	X	++
Thifensulfuron ME	79277-27-3	Herbicide	R					++	
Triallate	2303-17-5	Herbicide	R			X	++	++	++
Tribenuron ME	101200-48-0	Herbicide	R					++	
Trichlorfon	52-68-6	Insecticide	R			X	++		
Triclopyr	55335-06-3	Herbicide	R		X				++
Trifluralin	1582-09-8	Herbicide	R		X	X	++	++	++

^a Each transformation product is italicized and indented below its parent pesticide.

^b Chemical Abstracts Service Registry Number.

^c Class describes the most common classification for the active ingredient. Some active ingredients can be multipurpose (e.g., an insecticide and a fungicide). Transformation products may also have herbicidal, insecticidal or fungicidal properties, but the products are not classified here.

^d The registration status was determined using the Pest Management Regulatory Agency web database (PMRA, 2005); R - Registered; T - Transformation product; UNK - Unknown status; NR - Never registered in Canada; H - Historical.

^e Atl: Prince Edward Island, Nova Scotia and New Brunswick; QC: Quebec; ON₁: Ontario surface water study; ON₂: Ontario lake transect study; Prairie: Alberta, Saskatchewan and Manitoba; BC: British Columbia.

++ Active ingredients were monitored and detected.

X Active ingredients were monitored, but not detected.

3.0 OVERVIEW OF REGIONAL CHARACTERISTICS

Regional characteristics, including physical, chemical and meteorological conditions and/or specific regional agricultural practices are important considerations when developing a national surveillance program. While these characteristics are separate from, and unrelated to the properties of the pesticides themselves, they can have a major influence on the presence of pesticides in environmental media (i.e., surface water, groundwater, precipitation, soil, sediment, air and tissue). These media influence the likelihood and magnitude of exposure and therefore resulting adverse biological effects. This section provides a short review of regional characteristics in Canada.

3.1 Pesticide Use

The largest area of agricultural production in Canada is the prairie region of western Canada that includes Alberta, Saskatchewan and Manitoba. Due to the large land areas producing grains and oilseeds, more pesticides are applied in the prairies than in any other region of Canada. The sheer mass of pesticides being applied to the landscape increases the possibility of these products entering aquatic ecosystems. Interestingly, Chambers et al. (2000) reported that in the prairie provinces (Manitoba, Saskatchewan, and Alberta), less pesticide is used on a per hectare basis than in other agricultural regions of Canada. At the same time, the frequency of pesticide application is generally lower in the prairie provinces than in eastern Canada. This reflects the drier climate on the Prairies. Many pests (particularly insect and fungal pests) tend to be more abundant in regions with higher annual precipitation. In Prince Edward Island, for example, it is not uncommon for farmers to apply 12 to 15 applications of pesticides, primarily fungicides, during the potato-growing season (Murphy and Mutch, 2004). This intensity of application is not required in many other Canadian regions as moisture levels are lower, hence discouraging insect and fungal growth.

3.2 Precipitation

Regional differences in precipitation can influence the quantity of pesticides entering surface waters. Overall, there is a greater amount of precipitation in the regions east of Manitoba than in the prairie region of Canada (Martin et al., 2000). British Columbia has geographic regions, such as the Okanagan Basin, which are very dry, and coastal regions, which are temperate rainforests. Higher precipitation leads to a greater potential for pesticides to enter surface waters through surface runoff, leaching to groundwater, and soil erosion. Increased rainfall can also cause pest outbreaks, increasing the need for pesticide application. However, the extent to which these processes result in pesticides entering surface waters will also depend considerably on local topography, as well as hydrological and hydrogeological conditions. In Alberta (and Manitoba to a lesser extent), lower precipitation levels suggest a reduced frequency of pesticide surface runoff. However, when runoff does occur, the pesticide concentrations in the runoff water can be relatively high (Chambers et al., 2000; Donald et al., 2005). The dry climate and long winters in the prairie provinces may also reduce the rate of pesticide transformation

somewhat, relative to the eastern provinces. In the prairie provinces, the greatest loss of pesticides applied to farmland is generally via volatilization into the atmosphere, rather than surface runoff or soil erosion (Chambers et al., 2000). Precipitation intensity can have a great influence on the deposition of pesticide products. Donald et al. (2005) reported that high concentrations of pesticides are often associated with light precipitation.

3.3 Regional Air Flow Trajectory

The volatilization of pesticides is an important factor in the presence of some pesticides across Canada. Donald et al. (2005) reported that many of the pesticides detected in the Vanguard area in southeastern Saskatchewan likely originated in North and South Dakota, Kansas, Nebraska and Texas. For example, endosulfan, though detected in the Vanguard area, is not used in Saskatchewan, but is used extensively on vegetable and fruit crops in the United States (Donald et al., 2005). Long-range transport of pesticides will vary by region, depending upon the movement of air between regions and the pesticides entrained in the air mass (Donald et al., 2005; Struger et al., 2004; Haffner and Hites, 2003; van Dijk and Guicherit, 1999).

3.4 Soil Erosion

Soil erosion, and the resulting sedimentation/siltation effects on adjacent surface waters, can be a pathway for pesticides (which may be sorbed to soil particles or dissolved in soil pore water) to enter nearby water bodies (e.g., Chow et al., 2000). The rate and extent of soil erosion is primarily determined by soil type and texture, slope, amount of vegetation cover and other factors affecting the stability of banks and slopes and local meteorology (Chambers et al., 2000). Chow et al. (1999) reported that in the Saint John River Valley, New Brunswick, soil losses of 20 to 30 t/ha/yr can occur from potato fields, due to the rolling topography of the area. This soil loss can result in a substantial degradation of surface water quality in the impacted waterway. Quebec, Prince Edward Island and New Brunswick typically experience a higher frequency of soil erosion problems in agricultural regions.

Substantial soil erosion can occur due to wind action. This tends to be a much larger problem in the drier prairie provinces (such as Alberta) than in central or eastern Canada (Chambers et al., 2000). Soil erosion due to wind action can transport soil particles and sorbed pesticides considerable distances, and contaminate local airsheds, as well as surface water bodies that are located distant to where the pesticides were applied. Watercourses or water bodies located immediately downwind of a severely eroding field can be filled by wind-blown soil (Chambers et al., 2000). The amount of cultivated land in the Prairies that is considered by Agriculture and Agri-Food Canada to be at high or severe risk for wind erosion dropped from 15% (5 million hectares) to 6% (2 million hectares) between 1981 and 1996 (Chambers et al., 2000). This change was attributed to improved cropping systems and tillage practices.

In Quebec, agricultural regions are reported to have a generally low estimated risk of soil erosion from water, with 88% of cropland considered by Agriculture and Agri-Food Canada to be in the tolerable risk class in 1996 (Chambers et al., 2000). Quebec is considered unique among the provinces since it has no active cropland that is considered to be in the high and severe risk classes for soil erosion by water (Chambers et al., 2000).

3.5 Cropping Intensity

Cropping intensity within a region can have a significant impact on the type and concentration of pesticide residues detected. For example, of the five major potato-producing provinces (Prince Edward Island, Manitoba, New Brunswick, Alberta and Quebec), Prince Edward Island is unique in that it is the most intensively farmed potato-growing area in Canada (Statistics Canada, 2006). Of the 567,000 hectares of land in Prince Edward Island, approximately 111 300 hectares (20% of the province's total land area) are involved in potato production (Murphy and Mutch, 2004). Prince Edward Island is also the largest producer of potatoes in Canada (AAFC, 2004). As a result of this high potato farming intensity, there are few surface water bodies in Prince Edward Island that are not susceptible to potential impacts from pesticides used in potato production. Farming intensity is also high in the Lower Fraser Valley, British Columbia, where approximately 6,000 farms are located on 100 000 ha (Bellett, 2003). Over 44% of all pesticides sold in British Columbia are used in the Lower Fraser Valley. Given the high cropping intensity and pesticide use in this region, it is reasonable to assume that surface waters, wetlands and other environmental media in this area may have higher concentrations of pesticide products and transformation products than less intensively cropped areas of the province.

4.0 TECHNICAL APPROACH

4.1 Sampling Design

Designing a water quality surveillance program on a national scale is a challenging undertaking. The information collected across the country needs to be comparable, yet the uniqueness and individual priorities of each region must be acknowledged and reflected in the program design. Each regional surveillance component identified a list of vulnerable aquatic ecosystems and/or drinking water sources in high pesticide use areas that it wished to focus on in each of the three years of this program. Assessments of watershed vulnerability included factors such as estimates of pesticide use, runoff potential, and sensitivity of receiving habitats. Table 4 presents the focus of each of the regional components as a means of selecting potentially vulnerable aquatic ecosystems.

Table 4 *Selection of potentially vulnerable watersheds by each regional component*

Region	Focus of regional surveillance
British Columbia	<ul style="list-style-type: none"> • Agricultural and urban sites in the Lower Fraser Valley and the Okanagan Basin • Intense agricultural areas with high pesticide sales/use
Alberta, Saskatchewan and Manitoba	<ul style="list-style-type: none"> • Numerous prairie reservoirs, rural community tap water, rivers and sensitive wetlands. Includes Wascana Creek, both upstream and downstream of the City of Regina.
Ontario	<ul style="list-style-type: none"> • Great Lakes Areas of Concern and connecting channels, as well as smaller streams affected by both agricultural and urban activity in the Niagara Peninsula and Hamilton/Burlington areas • Southwestern Ontario lakes located within conservation areas or parks and having no major tributaries flowing through agricultural areas into the lakes • Northern Ontario reference lakes
Quebec	<ul style="list-style-type: none"> • Several main tributaries (Yamaska, Saint-François and Nicolet rivers) leading from intensive agricultural areas to the St. Lawrence River
Prince Edward Island, Nova Scotia and New Brunswick	<ul style="list-style-type: none"> • Several rivers in agricultural areas, including the Mill, Wilmot, Souris, Founds, Montague and Dunk rivers and North Brook, Prince Edward Island; Thomas Brook, Nova Scotia; and Buctouche Stream, Black Brook, Lanes Creek and Five Fingers Brook, New Brunswick • Groundwater from in-use potable water supplies in intensive agricultural areas of Prince Edward Island and Nova Scotia • Sediments, finfish and shellfish from the same river systems in Prince Edward Island as the surface water samples

All of the regional studies were conducted from the spring to early winter (generally from April to November), roughly corresponding to the growing season in Canada. This is also the groundwater recharge period. Large-scale agricultural application of pesticides and domestic use of pesticides generally occur during this period. Surface water samples collected early in the season (spring) may also have been affected by snowmelt runoff, which has the potential to mobilize pesticides and their transformation products. In many of the regional studies, surface water sampling was conducted after precipitation events to observe potential maximum pesticide concentrations due to increased mobility through such processes as surface runoff and atmospheric deposition. Table 5 presents the number of samples taken in each environmental medium (i.e., surface water, groundwater, drinking water, sediment, precipitation, tissue and air) in each of the regional studies.

Table 5 *Number of samples taken in each province as part of the National Water Quality Surveillance Program*

Province	Media sampled	Number of samples taken ^a			Total
		2003	2004	2005	
British Columbia	Groundwater	10	17	14	41
	Precipitation	0	5	3	8
	Surface water	26	70	42	138
Alberta	Reservoir	45	15	10	70
	Tap water	0	5	5	10
	Wetlands	0	20	0	20
	Rivers	0	0	14	14
Saskatchewan	Reservoir	54	18	11	83
	Tap water	0	6	6	12
	Wetlands	0	30	0	30
	Rivers	57	69	34	160
Manitoba	Reservoir	36	12	8	56
	Tap water	0	4	4	8
	Wetlands	0	10	0	10
	Rivers	12	12	35	59
Ontario (Latitudinal gradient study)	Surface water	61	71	36	168
	Precipitation	NR	24	NR	60
	Air	NR	NR	NR	12
Ontario (Surface water study)	Surface water	162	228	183	573
Quebec	Surface water	50	70	62	182
Prince Edward Island	Groundwater	108	122	125	355
	Surface water	27	15	40	82
	Sediment	0	30	0	30
	Shellfish	17	4	9	30
	Finfish	10	6	9	25
Nova Scotia	Surface water	0	19	29	48
	Groundwater	0	6	6	12
New Brunswick	Surface water	23	18	15	56

^a NR – Not reported.

4.2 Sampling Methods

The sampling methods used in the regional components of this national surveillance program were similar for most environmental media. A short description of the sampling approach in each of the regions is provided below.

4.2.1 British Columbia

Two 1-L samples were collected for each of surface water, groundwater and field runoff for each sampling location. One of the samples was used for analyzing one group of pesticides (known as the acid-extractable herbicides) and the second sample was analyzed for the remaining pesticides. Both sample types were preserved in the field to maintain the integrity of the sample. In 2003 and 2004, 20-L samples of water were collected from surface waters and groundwaters using a submersible pump and Teflon tubing. These 20-L samples were passed through a resin column (XAD-2), which removed the pesticides from the water onto the column for subsequent analysis. This method of collection usually increases the capability of detecting very low concentrations of chemicals in water. The comparison of results showed that, for this survey, the 1-L samples were sufficient to detect pesticides at low concentrations. Thus, the survey was continued in 2005 by using the 1-L samples. Usually, sampling for runoff, surface water and groundwater were conducted once during each season for each year. Rainwater samples were collected using the XAD resin columns. The rainwater samplers are designed to collect samples only when it is raining, so a period of about 60 days was required to collect enough rainfall for analysis.



Pesticide sampling in the lower Fraser Valley (Photos: Melissa Gledhill; Mark Sekela)

4.2.2 Alberta, Saskatchewan and Manitoba

Water samples were collected from a total of 15 reservoirs located in Manitoba, Saskatchewan and Alberta from 2003 to 2005. Samples were collected after snowmelt in March, twice per month from May to August, and then once in October and in January. Each sample was analyzed for 16 acidic herbicides, 13 neutral herbicides or their metabolites, and five sulfonyleurea herbicides. In addition, water samples were collected in July and August, and were analyzed for 13 organophosphate insecticides. Samples for nutrients, physical parameters and major ions were collected in August.



Collecting water samples on a Saskatchewan reservoir (Photo: David Donald)

Water samples were also collected from rivers in agricultural landscapes in Manitoba and Saskatchewan from 2003 to 2005. The pesticides monitored and the sampling frequencies were identical to the above description for reservoirs.

In July 2004, 60 wetlands were sampled for acid, neutral and sulfonyleurea herbicides. The wetlands were in clusters of 10, with one cluster of 10 in Manitoba, three in Saskatchewan, and two in Alberta. The clusters of 10 were distributed across a precipitation gradient, with a paired cluster in Saskatchewan (10 wetlands in cropland and 10 in nearby pasture).

All surface water samples were collected in pre-cleaned 1-L amber glass bottles from near the centre of aquatic ecosystems at mid-depth for rivers, at a depth of 30 cm for wetlands, at 2 m in reservoirs, and from the drinking water tap of rural water treatment plants.

4.2.3 Ontario

In 2003, large-volume samples (16 L) were collected up to six times in the St. Clair River, Detroit River, at Niagara-on-the-Lake in the Niagara River, Wolfe Island and two sites on the St. Lawrence River above and below Cornwall. One-litre samples were collected approximately eight to 12 times at four sites in the Hamilton Harbour Area of Concern, three sites in the Toronto Area of Concern and three sites in the Bay of Quinte Area of Concern, as well as five tributary locations in the Niagara Peninsula and the Hamilton/Burlington areas.

Samples were preserved, extracted and analyzed for triazines, phenoxy acid herbicides and organophosphorus insecticides. All samples were sub-sampled and analyzed for atrazine, metolachlor and diazinon using immunoassays. A maximum of 162 samples were analyzed for the three individual pesticide scans (organophosphate insecticides, triazine herbicides, and phenoxy acid herbicides). Replicate samples and field blanks were also collected monthly. In 2004, 228 samples were collected from 18 stream locations and 15 amphibian breeding locations and analyzed for triazine and phenoxy acid herbicides and organophosphorus insecticides. In 2005, 183 samples were collected at 21 stream locations and seven amphibian breeding locations and analyzed for triazine and phenoxy acid herbicides and organophosphorus insecticides.



**Pesticide sampling in Southern Ontario
(Photo: Janine Murray)**

Samples were preserved, extracted and analyzed for triazines, phenoxy acid herbicides and organophosphorus insecticides. All samples were sub-sampled and analyzed for atrazine, metolachlor and diazinon using immunoassays. A maximum of 162 samples were analyzed for the three individual pesticide scans (organophosphate insecticides, triazine herbicides, and phenoxy acid herbicides). Replicate samples and field blanks were also collected monthly. In 2004, 228 samples were collected from 18 stream locations and 15 amphibian breeding locations and analyzed for triazine and phenoxy acid herbicides and organophosphorus insecticides. In 2005, 183 samples were collected at 21 stream locations and seven amphibian breeding locations and analyzed for triazine and phenoxy acid herbicides and organophosphorus insecticides.

In the latitudinal transect lake study, field trips to collect lake water and install precipitation and passive air samplers were conducted starting in late April each year. Phytoplankton (<100 µm) were sampled by continuous centrifugation (1 000 L of centrifuged water at 6 L/min at specified sites) and zooplankton by a net haul (> 100 µm).

A Hydrolab (Rickly Hydrological Co., Columbus, OH) was used to determine the temperature profile in the water column. Surface water samples were collected for water chemistry and 19-L water samples were pumped through a glass fibre filter into stainless steel soft drink cans. Surface water samples (taken from depths of 1–4 m, depending on the lake) were collected from all lakes, and deep water samples (taken from depths of 4.5–50 m) were collected from lakes where the temperature profile indicated stratification. The filtered water was spiked with a solution containing d5-atrazine and δ -HCH, and then pumped through a resin column to extract the analytes. These columns were labelled, sealed and kept on ice for the duration of the field trip.

Precipitation was collected monthly using wet-only automated samplers, beginning in late May and ending in September in 2003 and 2004 and in October in 2005. XAD resin columns were then returned to the laboratory, where they were processed as described for water samples. Passive air samplers were deployed for approximately three months in each sampling year.

4.2.4 Quebec

The samples from the tributaries were collected from the tops of bridges, using metal sampling devices, each weighted with a lead block. The samples from the St. Lawrence River were collected using a Teflon pump. All samples were collected in 1-L clear glass bottles. The insides of the lids of the bottles containing the samples to be analyzed for organophosphorus pesticides, triazines, carbamates and substituted ureas were covered with aluminum foil. The insides of the lids of the bottles containing the samples to be analyzed for aryloxy acids were covered with Teflon and the samples were acidified to pH <2 by the addition of 5 mL/L sulphuric acid (H_2SO_4) 10 N. All samples were stored in a cooler until delivery to the laboratory and stored at 4°C until analysis.



Sampling for pesticides in Quebec
(Photo: Myriam Rondeau)

4.2.5 Prince Edward Island, Nova Scotia and New Brunswick

Surface water grab samples were collected from stream channels at each site in Prince Edward Island, Nova Scotia and New Brunswick, as indicated in Table 4. Grab samples of groundwater were taken from in-use potable water supplies (municipal, central and individual water supply wells) in each region (Table 4). Samples were held in 1-L pre-



Automated sampling station in PEI (Photo: Clair Murphy)

cleaned amber glass containers. Stream samples were normally collected 12–15 cm below the surface of the water. In Prince Edward Island in 2005, samples were collected using two TELEDYNE ISCO (model 6712) portable automatic samplers that were triggered to initiate a sampling based on rainfall intensity. Sediment samples from Prince Edward Island streams were collected in 200-mL amber glass containers using a disposable wood spatula. Samples were collected from natural deposition areas in the immediate proximity of the water sampling sites. Finfish were collected from Prince Edward Island streams using electrofishing techniques, while shellfish samples were collected by hand from the upper estuarine areas. The groundwater sampling program in Prince Edward Island included both a random Island-wide component and concentrated sampling in intensive potato growing areas. Groundwater samples collected in both Nova Scotia and Prince Edward Island were taken from existing plumbing outlets on individual water supply wells prior to any form of treatment. All samples were preserved in the field as required, placed on ice and forwarded for analysis to a laboratory that is certified by the Canadian Association for Environmental Analytical Laboratories.

4.3 Analytical Methods

Each regional component made arrangements for analytical support either through one of Environment Canada's laboratories, a provincial laboratory or a private laboratory.

4.3.1 *British Columbia*

Multi-residue pesticides were analyzed in aqueous samples containing none or negligible visible particulates (<1% solids). The samples were spiked with deuterium and ¹³C-labelled quantification standards in acetone. Samples were then liquid-liquid extracted with dichloromethane. The extract was dried over anhydrous sodium sulphate, reduced in volume and solvent exchanged to hexane in preparation for extract cleanup. Cleanup of the sample extracts were conducted using a microsilica chromatography column. The column was prepared by packing a 10% deactivated 0.75-g silica column into a glass wool-plugged transfer pipette. The column was moistened with 10 mL of hexane. The 1-mL extract was then loaded to the column drop by drop. The column was eluted with 5 mL of 10% methanol in dichloromethane. All eluates were collected and transferred to a round bottom flask; 5 mL of acetone and 1 mL of isooctane were added and the mixture was concentrated to 1 mL by rotary evaporation. The resulting extract was transferred to a centrifuge tube and reduced to 300 µL under a steady stream of nitrogen. The extract was then transferred to a microvial and spiked with labelled recovery (internal) standards prior to instrumental analysis.

For acidic herbicides analysis, aqueous samples were spiked with ¹³C isotope-labelled surrogate standard solution, hydrolyzed with sodium hydroxide, and cleaned up by dichloromethane extraction. The aqueous phase was acidified, extracted with dichloromethane, derivatized with diazomethane and analyzed by high-resolution gas chromatography/high-resolution mass spectrometry, using a DB-5 chromatographic column. Where necessary, extracts were cleaned up using aminopropyl solid phase extraction and Florisil columns. Analyte concentrations were determined by the isotope dilution/internal standard quantification method. Sample analyte concentrations were reported as total acid equivalent for each analyte.

4.3.2 *Alberta, Saskatchewan and Manitoba*

The sulfonylurea herbicides were quantified and their presence confirmed using a Micromass Quattro Ultima triple quadrupole mass spectrometer equipped with an electrospray ionization interface set to positive ion mode. Acid herbicides and organochlorine insecticides were analyzed by gas chromatography with a dual capillary column electron-capture detector. Neutral herbicides were analyzed by a dual capillary column gas chromatography electron-capture detector combined with a nitrogen-phosphorus detector. Dual column capillary gas liquid chromatography with electron capture and nitrogen-phosphorus detectors were used for the analysis of organophosphorus insecticides.

4.3.3 Ontario

The following is a brief description of the analytical procedures for the neutral herbicides, phenoxy acid herbicides and organophosphorus insecticides. Detailed analytical methods have been documented elsewhere (Environment Canada, 1997). All dichloromethane extracts were dried through sodium sulphate, exchanged into 2,2,4-trimethylpentane and concentrated to 1 mL. The neutral herbicide extracts were fractionated through 10% deactivated fluorisil and concentrated to a final volume of 10 mL. The organophosphorus extracts were eluted through 10% deactivated silica, fractionated, and concentrated to 1 mL final volume. All fractions were analyzed by gas chromatography and mass spectrometry detection and quantification.

For the phenoxy acid herbicides, acetone was added to the dichloromethane extracts to facilitate water evaporation, and the extracts were then concentrated to dryness. Next, samples were reconstituted with acetone, esterified using pentafluorobenzylbromide, and eluted through 5% deactivated silica. The fractions were concentrated to 10 mL final volume, and analyzed by gas chromatography/mass spectrometry.

Current-use pesticides in water, precipitation and passive air samples were extracted from XAD resin columns and quantified by gas chromatography/mass spectrometry as described by Muir et al. (2004). The XAD columns were eluted with methanol followed by dichloromethane. The extract was washed with 3% sodium chloride dried over anhydrous sodium sulphate. The dichloromethane phase was then carefully reduced in volume and applied to a small silica column (0.75 g, 10% deactivated with water) and rinsed with 10 mL hexane. The analytes were eluted with 10% methanol/dichloromethane and then exchanged into toluene for gas chromatographic analysis (final volume was 200 μ L).

Zooplankton were mixed with anhydrous sodium sulphate and Soxhlet extracted with dichloromethane. The extracts were applied to a gel permeation column (SX-3 Biobeads) in cyclohexane: dichloromethane (1:1) to separate co-extractive lipids from the majority of the current-use pesticides. The gel permeation column eluate was then evaporated to small volume in a rotary evaporator and transferred to a silica column, as described for water. Percent lipid was determined by drying and weighing the lipid fraction from the gel permeation column.

Current-use pesticides and transformation products (triazine/acetanilide herbicides, organophosphate insecticides and miscellaneous fungicides) were quantified by gas chromatography/-low-resolution mass spectrometry in both electron impact(EI) and electron capture negative ion (ECNI) modes using an Agilent 6890 gas chromatography and 5973 mass selective detector. Extracts were injected (pulsed splitless at 250°C) onto a Supelco MDN-5 column (30 m x 0.25 mm x 0.25 μ m film thickness) at an initial gas chromatography oven temperature of 80°C. Current-use pesticides were quantified using authentic external standards.

4.3.4 Quebec

Surface water analyses were conducted at the Centre d'Expertise en Analyse Environnementale du Québec. The pesticides were extracted using an octadecyl high performance liquid chromatography (HPLC) column (C-18), esterified with diazomethane in the case of the aryloxy acids. The analyses were performed using gas chromatography and mass spectrometry detection and quantification. The detailed analytical protocols are described in Centre d'Expertise en Analyse Environnementale du Québec documents (CEAEQ, 2006). Modifications were made to the methods to lower the detection limits for the station at Quebec City.

4.3.5 Prince Edward Island, Nova Scotia and New Brunswick

Samples from all media were analyzed for some or all of the 25 pesticides commonly used in the Atlantic provinces at laboratories certified by the Canadian Association for Environmental Analytical Laboratories (see Table 3 for a list of measured pesticides). The results of all water analysis represent a total concentration as the samples were not filtered before extraction. For the base neutral pesticide scan, samples were assessed with a solvent extraction and subsequent gas chromatography and mass spectrometry detection and quantification. For the dithiocarbamates, the analytical methodology used was derivatization followed by high performance liquid chromatography fluorescence (HPLC-fluorescence). In the case of imidacloprid, a Health Canada methodology for residues in food was followed. MCPA, 2,4-D and dicamba were analyzed using EPA Method B151A. The three laboratories used in the Atlantic study included Environment Canada's Environmental Quality Laboratory in Moncton, New Brunswick, the Atlantic Veterinary College in Charlottetown, Prince Edward Island, and the New Brunswick Research and Productivity Council in Fredericton.

4.4 Laboratory Quality Assurance/Quality Control

Approximately 10% of the laboratory analyses were dedicated to a quality assurance/quality control program over the three-year program. The quality assurance/quality control samples were prepared in one of four ways: 1) blind duplicate (field) samples with no spiking, 2) blind duplicate samples spiked with known concentrations of the individual analytes, 3) de-ionized water spiked with known concentrations of the pesticide product being analyzed and 4) de-ionized water blanks. With very few exceptions, the reproducibility of analysis in the blind duplicates was very high, and the rates of recovery of spikes were within the acceptable range of plus or minus 30 percent.

5.0 NATIONAL WATER QUALITY SURVEILLANCE PROGRAM RESULTS

The results of the national three-year water quality surveillance program are discussed below by region. Of the 141 pesticides and transformation products analyzed, 102 were detected across the country.

5.1 British Columbia

The objective of the British Columbia surveillance component was to identify and measure concentrations of current-use pesticides and some of their transformation products in the aquatic environment of British Columbia. The primary study areas included the Lower Fraser Valley and the Okanagan Basin (Figure 3).

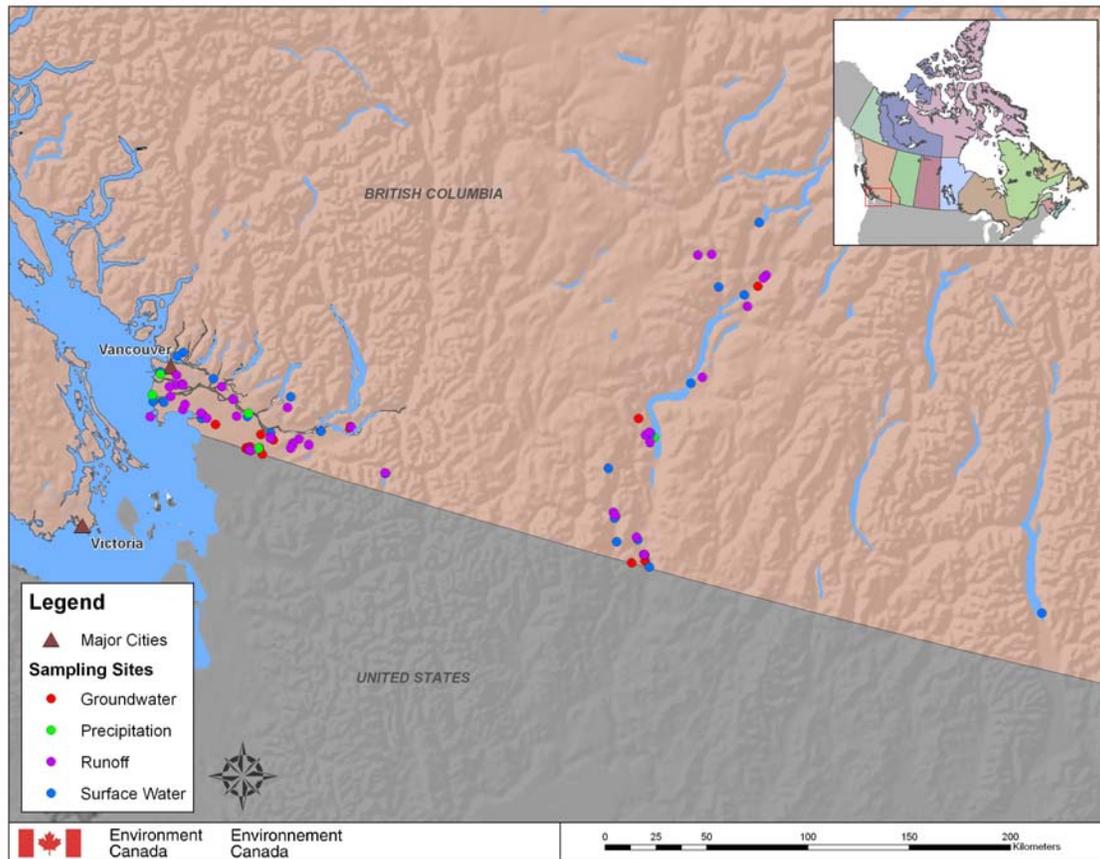


Figure 3 Water quality sampling sites in the Lower Fraser Valley and the Okanagan Basin, British Columbia, 2003–2005

These two regions of British Columbia are well-known agricultural areas where a wide variety of crops are grown, including berries, field vegetables, grapes, grains and forage crops in the Lower Fraser Valley and orchards, grapes and some vegetable crops in the Okanagan Basin. Sampling was conducted from surface waters (streams, rivers and lakes), groundwater, runoff from fields (e.g., drainage ditches adjacent to farm fields) and rainwater. Reference streams located a distance from human activities were also sampled to measure background pesticide concentrations. Sampling began in the fall of 2003 in the Lower Fraser Valley. In the spring and fall of 2004 and 2005, sampling occurred in both the Lower Fraser Valley and the Okanagan Basin. Sample collections occurred during periods of pesticide application and were timed to follow significant rainfall events.

Pesticides and/or their transformation products were detected at all sites sampled, including reference sites, in the Lower Fraser Valley and Okanagan Basin. Table 6 indicates the percentage of sites where each pesticide or its transformation product was detected.

Table 6 *Current-use pesticides and transformation products^a analyzed in samples^b from the Lower Fraser Valley and the Okanagan Basin, British Columbia, 2003–2005, and the percentage of sites where each was detected*

Insecticide	LFV^c	OB^d	Herbicide	LFV	OB
	(%)	(%)		(%)	(%)
Azinphos-methyl	14	29	2,4-D	63	52
Chlorpyrifos	58	29	Ametryn	25	3
<i>Chlorpyrifos-methyl</i>	14	39	Atrazine	75	71
<i>Chlorpyrifos-oxon</i>	6	0	<i>Desethylatrazine</i>	89	74
Cypermethrins	8	0	Bromoxynil	0	3
Diazinon	83	81	Butralin	3	0
<i>Diazinon-oxon</i>	69	61	Butylate	22	13
Dichlorvos	39	29	Cyanazine	3	0
Dimethoate	33	16	Dacthal (DCPA)	72	87
Disulfoton	6	0	Dicamba	71	48
<i>Disulfoton-sulfone</i>	22	3	Dimethenamid	22	16
Endosulfan, alpha	67	90	Ethalfluralin	8	0
Endosulfan, beta	89	84	Fluazifop	13	0
<i>Endosulfan-sulphate</i>	86	100	Flufenacet	0	0
Ethion	0	3	Hexazinone	19	23
Fenitrothion	6	0	Linuron	50	26
Fonofos	14	0	MCPA	79	84
Hexachlorocyclohexane (HCH), alpha	75	74	Mecoprop (MCP)	75	68
HCH, beta	61	32	Metolachlor	69	71
HCH, delta	42	23	Metribuzin	50	19
HCH, gamma (Lindane)	78	71	Pendimethalin	22	32
Malathion	22	3	Simazine	75	74
Methamidophos	17	3	Triallate	19	3
Methoprene	6	10	Triclopyr	63	19
Methoxychlor	14	3	Trifluralin	53	23
Mirex	28	35			
Naled (Dibrom)	14	3	Fungicides	LFV	OB
Octachlorostyrene	36	32		(%)	(%)
<i>Parathion-ethyl</i>	25	3	Captan	22	23
<i>Parathion-methyl</i>	0	0	Chlorothalonil	89	81
Permethrin	50	42	Flutriafol	39	29
Phorate	0	0	Hexachlorobenzene	42	68
Phosmet	22	35	Quintozene	92	61
Pirimiphos-methyl	6	6	Tebuconazol	44	13
Terbufos	0	6	Tecnazene	31	16

^a Each transformation product is italicized and indented below its parent pesticide.

^b Runoff samples were collected in the Lower Fraser Valley, but they were not included in this table because different analytical methods were used, and thus detections were not comparable.

^c Lower Fraser Valley.

^d Okanagan Basin.



Left: Raspberry spraying in Abbotsford, British Columbia; Right: Warning sign to alert of fungicide spraying at vineyard in Osoyoos, British Columbia (Photos: Mark Sekela)

5.1.1 Lower Fraser Valley

The insecticides most frequently detected (> 50% of samples) in the Lower Fraser Valley included endosulfan (alpha and beta) and its transformation product endosulfan-sulphate, diazinon and its transformation product diazinon-oxon, hexachlorocyclohexane (HCH—alpha, beta, and gamma [lindane]), chlorpyrifos and permethrin. The herbicides most commonly detected included atrazine and its transformation product desethylatrazine, MCPA, MCPP (mecoprop), simazine, dacthal, dicamba, metolachlor, 2,4-D, triclopyr, trifluralin, linuron and metribuzin. The most commonly detected fungicides included quinterozone, and chlorothalonil.

Pesticides present at the highest concentrations in precipitation, field runoff, surface water and groundwater are presented in Table 7. The highest pesticide concentrations in precipitation were observed for the fungicide chlorothalonil and the organophosphate insecticide diazinon and its transformation product diazinon-oxon. The highest concentrations in runoff were measured for the herbicide glyphosate, glyphosate's transformation product AMPA and the fungicide metalaxyl. Surface waters also had peak detections for the insecticide diazinon, followed by the herbicides 2,4-D and linuron. The highest detections in groundwater were for the herbicides simazine, MCPP (mecoprop) and atrazine. Some of these pesticides were also highest in sales for the Lower Fraser Valley. For example, glyphosate, atrazine, diazinon and chlorothalonil were among the top 10 pesticides sold.

The highest concentrations measured were usually in runoff samples. This was expected, as runoff samples were collected from water flowing directly from fields following pesticide applications. The locations sampled were also at points where the runoff entered larger, fish-bearing surface waters very soon after application. Groundwater samples had the lowest concentrations measured. This was also expected because surface water must percolate through the soil layers before it reaches the water table, providing the opportunity for various transformation processes by bacteria and fungi to occur.

Pesticides and their transformation products may also be adsorbed to soil if they have a high soil binding affinity.

5.1.2 Okanagan Basin

The detection frequencies for pesticides in the Okanagan Basin are shown in Table 6. The insecticides endosulfan (alpha and beta) and its transformation product endosulfan-sulphate, diazinon and its transformation product diazinon-oxon, and hexachlorocyclohexane (HCH–alpha and gamma [lindane]) were most frequently detected. The herbicides dacthal, MCPA, atrazine and its transformation product desethylatrazine, simazine, metolachlor, MCPP (mecoprop) and 2,4-D were the most frequently detected. The fungicides chlorothalonil, hexachlorobenzene and quintozene were the most frequently detected.

The ranges of detected concentrations for the top 10 pesticides or transformation products in each of the sampled media are provided in Table 7. Complete statistics for surface water in British Columbia are summarized in Table 8.



Bed sediment sampling for pesticides at Duck Lake in Kootenay, British Columbia (Photo: Melissa Gledhill)

Table 7 Pesticides and transformation products^a detected in the highest concentrations in each sample type in the Lower Fraser Valley and Okanagan Basin, British Columbia, sampling sites, 2003–2005

Lower Fraser Valley							
Precipitation		Runoff		Surface water		Groundwater	
Pesticide	Range (ng/L)	Pesticide	Range (ng/L)	Pesticide	Range (ng/L)	Pesticide	Range (ng/L)
Diazinon	0.46 – 106	Glyphosate	2 000 – 9 000	Diazinon	0.04 – 12 500	Simazine	0.05 – 90
Chlorothalonil	1.27 – 52.1	<i>AMPA</i>	3 000 – 6 000	2,4-D	0.62 – 1 230	MCPP	0.07 – 14.5
<i>Diazinon-oxon</i>	0.13 – 33.6	Metalaxyl	250 – 5 500	Linuron	0.41 – 1 050	Atrazine	0.009 – 10.7
Malathion	0.15 – 29.8	Dimethoate	200 – 3 000	MCPP	0.11 – 917	b-Endosulfan	0.001 – 5.11
Azinphos-methyl	0.32 – 22.9	Diazinon	100 – 2 710	Simazine	0.57 – 896	2,4-D	5.01
Atrazine	0.11 – 19.1	Metolachlor	20 – 1 350	MCPA	0.08 – 789	<i>Desethylatrazine</i>	0.001 – 4.93
<i>Chlorpyrifos-oxon</i>	1.79 – 10.8	Chlorpyrifos	100 – 750	Dimethoate	1.4 – 604	a-Endosulfan	0.001 – 3.17
Simazine	0.18 – 9.96	Atrazine	100 – 600	<i>Diazinon-oxon</i>	0.02 – 233	Dieldrin	0.001 – 2.23
Linuron	1.51 – 8.16	<i>Desethylatrazine</i>	10 – 510	Dicamba	0.08 – 179	Linuron	0.21 – 2.08
Metolachlor	0.02 – 6.34	Methoprene	500	Metolachlor	0.006 – 123	<i>Endosulfan-sulphate</i>	0.001 – 1.7
Okanagan Basin							
Precipitation		Runoff		Surface Water		Groundwater	
Pesticide	Range (ng/L)	Pesticide	Range (ng/L)	Pesticide	Range (ng/L)	Pesticide	Range (ng/L)
Azinphos-methyl	33.6 – 182	2,4-D	0.61 – 445	Simazine	0.82 – 2 370	<i>Desethylatrazine</i>	0.008 – 24.4
Chlorothalonil	5.13 – 18.1	Atrazine	0.15 – 428	Azinphos-methyl	1.04 – 135	Atrazine	0.006 – 21.5
Phosmet	16	Diazinon	0.09 – 214	MCPP	0.09 – 44.2	Simazine	0.12 – 9.15
Endosulfan b	5.15 – 14.7	<i>Endosulfan-sulphate</i>	0.03 – 109	2,4-D	0.59 – 41.8	Diazinon	0.007 – 2.14
Endosulfan a	4.43 – 13.1	Simazine	0.45 – 84.4	Diazinon	0.01 – 41.2	Permethrins	0.01 – 0.47
Diazinon	2.85 – 12.7	Endosulfan b	0.22 – 68.2	Quintozene	0.004 – 8.12	<i>Diazinon-oxon</i>	0.003 – 0.33
Simazine	2.21 – 4.73	Endosulfan a	0.114 – 44.6	Phosmet	0.004 – 6.68	MCPA	0.11 – 0.31
Malathion	2.13 – 4.61	Azinphos-methyl	1.08 – 25.5	Atrazine	0.016 – 6.36	Metolachlor	0.001 – 0.28
Dimethoate	2.35 – 3.85	<i>Diazinon-oxon</i>	0.03 – 20	<i>Diazinon-oxon</i>	0.12 – 6.24	Endosulfan a	0.003 – 0.22
<i>Diazinon-oxon</i>	1.24 – 3.78	Dimethoate	1.2 – 17.5	Methoprene	5.11	Dieldrin	0.002 – 0.17

^a Each transformation product is italicized and indented.

Table 8 Summary of pesticides and transformation products detected in surface water samples analyzed in the Lower Fraser Valley and the Okanagan Basin, British Columbia, 2003–2005

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
<i>Endosulfan-Sulphate</i>	96	94	97.9	0.011	<0.011	14.99	0.093	0.566	1.72	--
MCPA	92	83	90.2	0.05	<0.05	789	0.520	1.290	12.7	0
Dacthal	96	86	89.6	0.0007	<0.0007	0.3	0.004	0.014	0.048	0
HCH, alpha	90	78	86.7	0.006	<0.006	0.191	0.020	0.042	0.073	--
Diazinon	93	75	80.6	0.004	<0.004	12,500	0.118	1.900	9.7	4
MCPP	92	71	77.2	0.05	<0.05	917	0.202	3.345	37.98	0
Chlordane, gamma (trans)	90	69	76.7	0.0008	<0.0008	1.21	0.003	0.011	0.028	--
HCH, gamma	96	72	75.0	0.002	<0.002	0.674	0.015	0.035	0.080	0
<i>Desethylatrazine</i>	93	68	73.1	0.002	<0.002	15	0.010	0.082	0.814	0
Nonachlor, trans-	90	64	71.1	0.0005	<0.0005	0.307	0.003	0.011	0.029	--
Dicamba	92	64	69.6	0.05	<0.05	179	0.044	0.452	3.298	0
Chlorothalonil	96	66	68.8	0.001	<0.001	31.9	0.012	0.046	0.18	0
Simazine	93	62	66.7	0.089	<0.089	2,370	0.292	2.750	18.9	0
Quintozene	96	63	65.6	0.002	<0.002	8.12	0.011	0.020	0.047	0
beta-Endosulfan	96	62	64.6	0.001	<0.001	7.88	0.118	0.467	1.504	0
2,4-D	92	59	64.1	0.5	<0.5	1,230	0.680	2.720	22.95	0
Aldrin	90	57	63.3	0.0007	<0.0007	0.358	0.002	0.008	0.035	--
Chlordane, alpha (cis)	90	55	61.1	0.001	<0.001	0.444	0.003	0.006	0.029	--
<i>Diazinon-Oxon</i>	76	45	59.2	0.005	<0.005	233	0.021	0.128	0.384	5
Dieldrin	90	53	58.9	0.001	<0.001	2.27	0.010	0.049	0.166	--
alpha-Endosulfan	96	54	56.3	0.003	<0.003	5.47	0.046	0.125	0.382	0
4,4'-DDD	27	15	55.6	0.001	<0.001	1.2	0.012	0.029	0.073	--
Triclopyr	92	51	55.4	0.01	<0.01	4.77	0.025	0.079	0.288	0
<i>Heptachlor-Epoxyde</i>	90	47	52.2	0.001	<0.001	0.992	0.007	0.012	0.042	--
4,4'-DDE	27	14	51.9	0.006	<0.006	0.95	0.022	0.041	0.113	--
Heptachlor	90	44	48.9	0.0005	<0.0005	0.088	-	-	-	--
Atrazine	93	44	47.3	0.016	<0.016	64.5	-	-	-	0
HCH, beta	90	39	43.3	0.0013	<0.0013	0.766	-	-	-	--
Chlorpyrifos	96	41	42.7	0.0005	<0.0005	18.3	-	-	-	6

Table 8 Summary of pesticides and transformation products detected in surface water samples analyzed in the Lower Fraser Valley and the Okanagan Basin, British Columbia, 2003–2005

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
2,4'-DDD	27	10	37.0	0.001	<0.001	0.2	-	-	-	--
4,4'-DDT	27	10	37.0	0.004	<0.004	1.6	-	-	-	--
HCH, delta	90	33	36.7	0.002	<0.002	0.22	-	-	-	--
Metolachlor	92	33	35.9	0.004	<0.004	122.7	-	-	-	0
Octachlorostyrene	90	32	35.6	0.0009	<0.0009	0.255	-	-	-	--
Linuron	93	33	35.5	0.147	<0.147	1,050	-	-	-	0
Endrin	90	31	34.4	0.0008	<0.0008	0.253	-	-	-	--
Trifluralin	93	32	34.4	0.001	<0.001	1.38	-	-	-	0
Hexazinone	44	15	34.1	0.028	<0.028	38	-	-	-	0
Dichlorvos	96	31	32.3	0.001	<0.001	1.81	-	-	-	6
Permethrins	96	28	29.2	0.008	<0.008	2.36	-	-	-	0
Mirex	90	26	28.9	0.0003	<0.0003	0.29	-	-	-	--
2,4'-DDT	27	7	25.9	0.001	<0.001	0.19	-	-	-	--
Metribuzin	93	22	23.7	0.015	<0.015	2.74	-	-	-	0
<i>Oxychlorane</i>	90	21	23.3	0.001	<0.001	0.463	-	-	-	--
2,4'-DDE	27	5	18.5	0.001	<0.001	0.052	-	-	-	--
Nonachlor, cis-	90	16	17.8	0.0004	<0.0004	3.47	-	-	-	--
Tecnazene	96	17	17.7	0.0005	<0.0005	0.687	-	-	-	0
<i>Chlorpyrifos-Methyl</i>	96	17	17.7	0.0001	<0.0001	0.013	-	-	-	--
Dimethoate	85	15	17.6	0.075	<0.075	604	-	-	-	0
<i>Disulfoton Sulfone</i>	68	11	16.2	0.001	<0.001	5	-	-	-	--
<i>Endrin-Ketone</i>	90	14	15.6	0.0005	<0.0005	0.572	-	-	-	--
<i>Endrin-Aldehyde</i>	90	13	14.4	0.0008	<0.0008	0.091	-	-	-	--
Phosmet	90	12	13.3	0.0014	<0.0014	6.68	-	-	-	0
Pendimethalin	93	12	12.9	0.012	<0.012	2.1	-	-	-	0
Tebuconazol	80	9	11.3	0.012	<0.012	12.8	-	-	-	0
Ametryn	93	10	10.8	0.0015	<0.0015	0.33	-	-	-	0
Parathion-Ethyl	96	10	10.4	0.0024	<0.0024	4.83	-	-	-	0
Captan	82	7	8.5	0.007	<0.007	28.8	-	-	-	0
Fonofos	90	7	7.8	0.0002	<0.0002	1.286	-	-	-	0

Table 8 Summary of pesticides and transformation products detected in surface water samples analyzed in the Lower Fraser Valley and the Okanagan Basin, British Columbia, 2003–2005

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Naled	93	7	7.5	0.14	<0.14	25.5	-	-	-	0
Azinphos-Methyl	80	6	7.5	0.069	<0.069	135	-	-	-	1
Malathion	96	7	7.3	0.062	<0.062	75.1	-	-	-	0
Dimethenamid	93	6	6.5	0.0012	<0.0012	0.483	-	-	-	0
Methamidophos	79	5	6.3	0.04	<0.04	61.4	-	-	-	0
Hexachlorobenzene	90	5	5.6	0.001	<0.001	6.94	-	-	-	--
Triallate	93	5	5.4	0.012	<0.012	2.56	-	-	-	0
Disulfoton	48	2	4.2	0.026	<0.026	0.283	-	-	-	0
Fluazifop	85	3	3.5	0.5	<0.5	4.93	-	-	-	--
Pirimiphos-Methyl	90	3	3.3	0.001	<0.001	0.051	-	-	-	0
Methoxychlor	93	2	2.2	0.038	<0.038	34.5	-	-	-	0
Butylate	93	2	2.2	0.008	<0.008	1.16	-	-	-	0
Methoprene	93	2	2.2	0.977	<0.977	112	-	-	-	0
Cypermethrins	96	2	2.1	0.009	<0.009	3.09	-	-	-	2
Fenitrothion	90	1	1.1	0.004	<0.004	0.205	-	-	-	0
Ethalfuralin	93	1	1.1	0.004	<0.004	2.91	-	-	-	0
Cyanazine	93	0	0.0	0.081	<0.081	-	-	-	-	ND
<i>Chlorpyrifos-Oxon</i>	90	0	0.0	0.66	<0.66	-	-	-	-	ND
Ethion	96	0	0.0	0.059	<0.059	-	-	-	-	ND
<i>Parathion-Methyl</i>	96	0	0.0	0.042	<0.042	-	-	-	-	ND
Phorate	66	0	0.0	0.632	<0.632	-	-	-	-	ND
Terbufos	66	0	0.0	0.011	<0.011	-	-	-	-	ND
Alachlor	93	0	0.0	0.069	<0.069	-	-	-	-	ND
Butralin	93	0	0.0	0.0065	<0.0065	-	-	-	-	ND
Flufenacet	93	0	0.0	0.14	<0.14	-	-	-	-	ND
Bromoxynil	83	0	0.0	0.25	<0.25	-	-	-	-	ND

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection ≥50%.

^d Source of benchmarks: Cantox Environmental Inc., 2004.

^e NC: No comparison possible. (Method detection limit was above the benchmark).

5.2 Alberta, Saskatchewan and Manitoba

The Alberta, Saskatchewan and Manitoba component was designed to investigate the distribution and concentration of herbicides (particularly sulfonylureas), in prairie aquatic ecosystems, including reservoirs, tap water, wetlands and rivers. While the primary focus of this study was herbicides, other pesticides were also investigated. The sampling sites are illustrated in Figure 4.

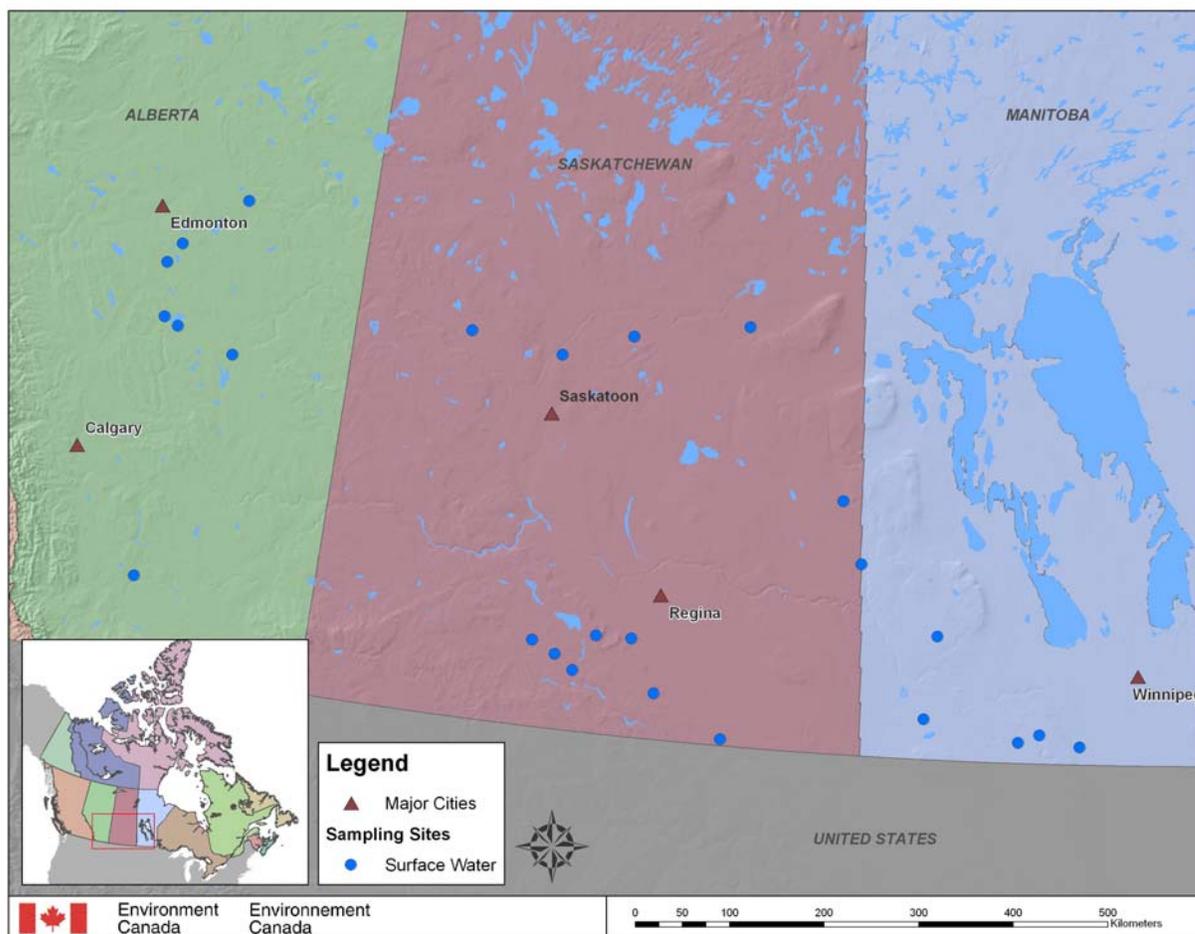


Figure 4 Water quality sampling sites in Alberta, Saskatchewan and Manitoba, 2003–2005

Wetlands

A total of 14 herbicides were detected in 60 wetlands at the end of the period when herbicides were being applied to crops (late June to early July 2004) (Table 9). The wetlands were located in Alberta, Saskatchewan and Manitoba and were in six clusters of 10 wetlands. Only 12% of wetland samples had sulfonylurea herbicides and none had neutral herbicides.

Table 9 Summary of pesticides and transformation products detected in wetlands analyzed in Alberta, Saskatchewan and Manitoba, 2004

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25 th percentile (ng/L) ^c	Median (ng/L) ^c	75 th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
2,4-D	60	60	100	0.47	< 0.47	4 290	44.70	68.80	114.00	1
MCPA	60	60	100	0.58	< 0.58	3 530	43.60	97.80	188.00	2
Bromoxynil	60	59	98.3	0.99	< 0.99	47.1	2.71	4.94	9.12	0
Clopyralid	60	59	98.3	0.59	< 0.59	1 520	7.35	17.20	90.60	0
Dicamba	60	55	91.7	0.73	< 0.73	1 270	2.45	5.13	11.70	0
2,4-DP (Dichlorprop)	60	52	86.7	0.42	< 0.42	79.4	2.27	8.96	29.10	0
Mecoprop	60	51	85.0	0.5	< 0.5	241	1.81	2.54	4.23	0
Picloram	60	9	15.0	0.66	< 0.66	1 550	-	-	-	0
Metsulfuron	60	5	8.3	1.0	< 1.0	77.8	-	-	-	NC
2,4,5-T	60	4	6.7	0.39	< 0.39	10	-	-	-	0
Fenoprop (Silvex)	60	3	5.0	0.4	< 0.4	5.32	-	-	-	0
2,3,6-TBA	60	2	3.3	1.1	< 1.1	7.6	-	-	-	0
Ethametsulfuron	60	2	3.3	1.0	< 1.0	1.26	-	-	-	NC
Imazethapyr	60	1	1.7	1.2	< 1.2	9.32	-	-	-	0
Metribuzin	59	1	1.7	20.7	< 20.7	63.9	-	-	-	0
2,4-DB	60	0	0.0	0.53	-	-	-	-	-	-
Atrazine	59	0	0.0	5.76	-	-	-	-	-	-
Benzoylprop-ethyl	59	0	0.0	26.2	-	-	-	-	-	-
Butylate	59	0	0.0	55.4	-	-	-	-	-	-
<i>Desethylatrazine</i>	59	0	0.0	26.8	-	-	-	-	-	-
<i>Desethylsimazine</i>	59	0	0.0	148	-	-	-	-	-	-
Diallate I	59	0	0.0	57.8	-	-	-	-	-	-
Diallate II	59	0	0.0	32.9	-	-	-	-	-	-
Diclofop-methyl	59	0	0.0	42.3	-	-	-	-	-	-
Imazamethabenz-methyl (A)	60	0	0.0	0.14	-	-	-	-	-	-
Imazamethabenz-methyl (B)	60	0	0.0	0.088	-	-	-	-	-	-
MCPB	60	0	0.0	0.63	-	-	-	-	-	-
Metolachlor	59	0	0.0	23.7	-	-	-	-	-	-
Simazine	59	0	0.0	16.4	-	-	-	-	-	-
Sulfosulfuron	60	0	0.0	1.0	-	-	-	-	-	-
Thifensulfuron	60	0	0.0	1.0	-	-	-	-	-	-

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection \geq 50%.

^d Source of benchmarks: Cantox Environmental Inc., 2004.

^e NC: No comparison possible. (Method detection limit was above the benchmark).

The median concentration of the most frequently detected herbicides in the wetlands near agricultural fields were these: MCPA, 98 ng/L; 2,4-D, 69 ng/L; clopyralid, 17.2 ng/L; dicamba, 5 ng/L; 2,4-DP (dichlorprop), 9 ng/L; mecoprop, 2.5 ng/L; and bromoxynil, 4.9 ng/L. These seven herbicides were detected in 82% to 100% of wetlands. Picloram was detected in 18% of wetlands with a maximum concentration of 1,550 ng/L. Metsulfuron was detected in 8% of wetlands with a maximum detected concentration of 78 ng/L (range: <1.0–77.8 ng/L). The herbicides 2,3,6-TBA, imazethapyr, 2,4,5-T, fenoprop and ethametsulfuron were detected in 6% of wetlands.

In southern Saskatchewan, pesticide concentrations were assessed in 10 wetlands in cropland and in 10 wetlands in pasture, all in the same geographic area. The mean concentration was 1 907 ng/L for all herbicides combined in the wetlands associated with crops and 281 ng/L for all herbicides combined in 10 wetlands in nearby pasture. In cropland, 2,4-D, dicamba and MCPA were found in several wetlands at concentrations greater than 1,000 ng/L. Concentrations of individual herbicides were less than 100 ng/L in pastures, except for a single detection of picloram (845 ng/L). Picloram is registered in Canada and is used for brush control in pastures.

Generally, the mean concentration of all herbicides combined in the six wetland clusters associated with cropland was directly related to total precipitation from the previous 15 days. For data collected in 2004, the maximum 15-day precipitation associated with a single wetland cluster was 45.5 mm. This quantity of rainfall would not have caused surface runoff. This suggests that atmospheric transport, deposition and perhaps direct transfer of herbicides from the atmosphere to wetlands is enhanced under humid conditions. This very general relationship between pesticide concentration in wetlands and precipitation has been identified elsewhere (Rawn et al., 1999).

Rivers

Pesticide levels were assessed at eight sites in six rivers located in either Manitoba or Saskatchewan. Water samples were collected from the rivers during spring and summer (Wood, Wascana, Long, Carrot) or throughout the year (Red, Assiniboine, Carrot at Turnberry, Manitoba). A total of 26 herbicides were detected in river water samples (Table 10). Median concentrations of frequently detected herbicides in river water were 2,4-D, 46 ng/L; MCPA, 12 ng/L; dicamba, 4 ng/L; clopyralid, 5 ng/L; bromoxynil, 1 ng/L; and 2,4-DP(dichlorprop), 1 ng/L (not including Wascana River site downstream from Regina). The herbicides detected in rivers were the same as those detected in reservoirs and wetlands, although concentrations in rivers were somewhat less than in the other aquatic systems. Atrazine and desethylatrazine were frequently detected in the Red River (Manitoba), but were rarely detected elsewhere (Wascana Creek downstream from Regina), or were not detected. Sulfonylurea herbicides were detected in 27% of river samples, with ethametsulfuron and tribenuron being the most frequently detected.

Table 10 Summary of pesticides detected in rivers analyzed in the Alberta, Saskatchewan, and Manitoba, 2003

Pesticide ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25 th percentile (ng/L) ^c	Median (ng/L) ^c	75 th percentile (ng/L) ^c
					Min	Max			
2,4-D	64	59	92.2	0.47	< 0.47	457	18.50	46.00	65.00
MCPA	64	59	92.2	0.58	< 0.58	176	5.74	11.95	23.85
Clopyralid	64	54	84.4	0.59	< 0.59	272	2.30	4.96	26.48
Dicamba	64	53	82.8	0.73	< 0.73	68.9	2.32	4.19	13.30
2,4-DP (Dichlorprop)	64	32	50.0	0.42	< 0.42	115	0.42	1.00	7.95
Bromoxynil	64	22	34.4	0.99	< 0.99	63.3	-	-	-
2,4,5-T	64	9	14.1	0.39	< 0.39	6.48	-	-	-
Imazamethabenz-methyl (A)	64	5	7.8	0.14	< 0.14	20.4	-	-	-
Fenoprop (Silvex)	64	5	7.8	0.4	< 0.4	3.32	-	-	-
Chlorpyrifos (Dursban)	13	1	7.7	14.8	< 14.8	38.8	-	-	-
2,3,6-TBA	64	4	6.3	1.1	< 1.1	4.89	-	-	-
<i>Desethylatrazine</i>	63	4	6.3	26.8	< 26.8	161	-	-	-
Metolachlor	63	4	6.3	23.7	< 23.7	285	-	-	-
Triallate	63	4	6.3	4.14	< 4.14	17.4	-	-	-
Imazamethabenz-methyl (B)	64	2	3.1	0.088	< 0.088	5.66	-	-	-
Imazethapyr	64	2	3.1	1.2	< 1.2	3.49	-	-	-
MCPB	64	2	3.1	0.63	< 0.63	5.73	-	-	-
2,4-DB	64	0	0.0	0.53	-	-	-	-	-
Azinphos-methyl (Guthion)	13	0	0.0	138	-	-	-	-	-
Benzoylprop-ethyl	63	0	0.0	26.2	-	-	-	-	-
Butylate	63	0	0.0	55.4	-	-	-	-	-
<i>Desethylsimazine</i>	63	0	0.0	148	-	-	-	-	-
Diallate I	63	0	0.0	57.8	-	-	-	-	-
Diallate II	63	0	0.0	32.9	-	-	-	-	-
Diazinon	13	0	0.0	15.5	-	-	-	-	-
Diclofop-methyl	63	0	0.0	42.3	-	-	-	-	-
Dimethoate	13	0	0.0	25.1	-	-	-	-	-
Disulfoton (Disyston)	13	0	0.0	47.1	-	-	-	-	-
Ethion	13	0	0.0	17.7	-	-	-	-	-
Fonofos	13	0	0.0	12.7	-	-	-	-	-

Table 10 Summary of pesticides detected in rivers analyzed in the Alberta, Saskatchewan, and Manitoba, 2003

Pesticide ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25 th percentile (ng/L) ^c	Median (ng/L) ^c	75 th percentile (ng/L) ^c
					Min	Max			
Malathion	13	0	0.0	14.7	-	-	-	-	-
Metribuzin	63	0	0.0	20.7	-	-	-	-	-
Naled (Dibrom)	13	0	0.0	79.5	-	-	-	-	-
Parathion	13	0	0.0	15.5	-	-	-	-	-
Phorate	13	0	0.0	11.6	-	-	-	-	-
Phosmet (Imidan)	13	0	0.0	157	-	-	-	-	-
Picloram	64	0	0.0	0.66	-	-	-	-	-
Simazine	63	0	0.0	16.4	-	-	-	-	-
Terbufos	13	0	0.0	8.3	-	-	-	-	-
Trifluralin	63	0	0.0	5.15	-	-	-	-	-

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection $\geq 50\%$.

Pesticide samples were collected from Wascana Creek, upstream and downstream from Regina. Mecoprop was not detected regularly in rivers, except in Wascana Creek downstream from Regina. Mean concentrations upstream (49 ng/L) were significantly less than downstream (322 ng/L). Two other herbicides also showed this upstream–downstream pattern, including 2,4-D (80 ng/L upstream compared with 378 ng/L downstream) and dicamba (200 ng/L upstream compared with 277 ng/L downstream). Mecoprop, dicamba and 2,4-D are commonly used on turf grass within the City of Regina to control broad-leaved weeds, such as dandelion.

Reservoirs

Concentrations of pesticides and transformation products were measured in 15 reservoirs located in Alberta, Saskatchewan and Manitoba in 2003–2005. Water samples were collected from April to February, with the majority of the sampling occurring between May and August. A total of 24 pesticides or transformation products were detected in reservoir water samples (Table 11). The most frequently detected analytes (> 30% of samples) were 2,4-D (n = 173, 100% detection), sulfosulfuron (n = 22, 100% detection), tribenuron ME (n = 23, 100% detection), MCPA (n = 173, 99.4% detection), ethametsulfuron ME (n = 71, 98.6% detection), clopyralid (n = 170, 98.3%), dicamba (n = 172, 86.1% detection), 2,4-DP (dichlorprop; n = 173, 81.5% detection), mecoprop (n = 173, 79.2% detection) and bromoxynil (n = 162, 46.3%).



Drinking water reservoir in Saskatchewan (Photo: David Donald)

Table 11 Summary of pesticides and transformation products detected in reservoir water analyzed in Alberta, Saskatchewan, and Manitoba, 2003–2004

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
2,4-D	206	205	99.5	0.47	< 0.47	1 850	23.85	66.30	129.00	0
MCPA	206	204	99.0	0.58	< 0.58	374	13.80	27.45	68.10	0
Clopyralid	206	202	98.1	0.59	< 0.59	1 050	4.61	13.00	41.20	0
Dicamba	206	177	85.9	0.73	0.4	1 040	2.10	3.82	10.40	0
2,4-DP (Dichlorprop)	206	168	81.6	0.42	< 0.42	113	1.47	5.78	15.10	0
Mecoprop	206	159	77.2	0.50	0.4	83.1	1.01	2.90	7.10	0
Bromoxynil	206	111	53.9	0.99	0.5	384	0.99	0.99	3.68	0
Ethametsulfuron	209	73	34.9	1.00	< 1.00	80.4	-	-	-	NC
Atrazine	198	55	27.8	5.76	1.7	52.7	-	-	-	0
<i>Desethylatrazine</i>	198	40	20.2	26.80	0.8	26.8	-	-	-	0
Chlorpyrifos (Dursban)	30	5	16.7	14.80	4.61	20.1	-	-	-	5
Imazamethabenz-methyl (A)	206	27	13.1	0.14	< 0.14	194	-	-	-	0
Picloram	206	27	13.1	0.66	< 0.66	457	-	-	-	0
Tribenuron	209	25	12.0	1.00	< 1.00	30.1	-	-	-	NC
<i>Desethylsimazine</i>	198	22	11.1	148.00	1.2	148	-	-	-	NC
2,4,5-T	206	22	10.7	0.39	< 0.39	4.18	-	-	-	0
Sulfosulfuron	209	22	10.5	1.00	< 1.00	36.09	-	-	-	0
Fenoprop (Silvex)	206	20	9.7	0.40	< 0.40	5.8	-	-	-	0
Imazamethabenz-methyl (B)	206	16	7.8	0.09	< 0.09	93.5	-	-	-	0
2,3,6-TBA	206	12	5.8	1.10	0.3	2.43	-	-	-	0
Imazethapyr	206	12	5.8	1.20	0.4	11	-	-	-	0
Trifluralin	198	7	3.5	5.15	0.6	18.5	-	-	-	0
Dimethoate (Cygon)	30	1	3.3	25.10	5.98	25.1	-	-	-	0
Butylate	198	5	2.5	55.40	1.1	55.4	-	-	-	0
MCPB	206	5	2.4	0.63	< 0.63	12.8	-	-	-	0
Thifensulfuron	209	5	2.4	1.00	< 1.00	12	-	-	-	NC
Diclofop-methyl	198	4	2.0	42.30	0.4	42.3	-	-	-	0
Simazine	198	3	1.5	16.40	1.7	16.4	-	-	-	0
Triallate	198	3	1.5	4.14	2.4	4.28	-	-	-	0
Metsulfuron	209	3	1.4	1.00	< 1.00	2.1	-	-	-	NC
Benzoylprop-ethyl	198	2	1.0	26.20	0.7	26.2	-	-	-	0
Metribuzin	198	1	0.5	20.70	< 20.70	185	-	-	-	0

Table 11 Summary of pesticides and transformation products detected in reservoir water analyzed in Alberta, Saskatchewan, and Manitoba, 2003–2004

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
2,4-DB	206	0	0.0	0.53	< 0.53	< 0.53	-	-	-	0
<i>Azinphos-methyl (Guthion)</i>	30	0	0.0	138.00	< 138.00	< 138.00	-	-	-	NC
<i>Diallate I</i>	198	0	0.0	57.80	< 57.80	< 57.80	-	-	-	NC
<i>Diallate II</i>	198	0	0.0	32.90	< 32.90	< 32.90	-	-	-	NC
<i>Diazinon</i>	30	0	0.0	15.50	< 15.50	< 15.50	-	-	-	0
<i>Disulfoton (Disyston)</i>	30	0	0.0	47.10	< 47.10	< 47.10	-	-	-	0
<i>Ethion</i>	30	0	0.0	17.70	< 17.70	< 17.70	-	-	-	NC
<i>Fonofos</i>	30	0	0.0	12.70	< 12.70	< 12.70	-	-	-	NC
<i>Malathion</i>	30	0	0.0	14.70	< 14.70	< 14.70	-	-	-	0
<i>Metolachlor</i>	198	0	0.0	23.70	< 23.70	< 23.70	-	-	-	0
<i>Naled (Dibrom)</i>	30	0	0.0	79.50	< 79.50	< 79.50	-	-	-	NC
<i>Parathion</i>	30	0	0.0	15.50	< 15.50	< 15.50	-	-	-	NC
<i>Phorate</i>	30	0	0.0	11.60	< 11.60	< 11.60	-	-	-	0
<i>Phosmet Total (Imidan)</i>	30	0	0.0	157.00	< 157.00	< 157.00	-	-	-	NC
<i>Terbufos</i>	30	0	0.0	8.30	< 8.30	< 8.30	-	-	-	0

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection ≥50%.

^d Source of benchmarks: Cantox Environmental Inc., 2004.

^e NC: No comparison possible. (Method detection limit was above the benchmark).

5.3 Ontario

In 2003, 162 water samples were analyzed from 21 sites including six Great Lakes connecting channel sites, 10 sites within three Canadian Great Lakes Areas of Concern and five small tributary sites in the Niagara Peninsula and Hamilton/Burlington areas of Ontario (Figure 5). Thirty-two of the samples were taken with large-volume water samples (16 L) to facilitate detection of trace analytes and all others with 1-L grab samples. Sixty-three percent (24/38) of the current-use pesticides and transformation products analyzed were detected. Some of the most frequently detected pesticides were 2,4-D (97.5%), atrazine (91.3%), dicamba (82.6%), MCPA (71.6%), metolachlor (44.1%), 2,4-DP (33.3%), clopyralid (27.2%) and diazinon (16.1%) (Table 12).

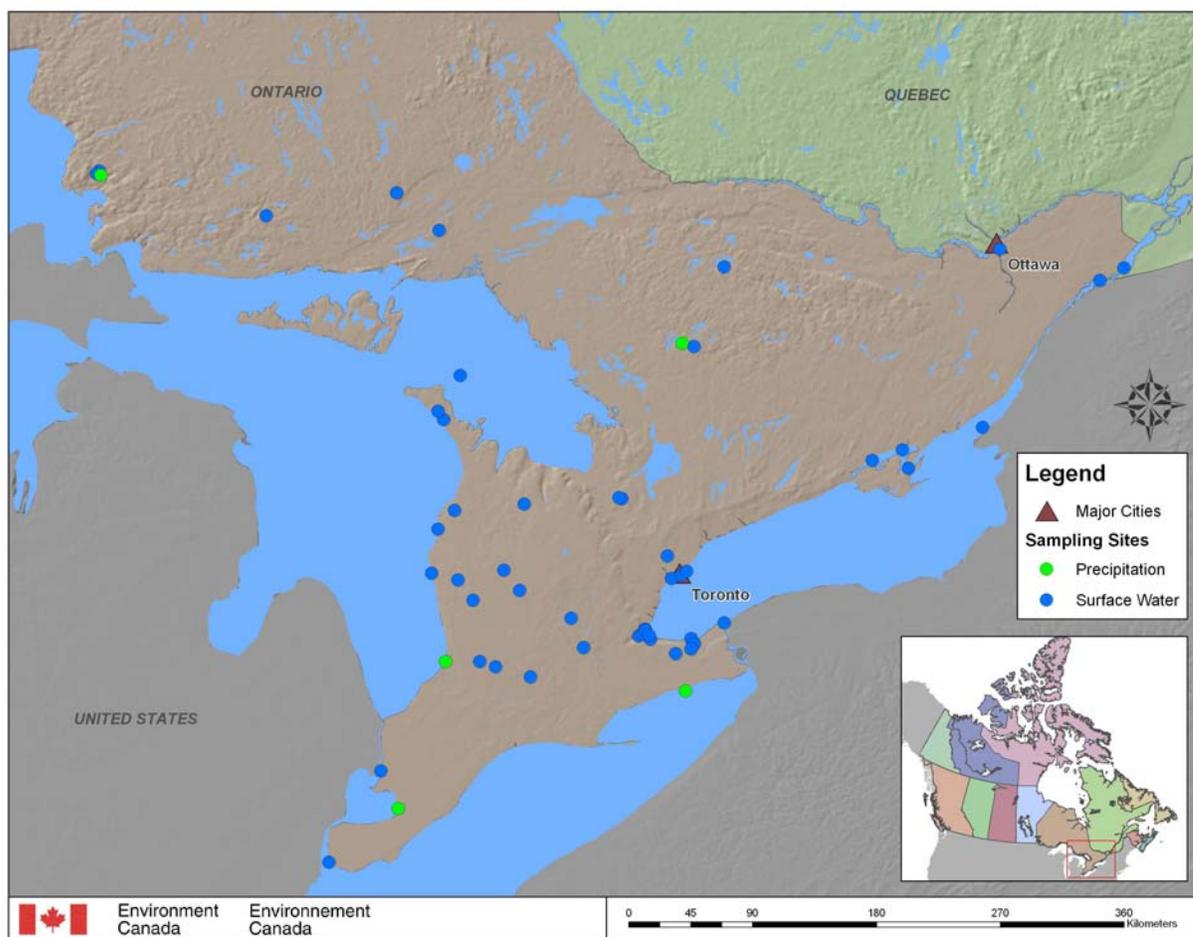


Figure 5 Water quality sampling sites in Ontario, 2003–2005

Table 12 Summary of pesticides and transformation products detected in surface water samples analyzed in Ontario, 2003

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
2,4-D	160	156	97.5	0.47	1.3	2 850	7.06	46.50	114.50	0
Atrazine	161	147	91.3	5.76	7.68	1 590	24.40	67.90	92.70	0
<i>Desethylatrazine</i>	161	94	58.4	26.8	27.4	472	13.40	39.00	72.80	0
Dicamba	161	133	82.6	0.73	0.75	826	1.68	9.07	23.80	0
MCPA	162	116	71.6	0.58	0.66	1 230	0.29	1.94	4.69	0
Metolachlor	161	71	44.1	23.7	24.3	1 560	-	-	-	0
2,4-DP (Dichlorprop)	162	54	33.3	0.42	0.42	6.62	-	-	-	0
Clopyralid	162	44	27.2	0.59	0.64	132	-	-	-	0
Simazine	161	43	26.7	16.4	18.40	1 070	-	-	-	0
<i>Desethylsimazine</i>	161	4	2.5	148	184	581	-	-	-	0
Diazinon	162	26	16.1	15.5	16.10	453	-	-	-	11
2,4,5-T	162	24	14.8	0.39	0.49	241	-	-	-	0
Bromoxynil	162	22	13.6	0.99	1.13	692	-	-	-	0
Metribuzin	161	17	10.6	20.7	21.0	1 230	-	-	-	2
Fenoprop (Silvex)	162	11	6.8	0.4	0.43	3.60	-	-	-	0
2,3,6-TBA	162	8	4.9	1.1	1.65	4.62	-	-	-	0
Imazethapyr	162	7	4.3	1.2	1.49	4.80	-	-	-	0
Chlorpyrifos	162	5	3.1	14.8	15.6	74.6	-	-	-	5
Imazamethabenz-methyl (A)	162	4	2.5	0.14	1.18	5.97	-	-	-	0
Azinphos-methyl	162	3	1.9	138	199	578	-	-	-	NC
Imazamethabenz-methyl (B)	162	2	1.2	0.088	2.90	9.31	-	-	-	0
Malathion	162	1	0.6	14.7	143	143	-	-	-	1
MCPB	162	1	0.6	0.63	2.74	2.74	-	-	-	0
2,4-DB	162	1	0.6	0.53	19.1	19.1	-	-	-	0
Benzoylprop-ethyl	161	0	0.0	26.2	-	-	-	-	-	-
Butylate	161	0	0.0	55.4	-	-	-	-	-	-
Diclofop-methyl	161	0	0.0	42.3	-	-	-	-	-	-
Diallate I	161	0	0.0	57.8	-	-	-	-	-	-
Diallate II	161	0	0.0	32.9	-	-	-	-	-	-
Ethion	162	0	0.0	17.7	-	-	-	-	-	-
Fonofos	162	0	0.0	12.7	-	-	-	-	-	-
Naled (Dibrom)	162	0	0.0	79.5	-	-	-	-	-	-
Parathion	162	0	0.0	15.5	-	-	-	-	-	-

Table 12 Summary of pesticides and transformation products detected in surface water samples analyzed in Ontario, 2003

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Phorate	162	0	0.0	11.6	-	-	-	-	-	-
Phosmet	162	0	0.0	157	-	-	-	-	-	-
Terbufos	162	0	0.0	8.30	--	--	--	--	--	--
Triallate	161	0	0.0	4.14	--	--	--	--	--	--
Trifluralin	161	0	0.0	5.15	--	--	--	--	--	--
					-	-	-	-	-	-

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection $\geq 50\%$.

^d Source of benchmarks: Cantox Environmental Inc., 2004.

^e NC: No comparison possible. (Method detection limit was above the benchmark).



Long-term pesticide monitoring site at 20 Mile Creek, Ontario (Photo: Janine Murray)

In 2004, a maximum of 228 water samples were analyzed from 18 small-stream tributary sites and 15 amphibian breeding sites (farm ponds and streams). Sixty-four per cent (23/36) of the analytes were detected in the samples. In 2004, the most frequently detected analytes were atrazine (92.9%), dicamba (82.5%), 2,4-D (80.7%), mecoprop (73.3%), metolachlor (58%), MCPA (56.1%), clopyralid (36.4%), bromoxynil (35.5%), 2,4-DP (30.7%) and simazine (18.3%) (Table 13). Although many of the sample locations were different from 2003 to 2004, several of the analytes, including atrazine, mecoprop, dicamba, 2,4-D and metolachlor, were commonly detected. As was the case in 2003, a large number of samples had multiple detections of pesticides.

Table 13 Summary of pesticides and transformation products detected in surface water samples analyzed in Ontario, 2004

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Atrazine	224	208	92.9	5.76	6.43	14 900	26.80	78.70	288.00	8
<i>Desethylatrazine</i>	224	132	58.9	26.8	27.0	519	13.40	32.10	58.55	0
Dicamba	228	188	82.5	0.73	0.73	105 000	1.90	11.25	53.40	2
2,4-D	228	184	80.7	0.47	0.71	8 240	1.84	12.75	61.95	3
Mecoprop	228	167	73.3	0.5	0.58	103 000	0.25	5.40	70.70	1
Metolachlor	224	130	58.0	23.7	24.0	5 290	11.90	38.60	135.50	0
MCPA	228	128	56.1	0.58	0.58	350	0.29	1.09	6.51	0
Clopyralid	228	83	36.4	0.59	0.61	11.3	-	-	-	0
Bromoxynil	228	81	35.5	0.99	1.00	110	-	-	-	0
2,4-DP (Dichlorprop)	228	70	30.7	0.42	0.45	110	-	-	-	0
Simazine	224	41	18.3	16.4	16.5	978	-	-	-	0
<i>Desethylsimazine</i>	224	1	0.5	148	206	206	-	-	-	0
Metribuzin	224	29	13.0	20.7	23.0	668	-	-	-	0
Diazinon	228	27	11.8	15.5	16.2	5 490	-	-	-	6
Fenoprop (Silvex)	228	11	4.8	0.4	0.55	3.8	-	-	-	0
Dimethoate	228	10	4.4	25.1	28.9	175	-	-	-	0
Chlorpyrifos	228	9	4.0	14.8	17.1	205	-	-	-	9
Azinphos-methyl	228	8	3.5	138	174	6 140	-	-	-	NC
2,3,6-TBA	228	6	2.6	1.1	1.43	11.4	-	-	-	0
Malathion	228	2	0.9	14.7	31.7	449	-	-	-	1
MCPB	228	1	0.4	0.63	4.14	4.14	-	-	-	0
Fonofos	228	1	0.4	12.7	41.4	41.4	-	-	-	NC
2,4-DB	228	1	0.4	0.053	365	365	-	-	-	0
Butylate	224	0	0.0	55.4	-	-	-	-	-	-
Diallate I	224	0	0.0	57.8	-	-	-	-	-	-
Diallate II	224	0	0.0	32.9	-	-	-	-	-	-
Diclofop-methyl	224	0	0.0	42.3	-	-	-	-	-	-
Disulfoton	228	0	0.0	47.1	-	-	-	-	-	-
Ethion	228	0	0.0	17.7	-	-	-	-	-	-
Naled (Dibrom)	228	0	0.0	79.5	-	-	-	-	-	-
Phorate	228	0	0.0	11.6	-	-	-	-	-	-
Phosmet	228	0	0.0	157	-	-	-	-	-	-
Picloram	228	0	0.0	0.66	-	-	-	-	-	-
Terbufos	228	0	0.0	8.3	-	-	-	-	-	-

Table 13 Summary of pesticides and transformation products detected in surface water samples analyzed in Ontario, 2004

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Triallate	224	0	0.0	4.14	-	-	-	-	-	-
Trifluralin	224	0	0.0	5.15	-	-	-	-	-	-

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection $\geq 50\%$.

^d Source of benchmarks: Cantox Environmental Inc., 2004.

^e NC: No comparison possible. (Method detection limit was above the benchmark).

In 2005, a maximum of 183 surface water samples were analyzed from 22 small-stream tributary sites and seven amphibian breeding sites located in southern Ontario. Sixty-four per cent (27/42) of the analytes screened for were detected in the samples (Table 14). In 2005, some of the most frequently detected analytes were atrazine (93.4%), 2,4-D (80.9%), dicamba (75.4%), mecoprop (58.5%), metolachlor (50.8%), MCPA (38.8%), 2,4-DP (33.3%), bromoxynil (25.1%) and simazine (14.2%). Eight analytes exceeded benchmarks or water quality guidelines. They included 2,4-D (3 sample), atrazine (8 samples), chlorpyrifos (9 samples), malathion (1 sample), metolachlor (1 sample), dicamba (2 samples), mecoprop (1 sample) and diazinon (4 samples).

In all three years (2003–2005), almost all of the collected samples had detections of two or more analytes. These data are summarized in Table 15.

Table 14 Summary of pesticides and transformation products detected in surface water samples analyzed in Ontario, 2005

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Atrazine	183	171	93.4	5.76	6.64	6 330	20.40	52.70	157.00	3
<i>Desethylatrazine</i>	183	114	62.3	26.8	27.4	1 800	13.4	37.7	66.9	NC
2,4-D	183	148	80.9	0.47	0.92	4 220	1.59	10.8	76.5	1
Dicamba	183	138	75.4	0.73	0.75	5 380	0.75	4.38	18.6	NC
Mecoprop	183	107	58.5	0.5	0.6	3 610	0.25	3.65	29.3	NC
Metolachlor	183	93	50.8	23.7	23.7	9 190	11.85	25.80	81.6	1
MCPA	183	71	38.8	0.58	1.04	69.1	-	-	-	NC
2,4-DP	183	61	33.3	0.42	0.44	809	-	-	-	NC
Clopyralid	183	47	25.7	0.59	0.64	88.2	-	-	-	3
Bromoxynil	183	46	25.1	0.99	1	45.8	-	-	-	NC
Simazine	183	26	14.2	16.4	16.9	2 050	-	-	-	NC
<i>Desethylsimazine</i>	183	7	3.8	148	167	353	-	-	-	NC
Metribuzin	183	14	7.7	20.7	23.1	1 210	-	-	-	1
2,4,5-T	183	10	5.5	0.39	2.68	9.3	-	-	-	NC
Fenoprop (Silvex)	183	10	5.5	0.4	0.56	3.35	-	-	-	NC
Chlorpyrifos	160	9	5.6	14.8	2.4	216	-	-	-	7
2,3,6-TBA	183	8	4.4	1.1	1.71	10.3	-	-	-	NC
Imazethapyr	174	9	5.2	1.2	2.48	146	-	-	-	NC
Diazinon	160	6	3.8	15.5	19.5	8 290	-	-	-	4
Azinphos-methyl	160	4	2.5	138	305	12 200	-	-	-	NC
Malathion	160	3	1.9	14.7	10.4	611	-	-	-	1
MCPB	183	2	1.1	0.63	2.81	7.97	-	-	-	NC
Dimethoate	160	2	1.3	25.1	24.7	33	-	-	-	NC
Trifluralin	183	2	1.1	5.15	5.21	11.8	-	-	-	NC
Benzoylprop-ethyl	183	1	0.6	26.2	159	159	-	-	-	NC
Diclofop-methyl	183	1	0.6	42.3	351	351	-	-	-	NC
Diallate I	183	1	0.6	57.8	67.1	67.1	-	-	-	NC
2,4-DB	183	0	0.0	0.53	-	-	-	-	-	-
Butylate	183	0	0.0	55.4	-	-	-	-	-	-
Disulfoton	160	0	0.0	47.1	-	-	-	-	-	-
Diallate II	183	0	0.0	32.9	-	-	-	-	-	-
Ethion	160	0	0.0	17.7	-	-	-	-	-	-
Fonofos	160	0	0.0	12.7	-	-	-	-	-	-

Table 14 Summary of pesticides and transformation products detected in surface water samples analyzed in Ontario, 2005

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Imazamethabenz-methyl (A)	174	0	0.0	0.14	-	-	-	-	-	-
Imazamethabenz-methyl (B)	174	0	0.0	0.09	-	-	-	-	-	-
Naled (Dibrom)	160	0	0.0	79.5	-	-	-	-	-	-
Parathion	160	0	0.0	15.5	-	-	-	-	-	-
Phorate	160	0	0.0	11.6	-	-	-	-	-	-
Phosmet	160	0	0.0	157	-	-	-	-	-	-
Picloram	183	0	0.0	0.66	-	-	-	-	-	-
Terbufos	160	0	0.0	8.3	-	-	-	-	-	-
Triallate	183	0	0.0	4.14	-	-	-	-	-	-

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection $\geq 50\%$.

^d Source of benchmarks: Cantox Environmental Inc., 2004.

^e NC: No comparison possible. (Method detection limit was above the benchmark).

Table 15 *Number of Ontario samples with one or more detected pesticide or transformation product(s) (2003–2005)*

Number of substances detected/Sample	1	2	3	4	5	6	7	8	9	> 10
Number of multiple detections 2003 (n = 138)	5	4	12	11	23	28	24	15	8	8
Number of multiple detections 2004 (n = 146)	2	3	10	16	17	8	30	18	26	16
Number of multiple detections 2005 (n = 179)	12	11	9	18	18	33	17	21	23	17

5.3.1 Pesticide Concentrations Over a Latitudinal Gradient in Ontario Lakes

The Ontario study also included a component that was designed to investigate pesticide concentrations and pesticide bioconcentration over a latitudinal gradient in Ontario lakes. Pesticide concentrations were determined in surface water, precipitation, air and zooplankton samples. Sample sites were located in northern and southern Ontario lakes (Figure 6). The study results are presented below.

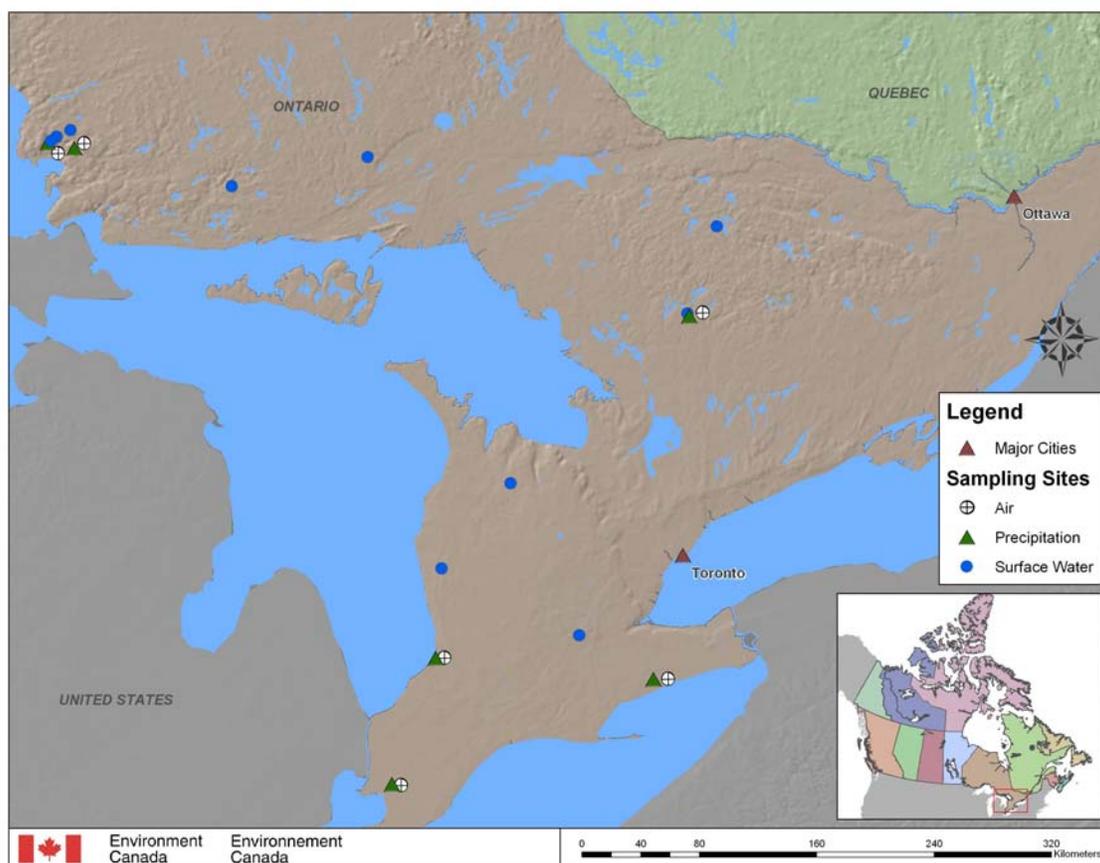


Figure 6 **Water quality sampling sites for the latitudinal gradient study in Ontario lakes, 2003–2005**

Lake Waters

A total of 168 large-volume water samples were collected from 10 lakes during the three-year study (Figure 6). The three southern lakes (Bell's, Turnbull, Wawanosh) were generally sampled four times per year (April to July), and the central lakes (Plastic, Opeongo) and northern lakes (Batchawana, Big Turkey, Windy, Wavy, Flack) three times per year (May to July). The central and northern lakes were sampled less often because of the greater distance and time required to sample at these locations (one week to make a complete circuit). Also, most northern lakes were still frozen at the end of April but unsafe to sample due to melting ice.

The frequency of detection of the 44 current-use pesticides (including three degradation products) analyzed for all three years ranged from 0 to 97% overall (Table 16). In 2004, for example, surface water samples had detectable concentrations of 30 of 44 analytes in the southern lakes, 22 of 44 in the central lakes, and 30 of 44 in the northern lakes. In 2005, 32 of 44 analytes were detected in the southern lakes and 24 of 44 in the central lakes. The frequency of detection was generally lower than the observations in 2003, where 40 of 55 analytes were detected in the southern and central lakes and 31 of 55 in two isolated northern lakes (Big Turkey, Batchawana). Chemicals with high frequencies of detection (> 50%) were atrazine, desethylatrazine, chlorpyrifos, diazinon, fonofos, endosulfan and metolachlor. Chlorothalonil, fonofos, metribuzin and trifluralin were detected more frequently in the south than in the north (Table 16).

Table 16 Summary of pesticides and transformation products detected in surface water from 10 isolated lakes in Ontario, 2003–2005

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c
					Min	Max			
Endosulfan a	163	158	97.0	0.004	< 0.004	0.42	0.013	0.027	0.057
<i>Desethylatrazine</i>	163	147	90.0	0.020	< 0.020	23.3	0.047	1.210	2.420
Metolachlor	163	144	89.0	0.005	< 0.005	24.1	0.209	0.500	1.080
Atrazine	163	132	85.0	0.020	< 0.020	37.4	1.030	2.090	3.700
Chlorothalonil	163	131	80.0	0.005	< 0.005	26.6	0.010	0.012	0.087
Chlorpyrifos	163	125	77.0	0.003	< 0.003	0.49	< 0.003	0.016	0.038
Endosulfan b									
<i>Endosulfan-sulphate</i>	163	110	67.0	0.004	< 0.004	0.89	0.004	0.047	0.108
Ametryn	163	74	60.0	0.020	< 0.020	3.02	< 0.020	< 0.020	0.226
Dyfonate	163	93	57.0	0.010	< 0.010	11.2	< 0.010	0.184	1.012
Diazinon	163	84	52.0	0.025	< 0.025	4.45	< 0.025	0.010	0.313
Naled	163	34	41.0	2.990	< 2.990	168	-	-	-
Alachlor	163	64	39.0	0.005	< 0.005	2.60	-	-	-
Dacthal (DCPA)	163	61	37.0	0.031	< 0.031	5.59	-	-	-
Myclobutanil	163	56	37.0	0.011	< 0.011	13.8	-	-	-
Metribuzin	163	49	30.0	0.001	< 0.001	23.1	-	-	-
Pendamethalin	163	49	30.0	0.008	< 0.008	8.22	-	-	-
Trifluralin	163	68	26.0	0.001	< 0.001	0.11	-	-	-
Disulfoton	163	41	25.0	0.010	< 0.010	4.09	-	-	-
Dimethoate	163	31	20.0	0.023	< 0.023	5.87	-	-	-
Terbacil	163	27	18.0	0.038	< 0.038	9.26	-	-	-
Flutriafol	163	21	13.0	0.005	< 0.005	6.61	-	-	-
Phorate	163	22	13.0	0.010	< 0.010	60.6	-	-	-
Linuron	163	19	12.0	0.046	< 0.046	4.10	-	-	-
Napropamide	163	10	12.0	0.012	< 0.012	2.06	-	-	-
Quizalofop-ethyl	163	19	12.0	0.036	< 0.036	4.12	-	-	-
Tefluthrin	163	18	11.0	0.001	< 0.001	0.10	-	-	-
Propiconazole	163	17	10.0	0.050	< 0.050	5.03	-	-	-
Dimethenamid	163	15	9.0	0.013	< 0.013	3.53	-	-	-
Lindane	163	13	8.0	0.005	< 0.005	61.0	-	-	-
Butylate	163	9	7.0	0.024	< 0.024	1.54	-	-	-
Simazine	163	12	7.0	0.047	< 0.047	5.91	-	-	-
<i>Diazinon-oxon</i>	163	6	4.0	0.025	< 0.025	2.90	-	-	-
Ethafluralin	163	3	3.0	0.005	< 0.005	0.09	-	-	-
Tebuconazol	163	5	3.0	0.003	< 0.003	0.94	-	-	-

Table 16 Summary of pesticides and transformation products detected in surface water from 10 isolated lakes in Ontario, 2003–2005

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c
					Min	Max			
Captan	163	3	2.0	0.193	< 0.193	29.8	-	-	-
EPTC	163	4	2.0	0.066	< 0.066	37.9	-	-	-
Malathion	163	3	2.0	0.001	< 0.001	2.20	-	-	-
Phosmet	163	3	2.0	0.010	< 0.010	11.5	-	-	-
Trichlorfon	163	3	2.0	0.752	< 0.752	64.5	-	-	-
Tecnazene (2356-TCNB)	163	2	1.0	0.004	< 0.004	0.81	-	-	-
Butralin	163	1	1.0	0.020	< 0.020	0.09	-	-	-
Cycloate	163	2	1.0	0.016	< 0.016	2.13	-	-	-
Phosalone	163	2	1.0	0.002	< 0.002	0.01	-	-	-
Terbufos	163	1	1.0	0.017	< 0.017	0.17	-	-	-
Triallate	163	0	0.0	-	-	-	-	-	-

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection $\geq 50\%$.

Concentrations were generally higher in the three southern lakes, as is evident by the number of current-use pesticides with concentrations greater than 1 ng/L (11 in southern lakes, six in central lakes, five in northern lakes) (Figure 7; note that the chemicals in the figure are arranged in order of fungicides, herbicides and insecticides). During the three-year study, chlorothalonil, atrazine, desethylatrazine, dacthal, EPTC, metolachlor, lindane, fonofos, naled, phorate and trichlorfon had the highest concentrations. In general, higher concentrations of two major herbicides, atrazine (including desethylatrazine) and metolachlor, were observed over three years in two southern Ontario lakes (Bell's, Wawanosh) than in the two central lakes (Plastic, Opeongo). The central lakes are more than 100 km from the nearest intensively farmed areas in Michigan and Ontario. Concentration differences between the southern and central lakes were greater for metolachlor than for atrazine.

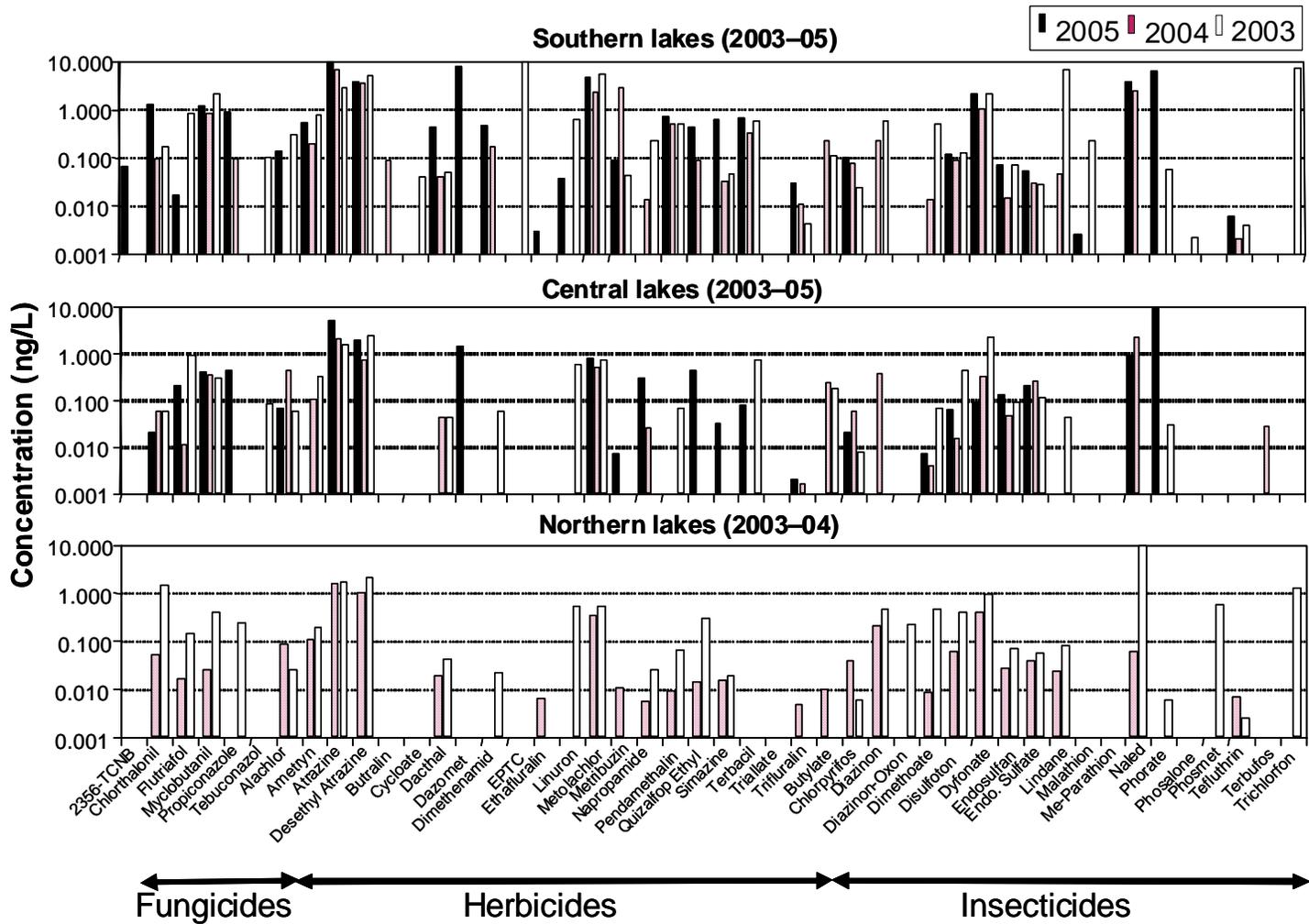


Figure 7 Mean concentrations of 46 current-use pesticides (including three degradation products) in southern, central and northern Ontario lakes, 2003–2005

The highest concentrations of atrazine and metolachlor were found in May, June and July, coinciding with post-emergence applications to corn crops in Ontario and the mid-west states of the United States. The lowest concentrations occurred in samples taken from the southern lakes in April and early August. Overall, there was greater month-to-month and year-to-year variation in concentrations of both herbicides in Bell's and Wawanosh lakes compared to the remote lakes. All lakes, except Turnbull, were sampled at two or more depths to determine whether the current-use pesticides remained in the epilimnion or were well distributed. In general, the concentrations were quite similar at all depths for atrazine and endosulfan in Opeongo Lake. In the case of atrazine, this is consistent with observations in the Great Lakes, which showed that the pesticide was present at similar concentrations at all depths (Schottler and Eisenreich, 1994).

Precipitation

A total of 60 rain samples were collected from April to September from 2003 to 2005. Overall detection frequency for 44 current-use pesticides, which were analyzed in all three years, ranged from 0 (ametryn, terbufos) to 100% (chlorothalonil) (Table 17). The frequency of detection was higher in the southern precipitation sampling locations than in the two remote locations (Turkey lakes and Dorset) in all three years. In the southern locations, average detection frequency was 71% (e.g., 31 of 45 analytes in 2005), while at the remote sites, detection frequency was 49% (e.g., 22 of 45 in 2005). Current-use pesticides with high frequency detections (> 80% of samples each year) were alachlor, atrazine/desethylatrazine, chlorothalonil, chlorpyrifos, dacthal, diazinon, endosulfan, metolachlor and pendimethalin, tefluthrin, and trifluralin. Dimethenamid, metolachlor, metribuzin, endosulfan and tefluthrin were not detected in the Turkey and Dorset samples, although they were widely detected in the south.

Table 17 Summary of pesticides and transformation products detected in precipitation at five sites in Ontario, 2003–2005

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c
					Min	Max			
Chlorothalonil	60	60	100	0.01	< 0.01	3 250	45.1	96.0	346
Metolachlor	60	59	98	0.01	< 0.01	849	0.81	4.32	30.6
<i>Endosulfan-sulphate</i>	60	59	98	0.01	< 0.01	17.1	0.42	0.97	1.84
Endosulfan a	60	56	93	0.01	< 0.01	76.6	0.32	1.65	5.57
Trifluralin	60	55	92	0.00	< 0.01	148	< 0.01	0.14	0.60
Tefluthrin	60	55	92	0.01	< 0.01	4.50	< 0.01	0.09	0.20
Metribuzin	60	54	90	0.00	< 0.01	58.0	< 0.01	< 0.01	0.36
Myclobutanil	60	54	90	0.02	< 0.02	25.6	< 0.02	< 0.02	0.19
Pendimethalin	60	53	88	0.02	< 0.02	477	0.42	2.48	28.1
Naled	60	52	87	3.00	< 3.00	5 440	< 3.00	< 3.00	5.80
Chlorpyrifos	60	49	82	0.01	< 0.01	144	0.13	0.81	2.47
Alachlor	60	46	77	0.01	< 0.01	54.5	< 0.01	< 0.01	2.30
Dacthal	60	45	75	0.63	< 0.63	18.6	0.63	0.48	0.97
Atrazine	60	45	75	0.04	< 0.04	431	0.71	4.25	40.98
Diazinon	60	36	60	0.05	< 0.05	260	< 0.05	1.54	4.68
<i>Desethylatrazine</i>	60	33	55	0.04	< 0.04	213	< 0.04	1.74	21.6
Lindane	60	33	55	0.01	< 0.01	41.9	< 0.01	< 0.01	< 0.01
Flutriafol	60	33	55	0.01	< 0.01	11.6	< 0.01	< 0.01	< 0.01
2356-TCNB	60	30	50	0.01	< 0.01	4.27	< 0.01	< 0.01	< 0.01
Fonofos	60	30	50	0.02	< 0.02	874	< 0.02	0.41	1.76
Phosalone	60	28	47	0.00	< 0.01	9.61	-	-	-
Dimethenamid	60	26	43	0.03	< 0.03	191	-	-	-
Terbacil	60	25	42	0.08	< 0.08	28.9	-	-	-
Phosmet	60	23	38	0.02	< 0.02	734	-	-	-
Malathion	60	21	35	0.01	< 0.01	10.2	-	-	-
Ethafuralin	60	20	33	0.01	< 0.01	5.17	-	-	-
Dimethoate	60	19	32	0.05	< 0.05	1120	-	-	-
Tebuconazol	60	19	32	0.01	< 0.01	36.0	-	-	-
Linuron	60	15	25	0.09	< 0.09	147	-	-	-
Simazine	60	12	20	0.09	< 0.09	1350	-	-	-
Disulfoton	60	10	17	0.02	< 0.02	3.82	-	-	-
Propiconazole	60	9	15	0.10	< 0.10	89.9	-	-	-
Quizalofop-ethyl	60	9	15	0.07	< 0.07	1.33	-	-	-
Phorate	60	7	12	0.02	< 0.02	17.8	-	-	-
Diazinon	60	3	5	0.05	< 0.05	45.0	-	-	-

Table 17 Summary of pesticides and transformation products detected in precipitation at five sites in Ontario, 2003–2005

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c
					Min	Max			
Napropamide	60	3	5	0.02	< 0.02	1.31	-	-	-
Butylate	60	2	3	0.05	< 0.05	1.72	-	-	-
Trichlorfon	60	2	3	1.50	< 1.50	57.5	-	-	-
Butralin	60	1	2	0.04	< 0.04	0.26	-	-	-
Captan	60	1	2	0.39	< 0.39	< 0.39	-	-	-
Cycloate	60	1	2	0.03	< 0.03	-	-	-	-
Ametryn	60	0	0	0.04	-	-	-	-	-
EPTC	60	0	0	0.13	-	-	-	-	-
Terbufos	60	0	0	0.03	-	-	-	-	-

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection \geq 50%.

Monthly fluxes of the major current-use pesticides in rain were calculated by dividing the quantity of each current-use pesticide (ng/month) by the sampler area (0.2025 m²). Fluxes of the five major current-use pesticides (chlorothalonil, atrazine, metolachlor, chlorpyrifos and pendimethalin) over the three-year period at Grand Bend near Lake Huron and at Dorset near Georgian Bay are shown in Figure 7. Fluxes of chlorothalonil were similar at both locations (from 0.5 to 20.0 µg/m² at Grand Bend and 0.1 to 11.5 µg/m² at Dorset); however, atrazine/desethylatrazine and metolachlor were 4 to >10-fold higher at Grand Bend.

Passive Air Samples

XAD-based passive air samplers were set up at the five precipitation sampling locations in 2004 and at all sampling sites except the one at Turkey Lake in 2005. Overall, 24 of 45 current-use pesticide analytes were detected in 2004 and 2005 (Table 18). The three southwestern Ontario locations (set up from April 1 to August 31) had a higher frequency of detection (21/45) than the two north/central locations in the non-agricultural areas (Dorset and Turkey lakes; set up from June 1 to Sept 30). The major current-use pesticides identified were similar to those found in precipitation, such as chlorpyrifos, diazinon, endosulfan and trifluralin, while others found in precipitation, such as atrazine, chlorothalonil, pendimethalin and simazine, were less frequently detected in air. The fact that the samplers in the north were not set up until the end of May could have influenced the results. Concentrations on the passive air samplers were estimated by assuming a sampling rate of 0.52 m³/day (Wania et al., 2003). Concentrations of major current-use pesticides ranged from 0.1 to 133 ng/m³ and were highest at the St. Clair site.

Table 18 Summary of pesticides and transformation products detected in air using XAD-passive samplers at four sites in Ontario, 2004–2005^a

Pesticide or transformation product ^b	Number of samples	Number of times detected	Frequency of detection (%)	Method detection limit (ng/m ³)	Range (ng/m ³)		25th percentile (ng/m ³) ^c	Median (ng/m ³) ^c	75th percentile (ng/m ³) ^c
					Min	Max			
Endosulfan a	12	11	92	0.001	< 0.001	10.5	0.531	1.14	3.21
Tefluthrin	12	11	92	0.001	< 0.001	0.176	0.010	0.056	0.135
Chlorothalonil	12	10	83	0.001	< 0.001	133	0.896	3.77	8.41
Chlorpyrifos	12	9	75	0.001	< 0.001	0.062	0.004	0.007	0.026
Metribuzin	12	9	75	0.000	< 0.001	0.039	0.007	0.012	0.030
<i>Endosulfan-sulphate</i>	12	8	67	0.001	< 0.001	0.225	< 0.001	0.022	0.060
Butylate	12	7	58	0.007	< 0.007	1.912	< 0.007	0.308	0.943
Metolachlor	12	7	58	0.001	< 0.001	2.12	< 0.001	0.151	0.373
Terbacil	12	7	58	0.011	< 0.011	3.17	< 0.011	0.645	1.277
Pendamethalin	12	6	50	0.002	< 0.002	5.70	< 0.002	0.055	0.301
Diazinon	12	5	42	0.007	< 0.007	0.341	-	-	-
Dacthal (DCPA)	12	4	33	0.020	< 0.093	0.048	-	-	-
Lindane	12	4	33	0.001	< 0.001	0.498	-	-	-
Atrazine	12	3	25	0.006	< 0.006	0.150	-	-	-
Phorate	12	3	25	0.003	< 0.003	1.26	-	-	-
Propiconazole	12	3	25	0.015	< 0.015	1.39	-	-	-
Captan	12	2	17	0.057	< 0.057	6.477	-	-	-
<i>Desethylatrazine</i>	12	2	17	0.006	< 0.006	0.035	-	-	-
Flutriafol	12	2	17	0.001	< 0.001	0.184	-	-	-
Terbufos	12	2	17	0.005	< 0.005	0.133	-	-	-
Alachlor	12	1	8	0.001	< 0.001	0.124	-	-	-
Dyfonate	12	1	8	0.003	< 0.003	0.608	-	-	-
Myclobutanil	12	1	8	0.003	< 0.003	0.014	-	-	-
Simazine	12	1	8	0.014	< 0.014	0.811	-	-	-
2356-TCNB	12	0	0	0.001	< 0.001	-	-	-	-
Ametryn	12	0	0	0.006	< 0.006	-	-	-	-
Butralin	12	0	0	0.006	< 0.006	-	-	-	-
Cycloate	12	0	0	0.005	< 0.005	-	-	-	-
<i>Diazinon-oxon</i>	12	0	0	0.007	< 0.007	-	-	-	-
Dimethenamid	12	0	0	0.004	< 0.004	-	-	-	-
Dimethoate	12	0	0	0.007	< 0.007	-	-	-	-
Disulfoton	12	0	0	0.003	< 0.003	-	-	-	-
EPTC	12	0	0	0.020	< 0.020	-	-	-	-
Ethafuralin	12	0	0	0.001	< 0.001	-	-	-	-
Linuron	12	0	0	0.014	< 0.014	-	-	-	-
Malathion	12	0	0	0.000	< 0.000	-	-	-	-
Naled	12	0	0	0.885	< 0.885	-	-	-	-
Napropamide	12	0	0	0.004	< 0.004	-	-	-	-
Phosalone	12	0	0	0.001	< 0.001	-	-	-	-
Phosmet	12	0	0	0.003	< 0.003	-	-	-	-
Quizalfop-ethyl	12	0	0	0.011	< 0.011	-	-	-	-
Tebuconazol	12	0	0	0.001	< 0.001	-	-	-	-
Triallate	12	0	0	0.001	< 0.001	-	-	-	-
Trichlorfon	12	0	0	0.222	< 0.222	-	-	-	-

^a Air concentrations (ng/m³) estimated by assuming a sampling rate of 0.52 m³/day (Wania et al., 2003).

^b Each transformation product is italicized and indented below its parent pesticide.

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection ≥50%.

5.4 Quebec

A total of 58 pesticides and/or transformation products were analyzed in surface waters from the St. Lawrence River and three of its main tributaries (the Yamaska, Nicolet and Saint-François rivers) (Figure 8). In 2003, samples were collected in the St. Lawrence and in the Nicolet, Yamaska and Saint-François rivers (n = 52). In 2004 and 2005, samples were collected (n = 70 and 62 respectively) at the same locations as in 2003 and at the outlet of Lake Saint-Pierre at Port-Saint-François.

Of the 58 substances analyzed, 28 were detected (tables 19 to 21). A combination of 7 to 9 pesticides—all herbicides—were detected in over 20% of the water samples from the St. Lawrence River and its tributaries each year. The substances detected in 50% or more of the samples from 2003 to 2005 were atrazine, metolachlor and the transformation product desethylatrazine. Atrazine and metolachlor are herbicides used primarily in the production of corn and soy in Quebec, which means the pesticides detected reflect the dominant cultures in the watersheds studied. The volume of active ingredients applied to fields in a drainage basin and the meteorological conditions during and after application have a strong influence on the presence of pesticides in surface waters. In Quebec, the maximum herbicide concentrations have generally been observed in the months immediately following their application.

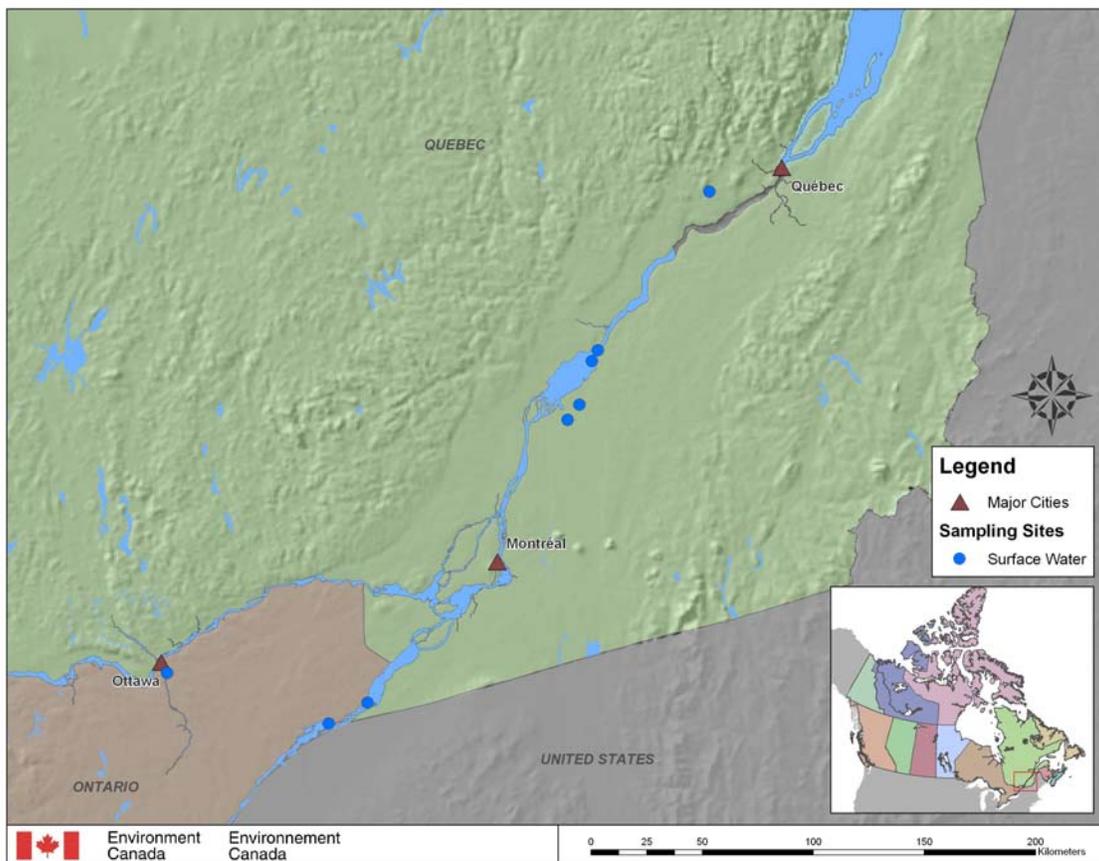


Figure 8 Water quality sampling sites in Quebec, 2003–2005

Table 19 Summary of pesticides and transformation products detected in surface water samples analyzed in Quebec, 2003

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Atrazine	52	42	80.8	20	<20	2 200	31	75	168	1
Metolachlor	52	33	63.5	10	<10	1 400	10	10	113	0
<i>Desethylatrazine</i>	52	26	50.0	40	<40	280	40	40	58	0
Dicamba	51	18	35.3	30	<30	1 900	-	-	-	0
Bentazone	51	12	23.5	30	<30	270	-	-	-	0
Dimethenamid	52	12	23.1	20	<20	520	-	-	-	0
Simazine	52	11	21.2	10	<10	20	-	-	-	0
Mecoprop	51	9	17.6	10	<10	160	-	-	-	0
<i>Deisopropylatrazine</i>	50	7	14.0	50	<50	120	-	-	-	NC
MCPA	51	6	11.8	10	<10	120	-	-	-	0
2,4-D	51	5	9.8	20	<20	120	-	-	-	0
Cyanazine	52	5	9.6	30	<30	30	-	-	-	0
Clopyralid	51	3	5.9	30	<30	80	-	-	-	0
Chlorpyrifos	52	2	3.8	20	<20	130	-	-	-	2
Chlorothalonil	50	2	3.8	60	<60	4 200	-	-	-	1
Dimethoate	50	1	2.0	40	<40	280	-	-	-	0
Metribuzin	50	1	2.0	20	<20	20	-	-	-	0
Myclobutanil	50	1	2.0	20	<20	40	-	-	-	0
Bromoxynil	51	1	2.0	20	<20	50	-	-	-	0
Diazinon	52	0	0.0	30	-	-	-	-	-	-
Diuron	52	0	0.0	250	-	-	-	-	-	-
EPTC	51	0	0.0	30	-	-	-	-	-	-
1-naphthol	50	0	0.0	60	-	-	-	-	-	-
2,4,5-T	51	0	0.0	10	-	-	-	-	-	-
2,4-DB	51	0	0.0	20	-	-	-	-	-	-
Azinphos-methyl	50	0	0.0	220	-	-	-	-	-	-
Bendiocarb	50	0	0.0	10	-	-	-	-	-	-
Butylate	50	0	0.0	30	-	-	-	-	-	-
Carbaryl	50	0	0.0	30	-	-	-	-	-	-
Carbofuran	50	0	0.0	60	-	-	-	-	-	-
Chlorfenvinphos	50	0	0.0	60	-	-	-	-	-	-
Chloroxuron	50	0	0.0	80	-	-	-	-	-	-
2,4-DP (Dichlorprop)	51	0	0.0	20	-	-	-	-	-	-
Dichlorvos	50	0	0.0	20	-	-	-	-	-	-
Diclofop-methyl	51	0	0.0	20	-	-	-	-	-	-

Table 19 Summary of pesticides and transformation products detected in surface water samples analyzed in Quebec, 2003

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Dinoseb	51	0	0.0	40	-	-	-	-	-	-
Disulfoton	18	0	0.0	30	-	-	-	-	-	-
Fenitrothion	49	0	0.0	40	-	-	-	-	-	-
Fenoprop (Silvex)	51	0	0.0	10	-	-	-	-	-	-
Fonofos	50	0	0.0	20	-	-	-	-	-	-
Linuron	49	0	0.0	40	-	-	-	-	-	-
Malathion	49	0	0.0	20	-	-	-	-	-	-
MCPB	51	0	0.0	10	-	-	-	-	-	-
Methidathion	50	0	0.0	20	-	-	-	-	-	-
Mevinphos	50	0	0.0	60	-	-	-	-	-	-
Parathion	50	0	0.0	160	-	-	-	-	-	-
<i>Parathion-methyl</i>	50	0	0.0	60	-	-	-	-	-	-
Phorate	38	0	0.0	70	-	-	-	-	-	-
Phosalone	50	0	0.0	30	-	-	-	-	-	-
Picloram	51	0	0.0	20	-	-	-	-	-	-
Tebuthiuron	50	0	0.0	240	-	-	-	-	-	-
Terbufos	38	0	0.0	40	-	-	-	-	-	-
Triclopyr	51	0	0.0	20	-	-	-	-	-	-
Trifluralin	50	0	0.0	50	-	-	-	-	-	-

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection $\geq 50\%$.

^d Source of benchmarks: Cantox Environmental Inc., 2004.

^e NC: No comparison possible. (no benchmark to compare with).

Table 20 Summary of pesticides and transformation products detected in surface water samples analyzed in Quebec, 2004

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Atrazine	69	63	91.3	20	<20	890	50	67	150	0
Metolachlor	69	53	76.8	10	<4	730	10	12	30	0
<i>Desethylatrazine</i>	69	39	56.5	40	<14	280	38	40	48	0
Simazine	69	34	49.3	2-10	<2	20	-	-	-	0
Dicamba	70	31	44.3	10-30	<10	430	-	-	-	0
2,4-D	70	25	35.7	10 - 20	<10	190	-	-	-	0
<i>Deisopropylatrazine</i>	69	23	33.3	3 - 50	<3	130	-	-	-	NC
Flumetsulam	11	3	27.3	20	<20	130	-	-	-	NC
Bentazone	70	19	27.1	20 - 30	<20	940	-	-	-	0
Mecoprop	70	13	18.6	5 - 10	<5	90	-	-	-	0
Dimethenamid	69	11	15.9	8 - 20	<8	120	-	-	-	0
MCPA	70	11	15.7	6-10	<6	110	-	-	-	0
Imazethapyr	11	1	9.09	10	<10	20	-	-	-	NC
Nicosulfuron	11	1	9.09	10	<10	10	-	-	-	NC
Dimethoate	69	6	8.70	5 - 40	<5	90	-	-	-	0
Disulfoton	68	4	5.88	5 - 30	<5	30	-	-	-	0
Clopyralid	70	3	4.29	20 - 30	<20	60	-	-	-	0
2,4-DB	70	2	2.86	9 - 20	<9	80	-	-	-	0
Bromoxynil	70	2	2.86	10 - 20	<10	40	-	-	-	0
Chlorpyrifos	69	1	1.45	6 - 20	<6	25	-	-	-	1
Myclobutanil	69	1	1.45	20	<20	40	-	-	-	0
1-naphthol	58	0	0.00	20 - 60	-	-	-	-	-	-
2,4,5-T	70	0	0.00	4 - 10	-	-	-	-	-	-
Azinphos-methyl	69	0	0.00	30 - 220	-	-	-	-	-	-
Bendiocarb	69	0	0.00	6 - 10	-	-	-	-	-	-
Butylate	68	0	0.00	3 - 30	-	-	-	-	-	-
Carbaryl	69	0	0.00	10 - 30	-	-	-	-	-	-
Carbofuran	69	0	0.00	3 - 60	-	-	-	-	-	-
Chlorfenvinphos	69	0	0.00	10 - 60	-	-	-	-	-	-
Chlorothalonil	69	0	0.00	10 - 60	-	-	-	-	-	-
Chloroxuron	69	0	0.00	20 - 80	-	-	-	-	-	-

Table 20 Summary of pesticides and transformation products detected in surface water samples analyzed in Quebec, 2004

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Cyanazine	69	0	0.00	8 - 30	-	-	-	-	-	-
Diazinon	69	0	0.00	5 - 30	-	-	-	-	-	-
Dichlorprop	70	0	0.00	10 - 20	-	-	-	-	-	-
Dichlorvos	61	0	0.00	10 - 20	-	-	-	-	-	-
Diclofop-methyl	70	0	0.00	8 - 20	-	-	-	-	-	-
Dinoseb	70	0	0.00	9 - 40	-	-	-	-	-	-
Diuron	69	0	0.00	80 - 250	-	-	-	-	-	-
EPTC	69	0	0.00	4 - 30	-	-	-	-	-	-
Fenitrothion	69	0	0.00	10 - 40	-	-	-	-	-	-
Fenoprop (Silvex)	70	0	0.00	3 - 10	-	-	-	-	-	-
Fonofos	69	0	0.00	2	-	-	-	-	-	-
Linuron	69	0	0.00	10 - 40	-	-	-	-	-	-
Malathion	69	0	0.00	4 - 20	-	-	-	-	-	-
MCPB	70	0	0.00	7 - 10	-	-	-	-	-	-
Methidathion	69	0	0.00	10 - 20	-	-	-	-	-	-
Metribuzin	69	0	0.00	6 - 20	-	-	-	-	-	-
Mevinphos	69	0	0.00	6 - 60	-	-	-	-	-	-
Parathion	69	0	0.00	20 - 160	-	-	-	-	-	-
<i>Parathion-methyl</i>	69	0	0.00	6 - 60	-	-	-	-	-	-
Phorate	69	0	0.00	9 - 70	-	-	-	-	-	-
Phosalone	69	0	0.00	8 - 30	-	-	-	-	-	-
Picloram	70	0	0.00	10 - 20	-	-	-	-	-	-
Rimsulfuron	11	0	0.00	10	-	-	-	-	-	-
Tebuthiuron	69	0	0.00	80 - 240	-	-	-	-	-	-
Terbufos	69	0	0.00	10	-	-	-	-	-	-
Triclopyr	70	0	0.00	9 - 20	-	-	-	-	-	-

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection $\geq 50\%$.

^d Source of benchmarks: Cantox Environmental Inc., 2004.

^e NC: No comparison possible. (no benchmark to compare with).

Table 21 Summary of pesticides and transformation products detected in surface water samples analyzed in Quebec, 2005

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Atrazine	62	59	95.2	20	< 20	1 400	50	70	147	0
Metolachlor	62	36	58.1	10	< 10	520	10	10	57.5	0
Dicamba	59	27	45.8	30	< 30	2 600	-	-	-	0
<i>Desethylatrazine</i>	62	28	45.2	40	< 40	150	-	-	-	0
Bentazone	59	18	30.5	30	< 30	4 600	-	-	-	0
2,4-D	59	13	22.0	20	< 20	340	-	-	-	0
MCPA	59	12	20.3	10	< 10	1 200	-	-	-	0
Dimethenamid	62	8	12.9	20	< 20	100	-	-	-	0
Mecoprop	59	7	11.9	10	< 10	180	-	-	-	0
Chlorpyrifos	62	6	9.7	20	< 20	240	-	-	-	6
Clopyralid	58	1	1.7	30	< 30	310	-	-	-	0
2,4-DB	59	1	1.7	20	< 20	40	-	-	-	0
Bromoxynil	59	1	1.7	20	< 20	270	-	-	-	0
Chloroxuron	62	1	1.6	80	< 80	90	-	-	-	0
<i>Deisopropylatrazine</i>	62	1	1.6	50	< 50	60	-	-	-	NC
Diuron	62	1	1.6	250	< 250	270	-	-	-	0
EPTC	62	1	1.6	30	< 30	330	-	-	-	0
Linuron	62	1	1.6	40	< 40	110	-	-	-	0
Myclobutanil	62	1	1.6	20	< 20	50	-	-	-	0
1-naphthol	57	0	0.0	60	-	-	-	-	-	-
2,4,5-T	59	0	0.0	10	-	-	-	-	-	-
Azinphos-methyl	62	0	0.0	220	-	-	-	-	-	-
Bendiocarb	62	0	0.0	10	-	-	-	-	-	-
Butylate	62	0	0.0	30	-	-	-	-	-	-
Carbaryl	62	0	0.0	30	-	-	-	-	-	-
Carbofuran	62	0	0.0	60	-	-	-	-	-	-
Chlorfenvinphos	62	0	0.0	60	-	-	-	-	-	-
Chlorothalonil	62	0	0.0	60	-	-	-	-	-	-
Cyanazine	62	0	0.0	30	-	-	-	-	-	-
Diazinon	62	0	0.0	30	-	-	-	-	-	-

Table 21 Summary of pesticides and transformation products detected in surface water samples analyzed in Quebec, 2005

Pesticide or transformation product ^a	Number of samples ^b	Number of times detected	Frequency of detection (%)	Method detection limit (ng/L)	Range (ng/L)		25th percentile (ng/L) ^c	Median (ng/L) ^c	75th percentile (ng/L) ^c	Number of samples above the benchmark ^{d,e}
					Min	Max				
Dichlorprop	59	0	0.0	20	-	-	-	-	-	-
Dichlorvos	62	0	0.0	20	-	-	-	-	-	-
Diclofop-methyl	60	0	0.0	20	-	-	-	-	-	-
Dimethoate	62	0	0.0	40	-	-	-	-	-	-
Dinoseb	59	0	0.0	40	-	-	-	-	-	-
Disulfoton	16	0	0.0	30	-	-	-	-	-	-
Fenitrothion	62	0	0.0	40	-	-	-	-	-	-
Fenoprop (Silvex)	59	0	0.0	10	-	-	-	-	-	-
Fonofos	62	0	0.0	20	-	-	-	-	-	-
Malathion	62	0	0.0	20	-	-	-	-	-	-
MCPB	59	0	0.0	10	-	-	-	-	-	-
Methidathion	62	0	0.0	20	-	-	-	-	-	-
Metribuzin	62	0	0.0	20	-	-	-	-	-	-
Mevinphos	62	0	0.0	60	-	-	-	-	-	-
Parathion	62	0	0.0	160	-	-	-	-	-	-
<i>Parathion-methyl</i>	62	0	0.0	60	-	-	-	-	-	-
Phorate	58	0	0.0	70	-	-	-	-	-	-
Phosalone	62	0	0.0	30	-	-	-	-	-	-
Picloram	59	0	0.0	20	-	-	-	-	-	-

^a Each transformation product is italicized and indented below its parent pesticide.

^b Total does not include samples that were not analyzed for any reason (i.e., sample was lost or destroyed).

^c Statistics (25th percentile, median, and 75th percentile) were calculated when the frequency of detection $\geq 50\%$.

^d Source of benchmarks: Cantox Environmental Inc., 2004.

^e NC: No comparison possible. (no benchmark to compare with).

5.5 Prince Edward Island, Nova Scotia and New Brunswick

The objective of the Atlantic component was to determine the presence, concentration, and potential risks associated with pesticides in groundwater, surface water, stream sediments and tissue in water systems draining intensive agricultural areas.

5.5.1 Surface Water

In Prince Edward Island, there were 12 detections of five active ingredients in the 27 surface water samples collected from July through October 2003. In 2004, active ingredients were detected in two of the 15 samples collected. There were no detections in the 40 samples collected from the Dunk River–North Brook and Wilmot River systems in 2005. In New Brunswick, there were 11 detections of six different active ingredients from the 23 samples collected in 2003, and in 2004, there were 31 detections of seven different products in the 19 samples collected. In 2005, there were 15 detections (11 from Black Brook and four from Lanes Creek) of eight different products. There were no detections at the Five Fingers Brook site in either 2003 or 2004, and no detections were found at the stream site near Buctouche Bay in 2003.

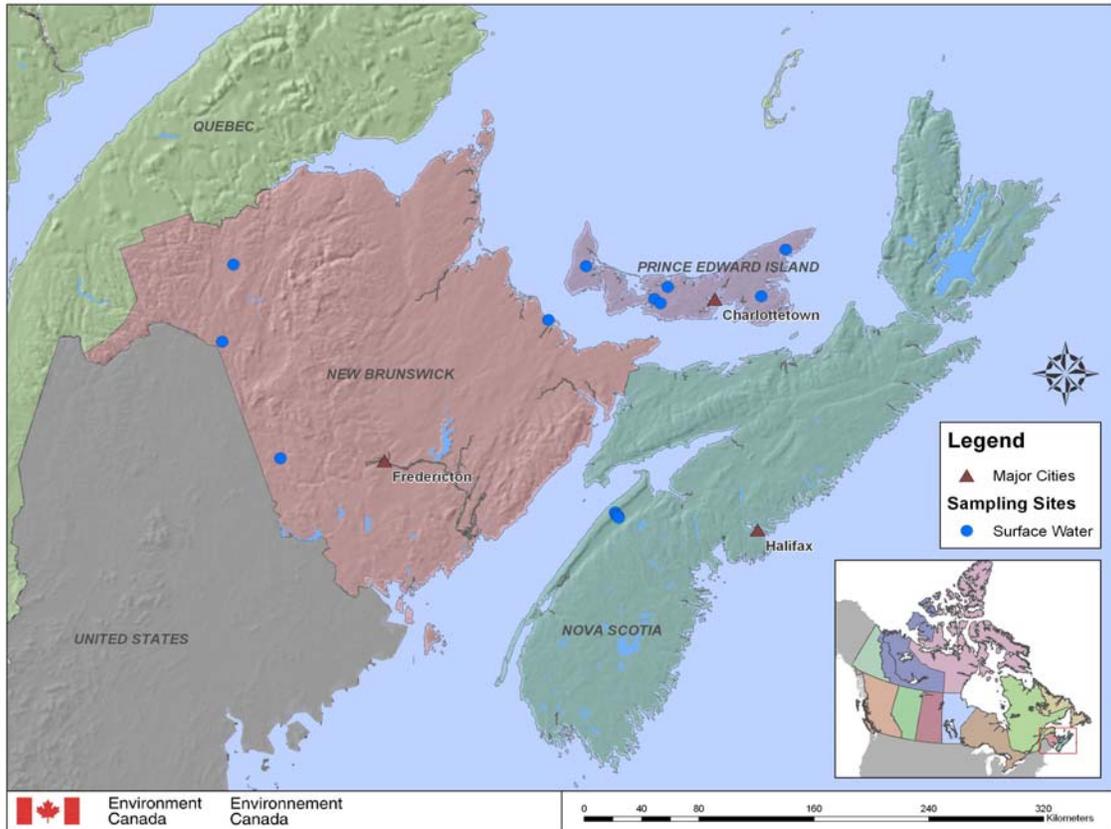


Figure 9 Water quality sampling sites in Prince Edward Island, Nova Scotia and New Brunswick, 2003–2005

Table 22 Summary of surface water results, Prince Edward Island, Nova Scotia and New Brunswick – 2003, 2004 and 2005

Province		New Brunswick			Prince Edward Island			Nova Scotia		
Total number of sites		4			6			4		
Number of samples by year		2003: 23 2004: 19 2005: 15			2003: 27 2004: 15 2005: 40			2003: 0 2004: 19 2005: 29		
Compound	Surface water guideline (µg/L)	Detections/ Number of samples ^a	Frequency of detection (%)	MDL ^b (µg/L)	Detections/ Number of samples ^a	Frequency of detection (%)	MDL ^b (µg/L)	Detections/ Number of samples ^a	Frequency of detection (%)	MDL ^b (µg/L)
2,4-D	4.0	0/57	0	0.1	0/82	0	0.1	0/48	0	0.1
Atrazine	1.8	0/57	0	0.03	0/82	0	0.05	12/48	25	0.03–0.15
Azinphos-methyl	0.005	5/57	9	0.05–5.0	0/82	0	0.05	1/48	2.0	0.03–0.06
Azoxystrobin		0/57	0	0.05	NA	0	0.05	0/48	0	0.05
Carbaryl	0.2	0/57	0	0.04	0/82	0	0.05	0/48	0	0.04
Carbofuran	1.8	0/57	0	0.04	2/82	2.4	0.05–0.59	0/48	0	0.04
Chlorothalonil	0.18	9/57	16	0.02–4.9	2/82	2.4	0.05–7.83	2/48	4.1	0.02–0.03
Cypermethrin	0.0002	0/57	0	0.08	0/82	0	0.05	0/48	0	0.08
Dicamba	10.0	0/33	0	0.6	0/55	0	0.6	0/48	0	0.6
Dimethoate	6.2	4/57	7.0	0.04–0.45	0/82	0	0.05	0/19	0	0.04
Dithiocarbamate (total)		2/57	3.6	25–114	0/82	0	25	NA		
Endosulfan a	0.02	1/57	2.4	0.02–0.1	0/82	0	0.05	0/48	0	0.02
Endosulfan b	0.056	2/57	3.6	0.01–0.2	0/82	0	0.05	0/48	0	0.01
Fonofos	0.008	0/57	0	0.02	0/82	0	0.05	0/48	0	0.02
Heptachlor - epoxide		0/57	0	0.02	NA			0/48	0	0.02
Hexazinone	0.07	0/57	0	0.06	4/82	4.9	0.06–0.24	0/48	0	0.06
Imidacloprid	0.38	2/57	4.0	0.1–0.3	0/82	0	0.1	0/48	0	0.1
Linuron	7.0	10/57	16	0.06–0.3	0/82	0	0.05	0/48	0	0.06
MCPA	2.6	1/57	1.8	0.1–0.1	0/82	0	0.1	1/48	2.1	0.1–0.2
Mecoprop	13.0	NA			NA			0/29	0	0.1
Metalaxyl	374	10/57	18.0	0.03–2.0	4/82	4.9	0.05–0.14	22/48	46	0.03–0.13
Metobromuron	10.0	0/56	0	0.03	0/82	0	0.05	0/48	0	0.03
Metribuzin	1.0	10/57	18.0	0.03–0.3	2/82	2.4	0.05–0.08	0/48	0	0.03
Permethrin	0.0004	1/57	2.4	0.06	0/82	0	0.05	0/48	0	0.06
Terbacil		0/33	0	0.08	NA			0/48	0	0.08

^a NA: not analyzed.^b Method detection limit.



Water sampling site in Prince Edward Island: during dry period (left) and after a rain event (right) (Photos: Clair Murphy)

A total of 48 surface water samples were collected in Nova Scotia during the June through October periods in 2004 and 2005 from four sites in the Thomas Brook watershed. There were 21 detections of three pesticides in the 19 samples analyzed in 2004, and 17 detections of four pesticide products in the 29 samples collected from the same watershed in 2005.

5.5.2 Stream Sediment

Sediment samples were collected as part of the Prince Edward Island monitoring program only. In 2003, there were nine detections of three different compounds, six in the Mill River and three in the Souris River samples. In 2004, there were a total of eight detections of dithiocarbamates in Wilmot River (3) and Founds River (5) samples. In 2005, dithiocarbamates were measured in all nine samples collected from the Wilmot River and Dunk River–North Brook sites. Table 23 provides a summary of the compounds measured and the frequency of detection.

Table 23 Summary of stream sediment results from the Mill, Wilmot, Founds and Souris rivers and from Dunk River–North Brook, Prince Edward Island – 2003, 2004 and 2005

Compound	Range ^a (µg/kg)	Detections/Number of samples	Frequency of detection (%)	Benchmark (MPC) ^b
Azinphos-methyl	< 5.0 – 18.7	3/54	5.5	0.89 (Netherlands)
Cypermethrin	< 5.0 – 17.3	3/54	5.5	0.39 (Netherlands)
Permethrin	< 5.0 – 10.9	3/27	11	0.87 (Netherlands)
Dithiocarbamates	< 100– 1 600	12/25	48	NA ^c

^a Method detection limit is indicated with a less than sign (<).

^b Maximum permissible concentration.

^c Not Available.

5.5.3 Groundwater

In Prince Edward Island, there were 108, 122 and 112 groundwater samples collected and analyzed as part of the 2003, 2004 and 2005 sampling programs, respectively. In all three years, the sampling occurred in late fall and early winter to coincide with the fall groundwater recharge period.

In 2003, there were low-level detections of chlorothalonil in two wells with concentrations of 100 and 400 ng/L, respectively. When the two wells were resampled, no product was detected. The herbicides atrazine and hexazinone were also detected at concentrations of 1 100 and 700 ng/L, respectively. On resample, each well showed a concentration of 640 ng/L, for the same two products.

In 2004, three herbicides and one fungicide were measured. In total, there were five detections of atrazine with concentrations ranging from 30 to 540 ng/L, two detections of metribuzin (100 and 180 ng/L) and single detections of hexazinone (560 ng/L) and metalaxyl (30 ng/L).

In 2005, there were five detections of atrazine at concentrations ranging from 30 to 650 ng/L, seven detections of metalaxyl (30 to 100 ng/L) and three detections of metribuzin with a maximum concentration of 190 ng/L.

During the summers of 2004 and 2005, groundwater sampling in Nova Scotia was conducted on two farm wells situated in the lower portion of the Thomas Brook watershed. There were no pesticide detections in the 12 samples analyzed.

5.5.4 Shellfish/Finfish Tissue

Over the course of the three-year program, a total of 20 shellfish and 23 finfish samples were collected from the same Prince Edward Island rivers as the surface water samples. No pesticides were detected in any of the samples collected over the three-year period.

6.0 IMPLICATIONS FOR WATER USES IN CANADA

Environmental quality managers, risk assessors and the public need interpretive tools and science-based guidance to assess the implications of surveillance results for water uses and potential risks to human health and the environment. The most commonly used tools are water quality guidelines, criteria or objectives that are designed to achieve specific protection goals (e.g., protection of 100% of freshwater aquatic species). In Canada, the Federal-Provincial-Territorial Committee on Drinking Water is responsible for the development of drinking water guidelines, which are published by Health Canada (Health Canada, 2006). The Canadian Council of Ministers of the Environment publishes Environmental Quality Guidelines for surface water, soil, sediment and tissue for the protection of the environment (CCME, 1999). Various other Canadian jurisdictions (e.g., provinces and territories) also publish water quality guidelines for the protection of aquatic life.

6.1 Protection of Drinking Water for Human Health

The Federal-Provincial-Territorial Committee on Drinking Water derives Guidelines for Canadian Drinking Water Quality for microbiological, physical, chemical and radiological parameters. The Guidelines for Canadian Drinking Water Quality are used by the provinces and territories to establish chemical-specific drinking water requirements in their jurisdictions. They provide reliable measures to identify potential drinking water problems. The guidelines are designed to protect human health, and they apply to all private and municipal water sources. Each Canadian drinking water quality guideline is reported as a maximum acceptable concentration that represents a level at or below which effects to human health are not expected over a lifetime of consumption (Health Canada, 1995, 2008). The maximum acceptable concentration is based on an acceptable daily intake, assuming that humans consume 1.5 L of drinking water a day over a period of 70 years. It is derived from available toxicity studies incorporating an uncertainty factor. An interim maximum acceptable concentration is derived when insufficient data or information are available to establish a maximum acceptable concentration. Interim maximum acceptable concentrations are based on the available information and incorporate larger safety factors. They are reviewed as new toxicity data and analytical detection methods become available (Health Canada, 1995). Drinking water quality guideline values are intended for application at the point of consumption (i.e., after treatment) rather than in source waters from which drinking water is obtained. There are currently only 26 Guidelines for Canadian Drinking Water Quality available for pesticides, as presented in Table 24. This study detected pesticides in drinking water

supplies for which no Guidelines for Canadian Drinking Water Quality exist (see section 6.1.1).

Table 24 Allowable pesticide concentrations under the Guidelines for Canadian Drinking Water Quality^a

	IMAC ^b (ng/L)	MAC ^c (ng/L)
Herbicides		
2,4-D	100 000	
Atrazine	5 000 ^d	
<i>Desethylatrazine^e</i>	5 000 ^d	
Bromoxynil	5 000	
Cyanazine	10 000	
Dicamba		120 000
Diuron		150 000
Glyphosate	280 000	
MCPA		2 000 ^f
Metolachlor	50 000	
Metribuzin		80 000
Paraquat (as dichloride)	10 000	
Picloram	190 000	
Simazine	10 000	
Trifluralin	45 000	
Insecticides		
Azinphos-methyl		20 000
Carbaryl		90 000
Carbofuran		90 000
Chlorpyrifos		90 000
Diazinon		20 000
Diclofop-methyl		9 000
Dimethoate	20 000	
Malathion		190 000
Methoxychlor		900 000
Parathion		50 000
Phorate		2 000
Terbufos	1 000	

^a Source: adapted from Health Canada, 2008.

^b Interim Maximum Acceptable Concentration.

^c Maximum Acceptable Concentration.

^d The guideline for atrazine applies to the sum of atrazine and its metabolites.

^e Each transformation product is italicized and indented below its parent pesticide.

^f MCPA guideline is undergoing review by Health Canada and MAC is not published in Health Canada (2008). The proposed MAC is 0.002mg/l or 2,000 ng/L (Health Canada 2008b).

6.1.1 Surveillance Data Comparisons to Canadian Drinking Water Quality Guidelines

Two of the five regional components of this national water quality surveillance program analyzed pesticides and their transformation products in drinking water (Alberta, Saskatchewan and Manitoba component and Prince Edward Island, Nova Scotia and New Brunswick component). In the Alberta, Saskatchewan and Manitoba component, the drinking water quality of several small rural communities was examined by sampling tap water in the communities. Tap water samples were collected in early July, well into the growing season. For comparison with the Guidelines for Canadian Drinking Water Quality, the maximum pesticide concentrations detected in tap water in 2004 and 2005 were used (Table 25).

Table 25 Comparison of maximum tap water pesticide concentrations in rural prairie communities with allowable pesticide concentrations under the Guidelines for Canadian Drinking Water Quality

Analyte	Number of samples	Minimum (ng/L)	Mean (ng/L)	Maximum (ng/L)	GCDWQ ^a (ng/L)
2,4-DP (Dichlorprop)	28	0.42	12.70	105.00	-
2,3,6-TBA	28	1.10	1.20	3.77	-
2,4,5-T	28	< 0.39	< 0.39	< 0.39	-
2,4-D	28	10.50	81.40	589.00	100 000
2,4-DB	28	0.53	0.53	0.53	-
Bromoxynil	28	0.99	12.80	227.00	5 000
Clopyralid	28	0.59	51.90	393.00	-
Dicamba	28	0.73	37.40	748.00	120 000
Imazamethabenz-methyl ^b	28	0.14	3.15	75.30	-
Imazethapyr	28	1.20	1.35	3.11	-
MCPA	28	0.58	96.50	865.00	2 000
MCPB	28	< 0.63	< 0.63	< 0.63	-
Mecoprop	28	0.50	5.74	42.10	-
Picloram	28	0.66	11.70	1740	-
Fenoprop (Silvex)	28	< 0.40	< 0.40	< 0.40	-
Atrazine	29	1.92	6.48	27.60	5 000 ^c
Desethylatrazine ^d	29	< 26.80	< 26.80	< 26.80	5 000 ^c
Benzoylprop-ethyl	29	< 26.20	< 26.20	< 26.20	-
Butylate	29	< 55.40	< 55.40	< 55.40	-
Diallate I	29	< 57.80	< 57.80	< 57.80	-
Diallate II	29	< 32.90	< 32.90	< 32.90	-
Diclofop-methyl	29	< 42.30	< 42.30	< 42.30	9 000
Metolachlor	29	< 23.70	< 23.70	< 23.70	50 000
Metribuzin	29	8.11	20.30	< 20.70	80 000
Simazine	29	2.93	15.94	< 16.40	10 000

Table 25 Comparison of maximum tap water pesticide concentrations in rural prairie communities with allowable pesticide concentrations under the Guidelines for Canadian Drinking Water Quality

Analyte	Number of samples	Minimum (ng/L)	Mean (ng/L)	Maximum (ng/L)	GCDWQ ^a (ng/L)
<i>Desethylsimazine</i> ^d	29	< 148.00	<148	< 148.00	-
Triallate	29	< 4.14	<4.14	< 4.14	-
Trifluralin	29	< 5.15	<5.15	< 5.15	45 000
Thifensulfuron ME	29	1.00	1.03	1.50	-
Metsulfuron ME	29	1.00	1.01	< 1.20	-
Ethametsulfuron ME	29	1.00	1.18	4.00	-
Sulfosulfuron	29	1.00	1.07	< 2.90	-
Tribenuron ME	29	1.00	1.28	4.00	-

^a The Guidelines for Canadian Drinking Water Quality (Health Canada, 2006) include interim maximum acceptable concentrations and maximum acceptable concentrations. See Table 24.

^b Two samples were analyzed at each site each year for imazamethabenz-methyl. The sample with the highest concentration was compared with the Canadian Drinking Water Quality Guidelines.

^c The Guideline for Canadian Drinking Water Quality for atrazine applies to atrazine and its transformation products.

^d Each transformation product is italicized and indented below its parent pesticide.

For those pesticides where a Canadian drinking water quality guideline was available (11 out of 36 pesticides), there were no samples that had maximum detected levels above the drinking water quality guideline value. In fact, all of the maximum values were usually one or two orders of magnitude lower than the guideline, with the exception of MCPA (Table 25).

Source Waters

Source waters are waters used to supply drinking water. They include natural or constructed reservoirs, lakes, rivers, groundwater aquifers and any other water source that ultimately is used for drinking water.

Drinking water reservoirs were sampled simultaneously in early July with the polished tap water. Drinking water contained an average of 6.4 herbicides (n = 28 samples), ranging from 3 to 15 herbicides depending on the location. Water treatment removed from 14% (clopyralid) to 56% (ethametsulfuron) of herbicides in the communities where the samples were taken (Table 26). When concentrations of a number of herbicides (bromoxynil, 2,4-DP(Dichlorprop), dicamba, mecoprop, imazethabenz, atrazine) were low in reservoir water (<20 ng/L), they were usually not detected in drinking water supplies (Donald et al., 2007).

Table 26 Mean concentrations of herbicides in reservoirs and the percent of herbicides removed by water treatment plants

Herbicide	Reservoir	Water treatment plant (Tap water)		
	Mean concentration n = 15 reservoirs (ng/L)	Mean removed (%)	Range (%)	Number of paired samples
2,4-D	123.0	39	0 – 84	28
MCPA	57.0	45	0 – 93	26
Clopyralid	28.0	14	0 – 88	27
Dichlorprop	16.0	29	0 – 55	19
Dicamba	6.6	38	0 – 95	19
Mecoprop	4.4	34	0 – 80	11
Bromoxynil	2.4	46	0 – 98	12
Ethametsulfuron	-	56	33 – 82	4
Picloram	-	33	16 – 45	3
Tribenuron	-	33	4 – 91	4
Imazethapar	-	38	0 – 79	3

The Prince Edward Island groundwater monitoring results were assessed against the Guidelines for Canadian Drinking Water Quality. In the absence of Canadian guidelines, chlorothalonil, metalaxyl and hexazinone detections were considered relative to Health Canada Guidance values of 70 000 ng/L and 700 000 ng/L and a United States Lifetime Health Advisory for drinking water of 400 000 ng/L, respectively (Health Canada, 2008; USEPA, 2006). There were 108, 122 and 112 groundwater samples collected and analyzed as part of the 2003, 2004 and 2005 sampling programs, respectively. In all three years, the sampling occurred in late fall and early winter to coincide with the fall groundwater recharge period. Samples were taken from active municipal, central or individual wells.

In 2003, there were low-level detections of chlorothalonil in two wells, with concentrations of 100 and 400 ng/L. When the two wells were sampled again, no product was detected. Atrazine and hexazinone were also detected, at concentrations of 1 100 and 700 ng/L. On re-sampling, each well showed a concentration of 640 ng/L for the same two products. In 2004, three herbicides and one fungicide were measured. In total, there were five detections of atrazine with concentrations ranging from 30 to 540 ng/l, two detections of metribuzin (100 and 180 ng/L) and single detections of hexazinone (560 ng/L) and metalaxyl (30 ng/L). In 2005, there were five detections of atrazine at concentrations ranging from 30 to 650 ng/L, seven detections of metalaxyl (30 to 100 ng/L) and three detections of metribuzin with a maximum concentration of 190 ng/L. All the pesticide detections found over the three-year program were several orders of magnitude below drinking water quality guidelines.

During the summers of 2004 and 2005, groundwater sampling in Nova Scotia was conducted in two farm wells situated in the lower portion of the Thomas Brook watershed. No pesticides were detected in the 12 samples analyzed.

6.2 Protection of Freshwater Aquatic Life

Pesticides that reach surface waters can cause a variety of ecological impacts, including the following:

- direct mortality (kills) of fish and other aquatic organisms
- various sub-lethal effects on aquatic organisms, such as impaired or altered reproduction, development, growth, behaviour and respiration, and increased vulnerability to other environmental stressors
- inhibition of photosynthesis in non-target aquatic plants
- bioaccumulation of active ingredients in aquatic organisms and biomagnification in wildlife that consume aquatic biota

The Canadian Water Quality Guidelines for the Protection of Aquatic Life provide concentrations for individual chemicals, such as pesticides, below which adverse biological effects are not expected to occur in the environment. Canadian Water Quality Guidelines for the Protection of Aquatic Life are available for only 30 pesticides (CCME, 1999; also see sidebar), meaning no Canadian Water Quality Guidelines for the Protection of Aquatic Life exist for approximately 75% of the pesticides included in the Pesticides Science Fund (PSF) water quality surveillance program. A further gap is the complete absence of guidelines for pesticide mixtures. Such mixtures are often detected in aquatic environments, but there are currently no tools to assist in interpreting the significance of such mixtures.

Pesticides listed in the Canadian Water Quality Guidelines for the Protection of Aquatic Life

- 2,4-D total (phenoxy herbicides)
- Aldicarb
- Atrazine
- Bromacil
- Bromoxynil
- Captan
- Carbaryl
- Carbofuran
- Chloropyrifos
- Chlorothalonil
- Cyanazine
- Deltamethrin
- Dicamba
- Diclofop-methyl
- Dimethoate
- Dinoseb
- Endosulfan
- Glyphosate
- Lindane (HCH, Gamma)
- Linuron
- MCPA total
- Metolachlor
- Metribuzin
- Pentachlorophenol
- Permethrin
- Picloram
- Simazine
- Tebuthiuron
- Trifluralin
- Triallate

6.2.1 Development of Science-based Water Quality Benchmarks for Current-Use Pesticides

In the absence of Canadian Water Quality Guidelines for the Protection of Aquatic Life for the majority of the pesticides in this project, Environment Canada initiated an international review and evaluation of existing science-based water quality benchmarks for current-use pesticides, and it commissioned the collection of key data to enable the development of additional benchmarks (Cantox Environmental Inc., 2004). For this work, a number of steps were taken, including these:

- 1) Available water quality guidelines for the protection of aquatic life for current-use pesticides were identified.
- 2) Toxicity data for pesticides lacking an interpretive tool (e.g., guideline, objective or criterion) were collected.
- 3) Benchmarks were derived for pesticides lacking other interpretive tools, including a description of the methods used to establish the benchmarks.

The Pesticide Science Fund National Water Quality Surveillance Program pesticide list was cross-referenced with the available Canadian Council of Ministers of the Environment Water Quality Guidelines for the Protection of Aquatic Life for pesticides (CCME, 1999). Next, federal and provincial sources were surveyed for water quality guidelines for the protection of aquatic ecosystems. Provincial guidelines from Ontario and Quebec were available for some of the pesticides lacking Canadian Council of Ministers of the Environment guidelines. For these pesticides, the lowest available provincial guideline was selected to serve as the Canadian benchmark for the protection of aquatic life. Provincial guidelines were given preference over international ones because they were derived from a Canadian perspective, taking into account such issues as the effects on Canadian species and the consideration of Canadian protection levels.

International sources, such as the United States Environmental Protection Agency, the Australian and New Zealand Environment and Conservation Council and the United Kingdom Department for Environment, Food and Agriculture were queried for the remaining current-use pesticides. The objectives and methods used internationally to develop guidelines differ from those of the Canadian Council of Ministers of the Environment water quality guideline protocol (CCME, 1991). Therefore, a review of the protocols used by other jurisdictions to derive water quality guidelines was undertaken. Using this review, decision criteria were developed to guide benchmark selection when Canadian Council of Ministers of the Environment guidelines or provincial guidelines were unavailable. The decision criteria were based on how similar the protocol objectives and methodologies used by other countries are to the Council protocol (CCME, 1991).

Although international sources reduced the number of pesticides in this national water quality surveillance program requiring a newly derived benchmark, a large group of pesticides (n = 41) still lacked a guideline, objective or criterion for the protection of

aquatic ecosystems. Aquatic toxicity data for these pesticides were collected and used to derive threshold values above which adverse effects to aquatic biota could occur. Data sources that were easily searchable and regularly updated were consulted (e.g., United States Environmental Protection Agency AQUIRE and Pesticide Ecotoxicity databases). Data were reviewed and the most sensitive study identified, generally following the recommended approach outlined in the Canadian Council of Ministers of the Environment protocol for the derivation of water quality guidelines for the protection of aquatic life (CCME, 1991). Application factors were applied to the most sensitive study, in keeping with the recommended approach in the Canadian Council of Ministers of the Environment water quality protocol (CCME, 1991). For chronic studies (e.g., Lowest Observed Effect Level, growth), each of the effect concentrations was multiplied by an application factor of 0.1. For acute studies (i.e., lethal concentration 50 [LC50] mortality), an application factor of 0.05 was used. This is equivalent to the Canadian Council of Ministers of the Environment application factor used for non-persistent substances (CCME, 1991). In situations where study information such as duration and endpoint was lacking, professional judgment was used to determine the appropriate application factor to apply. The end result was a table of 107 benchmarks for use with the surveillance data collected from Canadian surface waters in the Pesticide Science Fund National Water Quality Surveillance Program (Table 27).

Table 27 Science-based water quality benchmarks for 107 current-use pesticides^a

Pesticide/Class	CAS RN ^b	CCME Water Quality Guideline ^c	Benchmark (ng/L)
Herbicides			
2,4-D	94-75-7	4,000	4,000
2,4-DB	94-82-6	NG	25,000
2,4-DP (Dichlorprop)	120-36-5	NG	40,000
2,4,5-T	93-76-5	NG	1,000
2,3,6-TBA	50-31-7	NG	425,000
Alachlor	15972-60-8	NG	48,000
Ametryn	834-12-8	NG	500
Atrazine	1912-24-9	1,800	1,800
<i>Desethylatrazine^e</i>	6190-65-4	NG	72,000
Bentazone	25057-89-0	NG	510,000
Benzoylprop-ethyl	22212-55-1	NG	28,100
Bromoxynil	1689-84-5	5,000	5,000
Butylate	2008-41-5	NG	77,000
Butralin	33629-47-9	NG	14,000
Chloroxuron	1982-47-4	NG	240
Clopyralid	1702-17-6	NG	37,510,000
Cyanazine	21725-46-2	2,000 ^d	2,000
Dacthal (DCPA)	1861-32-1	NG	165,000
Diallate	2303-16-4	NG	135,000
Dicamba	1918-00-9	10,000 ^d	10,000
Diclofop-methyl	51338-27-3	6,100	6,100
Dimethenamid	87674-68-8	NG	5,600
Diuron	330-54-1	NG	1,600
EPTC	759-94-4	NG	39,000
Ethalfluralin	55283-68-6	NG	905
Flufenacet	142459-58-3	NG	245

Table 27 Science-based water quality benchmarks for 107 current-use pesticides^a

Pesticide/Class	CAS RN ^b	CCME Water Quality Guideline ^c	Benchmark (ng/L)
Glyphosate	1071-83-6	65,000 ^d	65,000
Hexazinone	51235-04-2	NG	70
Imidacloprid	13826-41-3	120	120
Imazamethabenz-methyl (A and B)	81405-85-8	NG	5,000,000
Imazethapyr	81335-77-5	NG	2 960 000
Linuron	330-55-2	7 000 ^d	7 000
MCPA	94-74-6	2 600 ^d	2 600
MCPB	94-81-5	NG	7 300
Mecoprop	93-65-2	NG	13 000
Metobromuron	3060-89-7	NG	10 000
Metolachlor	51218-45-2	7 800 ^d	7 800
Metribuzin	21087-64-9	1 000 ^d	1 000
Pendimethalin	40487-42-1	NG	620
Picloram	1918-02-1	29 000 ^d	29 000
Rimsulfuron	122931-48-0	NG	2 900
Fenoprop (Silvex)	93-72-1	NG	21 000
Simazine	122-34-9	10,000	10 000
Sulfosulfuron	141776-32-1	NG	100
Tebuthiuron	34014-18-1	1 600 ^d	1 600
Triallate	2303-17-5	240 ^d	240
Triclopyr	55335-06-3	NG	13 000
Trifluralin	1582-09-8	200	200
Insecticides			
Azinphos-methyl	86-50-0	NG	5
Carbaryl	63-25-2	200	200
Carbofuran	1563-66-2	1 800	1 800
Chlorfenvinphos	470-90-6	NG	30
Chlorpyrifos	2921-88-2	3.5	3.5
Cypermethrin	52315-07-8	NG	0.2
Diazinon	333-41-5	NG	80
<i>Diazinon-oxon^e</i>	962-58-3	NG	11
Naled (Dibrom)	300-76-5	NG	7
Dichlorvos	62-73-7	NG	1
Dimethoate	60-51-5	6 200 ^d	6 200
Disulfoton	298-04-4	NG	100
Endosulfan a	959-98-8	20	20
Endosulfan b	33213-65-9	NG	56
Ethion	563-12-2	NG	2.8
Fenitrothion	122-14-5	NG	10
Fonofos	944-22-9	NG	8
Imidacloprid	138261-41-3	NG	380
Lindane (g-BHC)	58-89-9	10	10
Malathion	121-75-5	NG	100
Methamidophos	10265-92-6	NG	1 300
Methidathion	950-37-8	NG	425
Methoprene	40596-69-8	NG	250
Methoxychlor	72-43-5	NG	40
Mevinphos	7786-34-7	NG	100
Parathion	56-38-2	NG	8
<i>Parathion-methyl^e</i>	298-00-0	NG	8

Table 27 Science-based water quality benchmarks for 107 current-use pesticides^a

Pesticide/Class	CAS RN ^b	CCME Water Quality Guideline ^c	Benchmark (ng/L)
Permethrin	52645-53-1	4	4
Phorate	298-02-2	NG	30
Phosalone	2310-17-0	NG	830
Phosmet	732-11-6	NG	45
Pirimiphos-methyl	29232-93-7	NG	15
Pyrethroids			
Deltamethrin	52918-63-5	0.4	0.4
Esfenvalerate	66230-04-4	NG	1
Terbufos	13071-79-9	NG	8.5
Fungicides			
Benomyl	17804-35-2	NG	260
Captan	133-06-2	1 300 ^d	1 300
Copper (Cu ²⁺)	7440-50-8	NG	2 000 to 4 000
Chlorothalonil	1897-45-6	180 ^d	180
Fosetyl-al	39148-24-8	NG	499 000
Total Dithiocarbamates		NG	
Mancozeb	8018-01-07	NG	2 000
Maneb	12427-38-2	NG	3 000
Ferbam	14484-64-1	NG	180
Thiram	137-26-8	NG	200
Ziram	137-30-4	NG	180
Metalaxyl	57837-19-1	NG	373 950
Metam	556-61-6	NG	2 750
Metiram	9006-42-2	NG	1 000
Myclobutanil	88671-89-0	NG	11 000
Quintozine	82-68-8	NG	5 000
Tebuconazole	107534-96-3	NG	15 150
Tecnazene	117-18-0	NG	1 000

^a Sources: Adapted from CCME, 1991; 1999; 2006 and Cantox Environmental Inc., 2004 – updated.

^b Chemical Abstracts Service Registry Number.

^c NG: No Canadian Council of Ministers of the Environment (CCME) water quality guideline available.

^d Interim CCME water quality guideline for the protection of aquatic life.

^e Each transformation product is italicized and indented below its parent pesticide.

The benchmark values are not meant to act as Canadian drinking water quality guidelines, replace existing guidelines, or be used in a regulatory manner. They are intended to help in evaluating the results of this study, in other words, to identify which pesticides may pose potential impacts and where. Guidelines, benchmarks and other similar tools like objectives and criteria are designed to aid risk assessors, risk managers and the public in determining whether there is a *potential* for adverse effects in the environment. The effects of pesticides, as with industrial chemicals and naturally occurring substances such as metals, are modified by physical and chemical factors in complex ecosystems. For example, a wide range of toxicity modifying factors (e.g., pH, temperature, chemical or biological ligands and many other factors) may be present and unaccounted for in the derivation of the guideline or benchmark. Similarly, benchmarks may have been derived for species not present in Canada, but which may be extremely sensitive to a particular active ingredient. If the benchmarks in Table 27 are exceeded by surveillance data maximum concentrations, further site-specific research would be

necessary to determine the cause of the exceedance and to determine whether aquatic biota are being adversely affected at that sampling location. An additional limitation of the benchmark approach is that benchmarks are specific to individual active ingredients.

A further gap, not directly addressed in this report, is the lack of any science-based benchmarks to interpret the effects of pesticide mixtures on aquatic ecosystems. In this national surveillance program, pesticides were rarely detected in isolation.

Benchmark Benefits

- Conservative values indicate where potential problems may exist.
- Benchmarks allow for rapid screening level assessment of surveillance data.
- Benchmarks reflect values based upon recognized scientific approaches.

Benchmark Limitations

- Benchmarks provide highly conservative values with high uncertainty.
- When they are set, benchmarks generally do not take site-specific conditions and toxicity-modifying factors into account.
- When benchmarks are used, the toxicity of pesticide mixtures is not accounted for.
- Benchmarks may have been derived using sensitive species not found in Canada.

6.2.2 National Water Quality Surveillance Program Data Comparisons to Canadian Water Quality Guidelines and Water Quality Benchmarks

In this section, concentrations of pesticides and transformation products in the sampled media are compared with water quality guidelines and benchmarks (Table 27).

British Columbia

Surface water samples from British Columbia (Table 8), for the three sampling years combined, were compared to selected benchmarks (Table 27). Benchmarks were available for 56 out of 85 pesticides or transformation products. The benchmarks for chlorpyrifos (3.5 ng/L) and dichlorvos (1 ng/L) were exceeded most often – six times each (n=96, for both). Diazinon exceeded its 80 ng/L benchmark in 4 of 93 samples, and diazinon-oxon exceeded its benchmark of 11 ng/L in 5 of 76 samples. The benchmark for cypermethrin (0.2 ng/L) was exceeded twice (n=96) and azinphos-methyl exceeded its benchmark (5 ng/L) in one sample (n=80).

Alberta, Saskatchewan and Manitoba

In the Alberta, Saskatchewan and Manitoba reservoir samples, none of the detected analytes (Table 11) exceeded benchmark values for the protection of aquatic life (Table 27). Several pesticides (ethion [n = 30], fonofos [n = 30], parathion [n = 30] and phosmet [n = 30]) had detection limits well above the benchmark values (ethion = 2.8 ng/L; fonofos = 8 ng/L; parathion = 8 ng/L; phosmet = 45 ng/L). None of these pesticides were detected above the method detection limit in the samples and in fact may not be present. Chlorpyrifos exceeded the benchmark (3.5 ng/L) four times out of 29 samples. However, the method detection limit was greater than the benchmark value. Lower detection limits, below the benchmark values, are required to assess the risks posed by all of these pesticides.

Many more pesticides, particularly the sulfonylurea pesticides, do not have benchmarks currently available for comparison.

In the prairie wetlands sampled, two pesticides (2,4-D and MCPA) were found to exceed aquatic life benchmarks. Out of 60 samples taken in wetlands across the region, the benchmark for 2,4-D was exceeded once, while the benchmark for MCPA was exceeded twice. These two pesticides were above the detection limit (DL) in all 60 samples (2,4-D DL 0.47 ng/L & MCPA DL, 0.58 ng/L; Table 9).

Ontario

Surface water samples were taken between the months of April and December in 2003, 2004 and 2005. In 2003, samples were analyzed for a maximum of 38 analytes (Table 12), while in 2004 and 2005, each sample was analyzed for a maximum of 36 and 42 analytes (Tables 13 and 14). The results of these analyses were compared to selected benchmarks (Table 27). Diazinon exceeded the benchmark in 25 samples over the three years followed by chlorpyrifos (21), atrazine (16), 2,4-D (6), dicamba (4), malathion (3), metribuzin (2), mecoprop (2) and metolachlor (1).

Quebec

Only three pesticides were observed at concentrations exceeding their benchmark (Tables 19 to 21 and 27): the herbicide atrazine and the fungicide chlorothalonil once in 2003. The insecticide chlorpyrifos exceeded its benchmark twice in 2003, once in 2004, and six times in 2005. It is important to note that since the detection limit of the method for chlorpyrifos is slightly higher than its benchmark, the number of samples for which the concentration exceeds the detection limit could be underestimated.

Prince Edward Island, Nova Scotia and New Brunswick

Prince Edward Island Surface Water – At the Wilmot River site in 2003, the fungicide chlorothalonil was found at a concentration of 640 ng/L in the October 1 sample, exceeding the benchmark of 180 ng/L. During the 48 hours prior to sampling, 28.7 mm of rain had fallen. In the Souris River in 2003, the herbicide hexazinone was detected in four of the nine surface water samples collected, at concentrations of 80, 120, 160 and 240 ng/L. The benchmark for hexazinone (70 ng/L) was exceeded in all four samples. This herbicide is extensively used for vegetation control in blueberry-growing areas. Concentrations in the stream water did not appear to be influenced by rainfall events. Chlorothalonil was measured at 7 830 ng/L in the Founds River on August 31, 2004, well above the benchmark of 180 ng/L. Heavy rainfall occurred on August 30 (23.3 mm) and August 31 (40.6 mm), which induced extensive runoff from treated fields.

Prince Edward Island Stream Sediment – Stream sediment samples were collected as part of the Prince Edward Island monitoring program only (Table 23). In 2003, there were nine detections of three compounds, six in Mill River and three in the Souris River samples. In 2004, there were eight detections of dithiocarbamates in Wilmot River (3) and Founds River (5) samples. In 2005, dithiocarbamates were measured in all four samples collected at the Wilmot River site and in all five samples collected from the Dunk River–North Brook site. Table 23 provides a summary of the compounds measured and the frequency of detection. Because there were no Canadian guidelines available, the results for three of the four products detected were assessed against guidelines used by the Netherlands. That comparison would suggest the potential for some level of risk to the benthic communities in these systems.

New Brunswick Surface Water – In Black Brook, chlorothalonil was measured in the July 23, 2003, sample as well as in both the duplicates collected on August 8, with concentrations of 4,000, 4,800 and 4,900 ng/L, respectively. These concentrations exceeded the benchmark (Table 27). Azinphos-methyl was found in the July 23 sample at a concentration of 5,000 ng/L, which exceeded the benchmark of 5 ng/L. The insecticide (beta) endosulfan was also detected at a concentration of 200 ng/L in the sample collected on August 8, 2003, exceeding the guideline of 56 ng/L. Substantial rainfall events occurred in the 24 hours before the July 23 and August 8 sampling dates, with 27.2 and 34.6 mm of rain, respectively, being measured at the Grand Falls monitoring station. The 2004 results for the Black Brook site showed similar pesticide residue patterns to those of 2003. Chlorothalonil was detected in five of the six samples analyzed, with four of the five concentrations exceeding the benchmark of 180 ng/L by an order of magnitude reaching a maximum of 7830 ng/L. Azinphos-methyl was detected in four of the six samples collected, with all of the concentrations measuring in excess of the benchmark (5 ng/L). There was also a single detection of the insecticide permethrin (110 ng/L), which exceeded the permethrin benchmark (0.4 ng/L). With the exception of one sampling date in 2004, all other samples were collected during, or immediately following, significant runoff-inducing rainfall events.

Canada-wide

Benchmark exceedances over the three years of the surveillance program occurred in surface waters in all regions. The analytes that commonly exceeded benchmarks across Canada included chlorothalonil, azinphos-methyl, permethrin, chlorpyrifos and diazinon. Several other active ingredients or their transformation products also exceeded benchmarks, but these tended to be more region specific and in most cases, less frequent. A short description follows for each of these five active ingredients.

Chlorothalonil is a commonly used fungicide in agricultural and domestic settings. It is distributed under a number of product names, including BRAVO 500 and Tattoo C (PMRA, 2006). Chlorothalonil's mode of action in fungi is the combination with and depletion of molecules known as thiols (particularly glutathione). This leads to the inhibition of a process known as glycolysis and ultimately interferes with cellular energy production inside fungus cells (Stenersen, 2004; Tomlin, 2000). Chlorothalonil is commonly used to address pink and grey snow mould on lawns and is used to treat early and late blight in a variety of agricultural crops, including potatoes and carrots. Chlorothalonil is commonly sold in British Columbia and the Atlantic provinces (see section 2.3). Chlorothalonil will readily biodegrade under aerobic and anaerobic conditions in aquatic ecosystems. Half-lives range from 0.18 to 8.8 days (HSDB, 2006). Adsorption from the water column to sediment and suspended material may occur (HSDB, 2006).

Azinphos-methyl is an organophosphate insecticide commonly used in the agricultural industry on field, fruit, vegetable and ornamental crops. It is a cholinesterase inhibitor. Azinphos-methyl is not among the top 10 pesticides sold in any region (section 2.2); however, the volume of insecticide sales is generally lower than herbicide sales in Canada. Common product names are Guthion and 240 EC, among others. This active ingredient has a water solubility of 28 mg/L, a log K_{ow} of 2.96 and a K_{oc} of 1 000. The soil half-life of azinphos-methyl is 68 days. Azinphos-methyl is expected to be somewhat mobile in soil (HSDB, 2006). The K_{oc} suggests that it will adsorb to suspended solids and sediment (HSDB, 2006). The low K_{ow} value suggests a low potential for bioaccumulation.

In Canada, permethrin is used in a number of insecticidal products (e.g., Ambush 500EC, RIPCORDER 400EC) designed to control a wide range of pests. It is not among the top 10 pesticides by sales volume in any of the regions examined in this national surveillance program (section 2.2). There is evidence that permethrin interferes with ATPase enzymes that maintain ionic concentration gradients across cell membranes (Solomon et al., 2001). It is used in agricultural, forestry and domestic practices. It is also used as a public health tool against disease vectors such as mosquitoes. Given these practical applications, there are many sources of permethrin in the environment. Permethrin is not expected to leach from soil (Carroll et al., 1981) or to contaminate groundwater (Wagenet et al. 1985) because it binds strongly to soil particles and is nearly insoluble in water (Carroll et al., 1981; US DASCs, 1990). Permethrin degrades rapidly in water, primarily through hydrolysis (Lutnicka et al., 1999). Aquatic invertebrates are generally more sensitive to permethrin than are fish or aquatic plants (Cantox Environmental Inc., 2004).

Chlorpyrifos is an insecticide commonly used in agricultural crops, including ornamentals and field crops. It also has limited commercial use, on golf courses and sod farms, for example. It is one of the top 10 pesticides sold in the Prairie Ecozone, but is not among the top 10 in any of the other regions studied. Chlorpyrifos is an organophosphorous pesticide, and its mode of action is through cholinesterase inhibition. Product names include LORSBAN, DURSBAN, along with many others. Based on a K_{oc} of 12 600, chlorpyrifos is expected to adsorb tightly to soil and have limited mobility (HSDB, 2006). It has a soil half-life of 56 days and water solubility of 1.4 mg/L. In water, it will adsorb to suspended solids and sediments (HSDB, 2006). Chlorpyrifos has a $\log K_{ow}$ of 4.7, which suggests that it will partition from water to lipids, and therefore has the potential to bioaccumulate in aquatic and terrestrial organisms.

Diazinon is an organophosphate insecticide used on ornamentals, livestock (e.g., cattle ear tags), and field and fruit crops (PMRA, 2006). It is commonly sold in British Columbia and the Atlantic provinces (see section 2.2). Product names include DIAZINON 50W and DIAZOL 50W, among others. A range of K_{oc} values from 191 to 1 842 indicates that diazinon is expected to adsorb to suspended solids and sediment (HSDB, 2006). Volatilization from water surfaces is not expected, based upon a Henry's Law constant of 1.1×10^{-7} atm m³/mole (HSDB, 2006).

These five active ingredients are registered for use in Canada under the *Pest Control Products Act* (Department of Justice, 2002). Surveillance data that exceeded Canadian Water Quality Guidelines for the protection of aquatic life, and/or science-based benchmarks suggest that current application practices for these pesticides in Canada could result in impacts in the aquatic environment. Further site-specific research is necessary to determine the cause of the exceedances, and to determine whether and how aquatic biota are being adversely affected at contaminated locations.

7.0 THE PATH FORWARD

The results from this first National Water Quality Surveillance Program suggest that continued monitoring of pesticides and transformation products in the Canadian environment is warranted. Further work needs to be conducted to characterize exposure patterns of current-use pesticides. The presence of pesticides not registered in Canada, and the fact that new pesticides are replacing some older pesticides, suggest that additional active ingredients and their transformation products, such as sulfonylureas, glufosinate, glyphosate, captan, metiram, mancozeb and pyrethroids, should be added to the surveillance list. Sulfonylureas are of particular interest as they are relatively new active ingredients and their use is increasing. No benchmarks are currently available for comparison to surveillance concentrations, and this data gap should be addressed for future surveillance programs. Samples collected in the Prairie Ecozone confirm the presence of sulfonylureas in prairie wetlands, rivers and reservoirs (Tables 9, 10 and 11).

One limitation to the addition of new pesticides (or their transformation products) is the lack of benchmarks and analytical methods. For those pesticides identified as high priority, but that do not have analytical methods with reasonable detection limits, an

effort should be made to develop and/or refine existing methods to address these priorities. For example, the analytical methods used in some regions were unable to discern individual dithiocarbamates like mancozeb, maneb and metiram. Given the importance of these fungicides, and the high sales volumes in Canada, a refined analytical method should be pursued. Likewise, high sales were recorded for the Lower Fraser Valley in British Columbia for the fumigant Metam (Vapam), but sensitive analytical methods were not available for Metam or its transformation products. In the Prairie Ecozone, ethion, fonofos, parathion and phosmet all had detection limits well above the benchmarks (Table 27). Refined analytical methods should be developed with detection limits below the benchmarks so that potential risk determinations can be made. Another important gap in assessing the environmental effects of pesticides is the presence and effects of adjuvants in formulated pesticide products. For some pesticides, such as glyphosate, the associated adjuvants have been shown to be more toxic than the active ingredient. Wan et al. (1989) found that the tallowamine (MON 0818) emulsifier used in some commercial glyphosate formulations, was five to 115 times more lethal than glyphosate to juvenile salmonids.

Glyphosate is the active ingredient with the highest sales volume in four of the five regions surveyed in this national water quality surveillance program, and yet was only measured in two of the provinces (British Columbia and Ontario). Future surveillance activities should include glyphosate in all environmental media due to the high sales volume.

Sample site locations are an important consideration for future surveillance activities. The vast majority of the sites in the present program were located close to regions of heavy agricultural activity. However, domestic use of pesticide products is also an important contributor to concentrations of pesticide products in the environment (Brimble et al., 2005). Domestic-sector applications are typically for cosmetic purposes like lawn treatment, and a lack of training increases the probability that pesticide products will be applied improperly and at higher rates than stated on the label (Brimble et al., 2005). The intensity of urban pesticide use in Canada is estimated to be 0.97 to 3.65 times higher than agricultural use (Brimble et al., 2005). Sampling of urban watersheds was only conducted in Ontario and British Columbia. Therefore, additional sampling sites located upstream and downstream of urban areas, close to storm sewers and in source waters affected by urban activity should be considered.

In all of the regional studies, individual active ingredients were rarely detected alone. The majority of the surface water samples contained more than one, and, in some cases, more than 10 individual active ingredients and transformation products (see Table 12, for example). The toxicity of chemical mixtures to humans and aquatic and terrestrial biota is an important consideration from a risk assessment, risk management and policy perspective. There are a number of scientific publications about and approaches to dealing with chemical mixtures (e.g., Faust et al., 2000; Williamson and Glozier, 2009). No Canadian guidelines, standards, criteria or objectives currently exist that address the issue of pesticide mixtures. However, Environment Canada, under the National Agri-Environmental Standards Initiative, is in the process of developing environmental quality benchmarks (referred to as performance standards) for pesticide mixtures (Williamson and Glozier, 2009).

In a surveillance program of this nature, effort should be taken to promote comparability of results and to facilitate the dissemination of surveillance information on a national scale. Meeting these objectives may involve the use of the same laboratories for analytical services, comparison and standardization of analytical methods; inter- and intra-laboratory comparisons using spiked samples; and field method standardization. The results of this program will also help determine the need for and benefits of a nationally consistent sampling design (e.g., grab samples at regular intervals, event-based sampling).

Overall, this three-year program provided excellent data on the presence and levels of pesticides and transformation products in the Canadian environment. Data collected from this National Water Quality Surveillance Program are critical to informing risk assessors and allowing for informed risk management, regulatory and policy decisions at all levels of government. The program has already contributed information to ongoing regulatory decisions in other departments (e.g., re-registration of lindane and endosulfan by PMRA) and to developing priority lists for the development of Ideal Performance Standards under the National Agri-Environmental Standards Initiative. Many of the analytes surveyed have not been analyzed in other international jurisdictions, so this program also provides leadership in the analysis of pesticides and transformation products in the environment.

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